BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (7), 1754—1757 (1976)

Solvation Effects on the Electron-Transfer Reaction of TCNQ Anion Radical and 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

Akihiko Yamagishi

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received October 15, 1975)

Rate constants were obtained with a temperature-jump apparatus for the electron-transfer reaction between 7,7,8,8-tetracyanoquinodimethane anion radical and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in acetonitrile/tetrahydrofuran (MeCN/THF) and in acetonitrile/water ($MeCN/H_2O$) mixtures. In MeCN/THF, the forward rate constant (k) was determined in three kinds of mixed solvents: $k=(5\pm2)\times10^9$ $M^{-1}s^{-1}$ (pure MeCN), $(2.2\pm0.2)\times10^9$ $M^{-1}s^{-1}$ (1: 2 MeCN/THF), and $(6\pm2)\times10^8$ $M^{-1}s^{-1}$ (1: 10 MeCN/THF) at 25±2 °C. In $MeCN/H_2O$ the forward rate constant increases with the square of the H_2O concentration in the range of $[H_2O]=2$—10 M; $k=k_0[H_2O]^2$ with $k_0=(1.0\pm0.2)\times10^6$ $M^{-3}s^{-1}$ at 25±2 °C. The results are discussed in terms of the specific solvation and the ion-pairing of ion radicals.

Recent studies of electron-transfer reactions of ion radicals demonstrate that the solvation structure of an ion radical affects the reaction rate drastically.[1] The specific solvation and ion-pairing with counter ions reduce the electron-transfer rate by a few orders of magnitudes.[1] The conclusion has been deduced mostly from ESR studies of the electron exchange between an ion radical and its parent molecule.

$$R^{\cdot+}\text{ (or }R^{\cdot-}) + R \rightleftarrows R + R^{\cdot+}\text{ (or }R^{\cdot-})$$

For a reaction of this kind, the free energy change of reaction, ΔF°, is zero.

The present paper gives the results of the temperature-jump study of the reaction between 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion radical and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).

$$\text{TCNQ}^{\cdot-} + \text{DDQ} \rightleftarrows \text{TCNQ} + \text{DDQ}^{\cdot-}, \qquad (1)$$

The electron affinity of DDQ is much greater than that of TCNQ, indicating that ΔF° of Reaction 1 is largely negative.[2,3] It was intended to see whether the specific solvation and the ion-pairing still cause an additional energy barrier even under the conditions of a negative free energy change, $\Delta F^\circ < 0$.

Experimental

Sodium (Na^+) and tetraethylammonium (NEt_4^+) salts of TCNQ and DDQ were prepared by the reduction with NaI and NEt_4I, respectively. $NaClO_4$ and $NaB(C_6H_5)_4$ were used without purification. NEt_4ClO_4 was prepared by the reaction of NEt_4OH with $HClO_4$. MeCN and THF were distilled with a distillation column of *ca.* 30 cm length, H_2O contents being 0.5 mg/ml (MeCN) and 1.7 mg/ml (THF). Both were stored under $CaCl_2$. H_2O was distilled after being deionized.

The instruments for equiliblrium, conductivity and rate measurements were described elsewhere.[4] As regards the temperature-jump apparatus, the rise time of temperature was determined by following the decrease of a $\text{DDQ}^{\cdot-}$ dimer at 700 nm after the temperature-jump; *e.g.* for 1: 10 MeCN/THF solvent containing 0.01 M NEt_4ClO_4 and *ca.* 10^{-3} M NEt_4^+-$\text{DDQ}^{\cdot-}$, the 90% temperature rise was attained within 10 μs. Equilibrium measurements were carried out at 25 ±1 °C. For temperature-jump measurements, samples were kept at 20 ±1 °C. The difference in temperature between static and kinetic results was neglected.

