December, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3475—3479 (1975)

A Temperature-Jump Study of Electron-Transfer Reactions Involving Ion Radicals: Reactions of the Cation Radicals of Phenothiazine and Aromatic *p*-Diamines

Akihiko YAMAGISHI

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

(Received May 16, 1975)

The reversible one-electron-transfer reactions of the following cation radicals were studied by temperature-jump and stopped-flow methods: phenothiazine (PhZ)/*N,N,N′,N′*-tetramethyl-*p*-phenylenediamine cation (TMPD$^{+\cdot}$), PhZ/*N,N*-dimethyl-*p*-phenylenediamine cation (DMPD$^{+\cdot}$), DMPD/TMPD$^{+\cdot}$ and DMPD/*N,N,N′,N′*-tetramethylbenzidine cation (TMBZ$^{+\cdot}$). The solvent used was either 1 : 3 ethanol–water or acetonitrile. For PhZ/TMPD$^{+\cdot}$, PhZ/DMPD$^{+\cdot}$ in ethanol-water and also for DMPD/TMPD$^{+\cdot}$ in acetonitrile, the backward reaction corresponding to the negative free energy change of reaction ($\Delta F^\circ < 0$) proceeds almost at the diffusion controlled rate. The backward rate constant for DMPD/TMPD^{+} in ethanol-water, $(6\pm1)\times10^8\ \mathrm{M^{-1}\,s^{-1}}$, is slightly less than a diffusion controlled one even for $\Delta F^\circ < 0$. The results are discussed as compared with the previous study on 7,7,8,8-tetracyanoquinodimethane/substituted-*p*-benzoquinone anions.

In a previous paper, a study on the reversible one-electron-transfer reactions between 7,7,8,8-tetracyanoquinodimethane anion radical and substituted *p*-benzoquinones was given, attention being paid to the dependence of the rate constant on the free energy change of reaction.[1] It was revealed that the electron-transfer reaction proceeds with no activation free energy when the free energy change of reaction is negative. This result can not be interpreted by the application of the Marcus theory.[2]

The above results provide two possibilities for the mechanism of the electron-transfer; (i) there exists a non-equilibrium polarization of solvents at the activated state,[2] but the potential barrier due to it is much smaller than that expected by the theory, and (ii) the electronic interaction between electron donor and acceptor is so large as to cause an appreciable lowering of the potential surfaces. These two mechanisms could be discriminated, if it were possible to detect the relaxation process of solvent polarization before and after the electronic transition or to prove kinetically the existence of an intermediate complex as has been done in the innersphere electron-transfer reactions of metal ions.[3] At present, however, neither of these two approaches seems to be possible.

We have studied the reactions of cation radicals with the purpose of attacking the above problem from another approach. The reacting pairs studied differ from each other in molecular size, electronic structure and kind of substituent to varying extent. Accordingly the electronic interaction between an electron donor (neutral molecule) and an acceptor (cation radical) would vary a great deal from one extreme in which a stable intermediate (dimer cation) is possible, to the other extreme in which the overlap of electron clouds is hardly possible. By examining these effects on the reaction rates, we intended to see how far the electronic interaction between reactants dominates the electron-transfer rates.

Experimental

Phenothiazine (PhZ) was sublimed once. The dihydrochlorides of *N,N,N′,N′*-tetramehyl-*p*-phenylenediamine (TMPD) and *N,N*-dimethyl-*p*-phenylenediamine (DMPD) were used without purification. The free base of DMPD was obtained by neutralizing it with NaOH and then extracting with diethylether. The obtained free base was sublimed once. *N,N,N′,N′*-Tetramethylbenzidine(TMBZ) was used without purification.