Results

Reactions in MeCN/THF. The apparent equilibrium constant of Reaction 1 in MeCN/THF was determined in the same way as for MeCN solvent.[5]

$$K_{ap} = [\text{TCNQ}][\text{DDQ}^{\cdot-}]_t/[\text{TCNQ}^{\cdot-}]_t[\text{DDQ}]$$

where $[\ ]_t$ denotes the total concentration of each ion radical, since an ion radical is present as either a free ion or an ion-paired ion. $[\text{TCNQ}^{\cdot-}]_t$ is calculated from the absorbance at 842 nm, assuming $\varepsilon=4.33\times10^4$ for all the solvents. $[\text{DDQ}^{\cdot-}]_t$ is equated to $[\text{DDQ}^{\cdot-}]_t=[\text{DDQ}^{\cdot-}]^0+\Delta[\text{TCNQ}^{\cdot-}]$, where $[\text{DDQ}^{\cdot-}]^0$ is the initial concentration of $\text{DDQ}^{\cdot-}$ and $\Delta[\text{TCNQ}^{\cdot-}]$ the decrease of $\text{TCNQ}^{\cdot-}$ when DDQ is added. K_{ap} thus obtained is plotted against the volume percent of THF (Fig. 1).

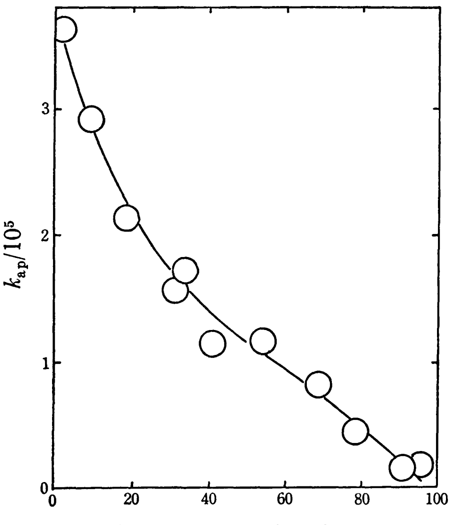

Fig. 1. K_{ap} obtained in MeCN/THF mixtures.

K_{ap} was also obtained in the presence of various amounts of added salts. The results are given in Table 1. The addition of $NaClO_4$ gives a negligible effect on K_{ap} in pure MeCN. In 1: 2 MeCN/THF, however, K_{ap} increases as $[NaClO_4]$ increases. In 1: 10 MeCN/THF, the small amount of $NaB(C_6H_5)_4$ increases K_{ap} remarkably, while further addition of the salt decreases K_{ap}.

Table 1. The effect of Na^+ on K_{ap}

a) In MeCN; $K^0_{ap}=3.6\times10^5$ a)				
$[NaClO_4]/M$	0.012	0.041	0.12	0.21
K_{ap}/K^0_{ap} at 25 °C	1.0	1.0	1.0	1.0
b) In 1:2 MeCN/THF; $K^0_{ap}=8.2\times10^4$ a)				
$[NaClO_4]/M$	0.0072	0.025	0.057	0.087
K_{ap}/K^0_{ap}	1.3	1.5	1.5	1.7
c) In 1:10 MeCN/THF; $K^0_{ap}=1.0\times10^4$ a)				
$[NaB(C_6H_5)_4]/M$	0.0011	0.0022	0.0043	0.01
K_{ap}/K^0_{ap}	1.5	1.5	1.4	1.1

a) K^0_{ap} denotes K_{ap} at $[Na^+]=0$.

Table 2. The molar conductivity, λ, of $NEt_4^+TCNQ^{\cdot-}$ and $NEt_4^+DDQ^{\cdot-}$

a) $NEt_4^+TCNQ^{\cdot-}$ in MeCN					
$[NEt_4^+TCNQ^{\cdot-}]\times10^6/M$	2.2	4.5	8.8	14	
λ	145	132	123	111	
b) $NEt_4^+TCNQ^{\cdot-}$ in 1:2 MeCN/THF					
$[NEt_4^+TCNQ^{\cdot-}]\times10^6/M$	5.3	10	21		
λ	112	112	107		
c) $NEt_4^+TCNQ^{\cdot-}$ in THF					
$[NEt_4^+TCNQ^{\cdot-}]\times10^6/M$	2.1	3.7	5.9	9.1	
λ	65.5	61.7	60.7	57.0	
d) NEt_4^+ $DDQ^{\cdot-}$ in MeCN					
$[NEt_4^+DDQ^{\cdot-}]\times10^5/M$	6.3	9.5	14	32	
λ	240	238	240	232	
e) $NEt_4^+DDQ^{\cdot-}$ in THF					
$[NEt_4DDQ^{\cdot-}]\times10^5/M$	1.2	2.5	4.9	9.3	16
λ	123	91.8	66.9	49.5	40.1