Perchlorate salts of TMPD and DMPD (TMPD$^{+\cdot}$ClO$_4^-$ and DMPD$^{+\cdot}$ClO$_4^-$, respectively) were prepared according to the method of Michaelis and Granich.[4] Phenothiazine picrate (PhZ$^{+\cdot}$Pic$^-$) was supplied by Dr. Y. Iida. The cation radical of TMBZ was generated by electrolytic oxidation in acetonitrile, using a platinum electrode in 0.01 M tetra-*n*-propylammonium perchlrorate. The stability of these salts in various media was studied. Acetonitrile was distilled once using a distillating column of *ca.* 50 cm length (water content 0.5 mg/ml). Ethanol was distilled once. Water was deionized and distilled once.

The electronic spectra were measured with an EPS-3T spectrophotometer. pH was measured with a Radiometer equipped with G 200B glass electrode and K 100 reference calomel electrode. The concentration of proton in 1 : 3 ethanol-water solvent was calculated by means of the equation $\mathrm{p[H^+]} = \mathrm{pH} - \alpha$ ($\alpha = 0.11$). This relation is obtained by measuring the pH of an ethanol-water mixture containing 10^{-2}—10^{-3} M of HClO$_4$. The variation of α with ionic strength (0—0.01 M) is neglected in calculating the proton concentration.

The rate of reaction was measured with a Union-Giken temperature-jump apparatus or a Union-Giken rapid-scan stopped-flow spectrophotometer. 0.01 M tetra-*n*-propylammonium perchlorate was added as a supporting electrolyte in measuring the rate in acetonitrile with a temperature-jump apparatus. Equilibrium and kinetic measurements were carried out at 10 °C. The effect of temperature at temperature-jump (2—5 °C) on the rate constants was considered to be negligible.

Results

A. Phenothiazine (PhZ) and N,N,N′,N′*-Tetramethyl-*p*-Phenylenediamine (TMPD) Cation Radical System.* TMPD$^{+\cdot}$ClO$_4^-$ is stable in both water and ethanol at pH less than 8. Phenothiazine picrate (PhZ$^{+\cdot}$Pic$^-$) is stable in water at pH less than 3, but it decomposes rapidly in ethanol at any pH. The reaction between PhZ and TMPD$^{+\cdot}$ was, therefore, investigated in 1 : 3 ethanol–water solvent in the presence of more than 10^{-3} M HCl, since PhZ hardly dissolves in pure

Table 1. EQUILIBRIUM CONSTANT OF THE PhZ AND TMPD$^{\dot{+}}$ SYSTEM

HCl/M	K_{ap}	$K_{ap}[H^+]^{-2}$/M^{-2}
4.5×10^{-3}	2.2×10^{-2}	1.1×10^{3}
9.1×10^{-3}	6.6×10^{-2}	0.80×10^{3}
18×10^{-3}	26×10^{-2}	0.80×10^{3}
35×10^{-3}	120×10^{-2}	1.0×10^{3}
67×10^{-3}	490×10^{-2}	1.1×10^{3}
		av. 0.96×10^{3}

water. The apparent equilibrium constant defined by

$$K_{ap} = [PhZ^{\dot{+}}][TMPD]_t/[PhZ][TMPD^{\dot{+}}]$$

is determined spectrophotometrically, adding a known amount of PhZ into a TMPD$^{\dot{+}}$ClO$_4^-$ solution at a constant HCl concentration. Parenthesis [ ]$_t$ represents the total concentration of TMPD, since TMPD is present as TMPDH$^+$ and TMPDH$_2^{++}$ in the pH region (1.3—2.5). [PhZ$^{\dot{+}}$] and [TMPD$^{\dot{+}}$] are determined, using the values ε_{437} (PhZ$^{\dot{+}}$) 5.7×10^3 and ε_{612} (TMPD$^{\dot{+}}$) 1.1×10^4, respectively.[5,6)] [TMPD]$_t$ is equated to the decrease of TMPD$^{\dot{+}}$. The presence of the isosbestic point at 520 nm confirms the view that the one-electron-transfer reaction occurs between PhZ and TMPD$^{\dot{+}}$.

$$PhZ + TMPD^{\dot{+}} \rightleftharpoons PhZ^{\dot{+}} + TMPD \qquad (1)$$

K_{ap} is remarkably dependent on [H$^+$] as seen in Table 1. The observed H$^+$ dependence of K_{ap} is ascribed to the protonation of TMPD in acidic media.