In order to obtain the dissociation constants of ion radical salts, the molar conductivities of $NEt_4^+TCNQ^{\cdot-}$ and $NEt_4^+DDQ^{\cdot-}$ were measured in MeCN/THF (Table 2). The dissociation constant, K_D, for

$$NEt_4^+R^{\cdot-} \rightleftharpoons NEt_4^+ + R^{\cdot-}$$

is roughly estimated by means of the equation.

$$K_D = \frac{C\lambda^2}{\lambda_\infty^2}. \tag{2}$$

Where C is the total concentration of an ion radical salt and λ_∞ the molar conductivity at infinite dilution. For $NEt_4^+DDQ^{\cdot-}$ in THF, K_D is obtained to be $(4.9\pm1.0)\times10^{-5}$ M at 25±2 °C. In the other solvents, however, K_D defined by Eq. 2 gives no constant value, making the estimation of K_D impossible.

Temperature-jump studies were performed in MeCN, 1:2 MeCN/THF, and 1:10 MeCN/THF in order to obtain the rate constans of Reaction 1. With a temperature-rise, the trasient increase of $TCNQ^{\cdot-}$ is observed at 745 nm in all the solvents. k_{obs} defined by

$$-\frac{d\Delta[TCNQ^{\cdot-}]}{dt} = k_{obs}\Delta[TCNQ^{\cdot-}] \tag{3}$$

is related to the forward rate constant as follows.[5]

$$k_{obs} = k\{[TCNQ^{\cdot-}]_{t,e}+[DDQ]_e\}, \tag{4}$$

where $[\ ]_e$ denotes the equilibrium concentration at an elevated temperature. The k values determined at various concentrations of supporting electrolytes are given in Table 3.

Table 3. k at various concentrations of counter ions at 25 °C

a) MeCN				
$[NEt_4ClO_4]/M$	0.012			
$k\times10^{-9}/M^{-1}s^{-1}$	5±2			
b) 1:2 MeCN/THF				
$[NEt_4ClO_4]/M$	0.0012	0.0024	0.0050	0.010
$k\times10^{-9}/M^{-1}s^{-1}$	2.6±0.5	2.2±0.5	2.2±0.5	2.2±0.5
c) 1:10 MeCN/THF				
$[NaB(C_6H_5)_4]/M$	0.006	0.012	0.024	
$k\times10^{-8}/M^{-1}s^{-1}$	7±2	5±2	6±2	

Reactions in $MeCN/H_2O$: The apparent equilibrium constant of Reaction 1 in $MeCN/H_2O$ was determined in the same way as in MeCN/THF. A large uncertainty in K_{ap} arises in the higher concentration of H_2O, since $DDQ^{\cdot-}$ decomposes gradually in such regions and DDQ is reduced to $DDQ^{\cdot-}$. K_{ap} thus obtained is plotted against the volume percent of H_2O (Fig. 2).

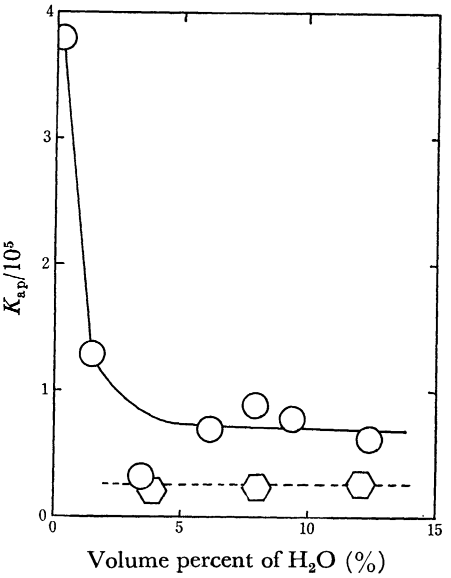

Fig. 2. K_{ap} obtained in $MeCN/H_2O$ mixtures; A solid line is determined by spectrophotometric measurements and a dotted line by rate measurements.

The rates of Reaction 1 in $MeCN/H_2O$ mixtures were determined using a temperature-jump apparatus. In $MeCN/H_2O$, the trasient increase of $TCNQ^{\cdot-}$ is observed at 745 nm with temperature-rise. k_{obs} defined by Eq. 3 is determined by varying the concentrations of $TCNQ^{\cdot-}$ and DDQ at constant concentrations of TCNQ and $DDQ^{\cdot-}$. Under these conditions, Eq. 4 is transformed into

$$k_{obs} = k\{[TCNQ^{\cdot-}]_e + C/[TCNQ^{\cdot-}]_e\}, \tag{5}$$

where C is a constant given by

$$C = [TCNQ]_e[DDQ^{\cdot-}]_{t,e}/K_{ap}.$$

The dependence of k_{obsd} on $[TCNQ^{\cdot-}]_e$ is shown in Fig. 3. As expected from Eq. 5, k_{obsd} becomes minimum for a certain value of $[TCNQ^{\cdot-}]_e$. This concentration is denoted by $[TCNQ^{\cdot-}]_e$*. It is apparent from Eq. 5 that $[TCNQ^{\cdot-}]_e$ is equal to $[DDQ]_e$ at $[TCNQ^{\cdot-}]_e^*$. Using

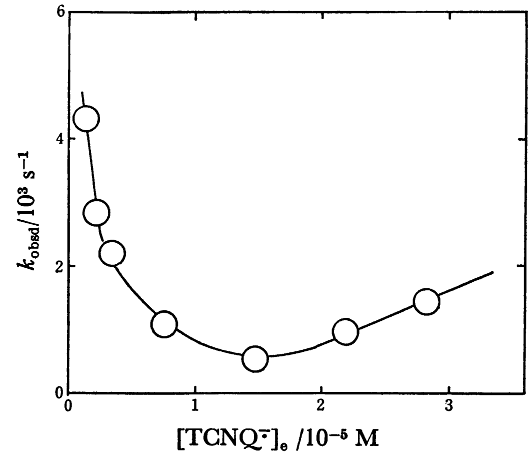

Fig. 3. Dependence of k_{obsd} on $[\mathrm{TCNQ}^{\overline{\cdot}}]_{\mathrm{e}}$ in 9: 1 MeCN/H_2O; [TCNQ] 1.1×10^{-3} M and $[\mathrm{NEt_4}^{+}\mathrm{DDQ}^{\overline{\cdot}}]$ 4.1×10^{-4} M.

the value of $[\mathrm{TCNQ}^{\overline{\cdot}}]_{\mathrm{e}}{}^{*}$, K_{ap} is determined by

$$K_{\mathrm{ap}} = [\mathrm{TCNQ}]_{\mathrm{e}}[\mathrm{DDQ}^{\overline{\cdot}}]_{\mathrm{t,e}}/[\mathrm{TCNQ}^{\overline{\cdot}}]_{\mathrm{e}}{}^{*2}.$$

K_{ap} obtained in this way agrees with the one obtained by the equilibrium measurements within a factor of 5 (a dotted curve, Fig. 2).

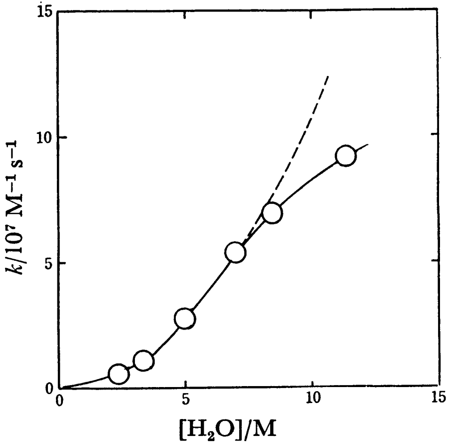

Fig. 4. Dependence of k on the H_2O concentration. A dotted curve denotes the calculated values according to Eq. 6.