$$TMPD + H^+ \rightleftharpoons TMPDH^+;\ K_{a1} \qquad (2)$$

$$TMPDH^+ + H^+ \rightleftharpoons TMPDH_2^{++};\ K_{a2} \qquad (3)$$

Assuming that no protonation takes place on either PhZ or cation radicals, K_{ap} is expressed as

$$K_{ap} = (1+K_{a1}[H^+]+K_{a1}K_{a2}[H^+]^2)K$$

where K_{a1}, K_{a2} and K are the equilibrium constants of reactions (2), (3) and (1), respectively. K_{a1} and K_{a2} are determined by the pH titration of TMPD·2HCl with 0.02 M NaOH.

$$K_{a1} = (3.3\pm1)\times10^6\ M^{-1}$$

$$K_{a2} = (3\pm2)\times10^2\ M^{-1} \text{ in } 1:3 \text{ ethanol-water}$$

The relations $1 \ll K_{a1}[H^+] \ll K_{a1}K_{a2}[H^+]^2$ hold in the pH range (1.3—2.5). Thus K_{ap} is reduced to

$$K_{ap} = K_{a1}K_{a2}K[H^+]^2$$

This expression agrees with the observed H$^+$ dependence of K_{ap} (the last column, Table 1). The true equilibrium constant K of reaction (1) is determined to be 0.96×10^{-6} at 10 °C, which leads to 7.8 kcal mol^{-1} for the free energy change of reaction (1).

The relaxation time observed by the temperature-jump experiments (*ca.* 1 s) exceeds the duration within which a raised temperature is maintained (*ca.* 0.5 s). The rate of this system is, therefore, followed with a stopped-flow apparatus. The backward rate of reaction (1) is obtained by mixing the PhZ$^{\dot{+}}$Pic$^-$ solution with the TMPD·2HCl solution under the conditions of a large excess of TMPD·2HCl over PhZ$^{\dot{+}}$Pic$^-$. The decrease of PhZ$^{\dot{+}}$ is exponential with time, leading to the following rate equation (Table 2),

Table 2. PSEUDO FIRST-ORDER RATE CONSTANT k_{obsd} OF THE REACTION BETWEEN PhZ$^{\dot{+}}$ AND TMPD

a) Dependence of k_{obsd} on [TMPD]. The initial concentrations of PhZ$^{\dot{+}}$ and HCl are [PhZ$^{\dot{+}}$]$_0$ 3.0×10^{-6} M and [HCl]$_0$ 3.0×10^{-2} M, respectively.

TMPD/M	k_{obsd}/s^{-1}	k_{obsd}[TMPD]$^{-1}$/M^{-1} s^{-1}
1.4×10^{-4}	2.5	1.8×10^{4}
2.7×10^{-4}	4.2	1.6×10^{4}
4.1×10^{-4}	5.8	1.4×10^{4}
$6{\cdot}7\times10^{-4}$	7.8	1.2×10^{4}
		av. 1.5×10^{4}

b) Dependence of k_{obs} on [H$^+$]. [PhZ$^{\dot{+}}$]$_0$ 1.9×10^{-6} M and [TMPD]$_0$ 3.2×10^{-4} M.

HCl/M	k_{obsd}/s^{-1}	$k_{obsd}[H^+]^{-2}$/M^{-2} s^{-1}
9.4×10^{-2}	0.72	3.4×10^{-3}
5.6×10^{-2}	1.7	5.2×10^{-3}
3.8×10^{-2}	2.7	3.8×10^{-3}
1.9×10^{-2}	7.9	2.7×10^{-3}
		av. 3.8×10^{-3}

$$-d[PhZ^{\dot{+}}]/dt = k_b[TMPD]_t[H^+]^{-2}[PhZ^{\dot{+}}], \qquad (4)$$

$$k_b = 12 \pm 2\ M\ s^{-1}$$

where the contribution of the forward rate is neglected, since the equilibrium concentration of PhZ$^{\dot{+}}$ is zero.