Figure 4 gives the dependence of k on the concentration of H_2O. It is concluded that k increases with the square of the H_2O concentration from 2 to 10 M.[6)]

$$k = k_0[H_2O]^2$$

$$k_0 = (1.0\pm0.2)\times10^6\ \mathrm{M}^{-3}\ \mathrm{s}^{-1} \text{ at } 25\pm2^{\circ}\mathrm{C}. \qquad (6)$$

Discussion

The effect of THF on the equilibrium and the rates of Reaction 1 is interpreted in terms of the ion-pairing of ion radicals.

$$\begin{tikzcd}
\mathrm{TCNQ}^{\overline{\cdot}} + \mathrm{DDQ} \arrow[r, shift left, "k_1"] \arrow[d, shift right, "\mathrm{M}^+"'] & \mathrm{TCNQ} + \mathrm{DDQ}^{\overline{\cdot}} \arrow[l, shift left] \arrow[d, shift left, "\mathrm{M}^+"] \\
\mathrm{M}^+\mathrm{TCNQ}^{\overline{\cdot}} + \mathrm{DDQ} \arrow[u, shift right] \arrow[r, shift left, "k_2"] & \mathrm{TCNQ} + \mathrm{M}^+\mathrm{DDQ}^{\overline{\cdot}} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd} \qquad (7)$$

K_{ap} is expressed in terms of the dissociation constants of $\mathrm{M}^+\mathrm{TCNQ}^{\overline{\cdot}}$ and $\mathrm{M}^+\mathrm{DDQ}^{\overline{\cdot}}$, $K_{\mathrm{D}}^{\mathrm{T}}$ and $K_{\mathrm{D}}^{\mathrm{D}}$, respectively, as follows.

$$K_{\mathrm{ap}} = K_0(1+[\mathrm{M}^+]/K_{\mathrm{D}}^{\mathrm{D}})/(1+[\mathrm{M}^+]/K_{\mathrm{D}}^{\mathrm{T}}) \qquad (8)$$

where K_0 is the equilibrium constant for the electron-transfer reaction of free ions.

$$K_0 = \frac{[\mathrm{TCNQ}][\mathrm{DDQ}^{\overline{\cdot}}]}{[\mathrm{TCNQ}^{\overline{\cdot}}][\mathrm{DDQ}]}$$

K_{ap} in MeCN only slightly varies with the addition of $\mathrm{NaClO_4}$ (Table 1). This indicates that $K_{\mathrm{D}}^{\mathrm{T}}$ is nearly equal to $K_{\mathrm{D}}^{\mathrm{D}}$ previously determined to be 0.40 M.[4)] On the other hand, K_{ap} in 1 : 10 MeCN/THF increases rapidly until it reaches a constant value. According to Eq. 8, this implies that $K_{\mathrm{D}}^{\mathrm{D}}$ is smaller than $K_{\mathrm{D}}^{\mathrm{T}}$ in this medium. From the limiting value of $K_{\mathrm{ap}}/K^0{}_{\mathrm{ap}}=1.5$ at the region of $[\mathrm{NaB(C_6H_5)_4}]=0.0011-0.0022$ M, $K_{\mathrm{D}}^{\mathrm{T}}$ is equated to 1.5 $K_{\mathrm{D}}^{\mathrm{D}}$. Assuming that $K_{\mathrm{D}}^{\mathrm{D}}$ in 1 : 10 MeCN/THF does not differ from $K_{\mathrm{D}}^{\mathrm{D}}$ in THF ($4.9\pm1.0\times10^{-5}$ M), $K_{\mathrm{D}}^{\mathrm{D}}$ and $K_{\mathrm{D}}^{\mathrm{T}}$ are roughly estimated to be 5×10^{-5} M and 8×10^{-5} M, respectively.

Under the scheme of Eq. 7, k is expressed in terms of $K_{\mathrm{D}}^{\mathrm{T}}$ and $K_{\mathrm{D}}^{\mathrm{D}}$ as follows.

$$k = k_1\left(\frac{K_{\mathrm{D}}^{\mathrm{T}}}{[\mathrm{M}^+]+K_{\mathrm{D}}^{\mathrm{T}}}\right) + k_2\left(\frac{[\mathrm{M}^+]}{[\mathrm{M}^+]+K_{\mathrm{D}}^{\mathrm{T}}}\right), \qquad (9)$$

where k_1 and k_2 are the forward rate constants for the reactions between $\mathrm{TCNQ}^{\overline{\cdot}}$ and DDQ and between $\mathrm{M}^+\mathrm{TCNQ}^{\overline{\cdot}}$ and DDQ, respectively. In deriving the equation, the rate of ion-pairing of $\mathrm{TCNQ}^{\overline{\cdot}}$ with M^+ is assumed to be much greater than that of electron-transfer. Taking $[\mathrm{Na}^+]\approx[\mathrm{NaB(C_6H_5)_4}]\approx10^{-2}$ M and $K_{\mathrm{D}}^{\mathrm{T}}\approx8\times10^{-5}$ M in 1 : 10 MeCN/THF, k is simply equated to k_2 in this solvent. k_2 in 1: 10 MeCN/THF is about one order smaller than in MeCN. It is concluded that the transfer process of Na^+ causes an additional energy barrier even under the conditions of a negative free energy change, $\Delta F^{\circ} < 0$.

The effects of H_2O on the equilibrium and rate constants are most likely ascribed to the capacity of H_2O for hydrogen-bonding. As regards DDQ and its anion radical, the formation of hydrogen bond with H_2O has been confirmed by polarographic investigations.[3)] The decrease of K_{ap} in MeCN/H_2O indicates that the free energy change of reaction, ΔF°, becomes less negative. This seems closely related to the fact that the electron affinity of DDQ decreases in hydroxylic solvents like H_2O and ethanol.[3)] The specific solvation of DDQ and $\mathrm{DDQ}^{\overline{\cdot}}$ by H_2O is thus concluded from Fig. 2 to be completed at the concentration of $[H_2O]=$ 6 vol. %.

The kinetic result shown in Fig. 4 implies that H_2O acts catalytically in electron-transfer. From the dependence of the forward rate on $[H_2O]$ (Eq. 6), it is suggested that a part of DDQ is solvated by two H_2O molecules to form $\mathrm{DDQ}(H_2O)_2$, and that electron-transfer takes place through this species.

$$\mathrm{TCNQ}^{\overline{\cdot}} + \mathrm{DDQ}(H_2O)_2 \rightleftharpoons \mathrm{TCNQ} + \mathrm{DDQ}^{\overline{\cdot}}(H_2O)_2 \qquad (8)$$

It is assumed herewith that TCNQ does not form hydrogen-bond with H_2O in the investigated region of

[H_2O] since a carbon atom is a weaker proton acceptor than an oxygen atom.[7]

The author thanks Prof. Masatoshi Fujimoto for his encouragement. This work was supported by the ministry of Education.

References

1) N. Hirota, "Radical Ions," E. T. Kaiser and L. Kevan, Ed. Interscience, New York, N. Y. (1968), p. 35.

2) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

3) M. E. Peover, *Trans. Faraday Soc.*, **58**, 1656 (1962).

4) A. Yamagishi, *Bull. Chem. Soc. Jpn.*, **48**, 2440 (1975).

5) A. Yamagishi, *Chem. Lett.*, **1975**, 899.

6) Since the activity of H_2O in MeCN is not available, k is plotted against [H_2O]. At the higher concentration, the effect of aggregation of H_2O molecules should not be neglected. *Cf.* A. Rainis, R. Tung, and M. Szwarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).

7) M. L. Ahrens, M. Eigen, W. Krusc, and G. Maaass, *Ber. Bunsenges. Phys. Chem.*, **74**, 382 (1970).