The forward rate is obtained by mixing the TMPD$^{\dot{+}}$ClO$^-$ solution with the PhZ solution under the conditions of a large excess of TMPD$^{\dot{+}}$ClO$_4^-$ over PhZ. The pseudo first order rate constant of the decrease of TMPD$^{\dot{+}}$ is plotted against [H$^+$] in Fig. 1. Although k_{obsd} increases slightly with the increase in [H$^+$], it approaches a constant value k_f as [H$^+$] decreases. Thus the rate equation in the low [H$^+$] region is given by

$$-d[PhZ]/dt = k_f[PhZ][TMPD^{\dot{+}}] \qquad (5)$$

$$k_f = (8\pm2)\times10^3\ M^{-1}\ s^{-1}$$

The ratio k_f/k_b is equal to $(0.7\pm0.2)\times10^3$ M^{-2} which agrees with the equilibrium constant $K_{ap}[H^+]^{-2}$= 0.96×10^3 M^{-2} (Table 1).

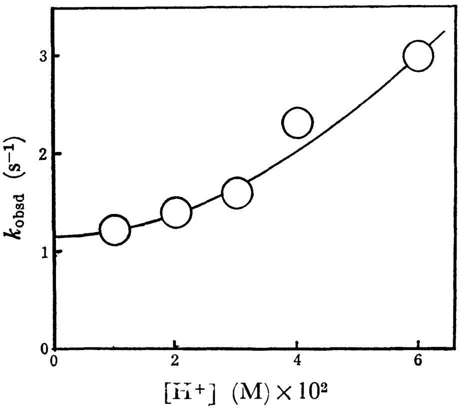

Fig. 1. The dependence of k_{obsd} on [H$^+$] in the reaction between TMPD$^{\dot{+}}$ and PhZ in 1 : 3 ethanol-water. [TMPD$^{\dot{+}}$]$_0$ 1.7×10^{-4} M and [PhZ] 9.0×10^{-6} M.

The H^+ dependence of the backward rate could be interpreted by the assumption that the overall reaction proceeds only through the neutral form of TMPD, and through neither $TMPDH^+$ nor $TMPDH_2^{++}$. Under this assumption, k_f and k_b in Eqs. (5) and (4) are related to the forward and backward rate constants of Reaction (1), $\overrightarrow{k}$ and $\overleftarrow{k}$, respectively, as follows,

$$k_f = \overrightarrow{k} \text{ and } k_b = \overleftarrow{k}/K_{a1}K_{a2}$$

Thus

$$\overrightarrow{k} = (8\pm2) \times 10^3\ \mathrm{M^{-1}\,s^{-1}}$$

$$\overleftarrow{k} = (1.4\pm0.7) \times 10^{10}\ \mathrm{mol^{-1}\,s^{-1}}.$$

The large uncertainty in $\overleftarrow{k}$ arises from the uncertainty of determining K_{a2}. The inertness of $TMPDH^+$ and $TMPDH_2^{++}$ in donating an electron was observed in both $TMPD^{+\cdot}$/DMPD and $TMPD^{+\cdot}$/TMPD systems.[7,8] The origin of the increase of k_f in the high $[H^+]$ region is uncertain.

B. Phenothiazine (PhZ) and N,N-*Dimethyl*-p-*Phenylenediamine (DMPD) Cation Radical System.* $DMPD^{+\cdot}ClO_4^-$ is less stable than $TMPD^{+\cdot}ClO_4$. It decomposes gradually in 1 : 3 ethanol–water solvents. The decomposition is, however, depressed in the presence of excess TMPD. K_{ap} is determined by adding $PhZ^{+\cdot}Pic^-$ to the DMPD solution (Table 3). $[DMPD^{+\cdot}]$ is calculated from the absorbance, using $\varepsilon_{555}=6.4\times10^3$.[6] In the $[H^+]$ range investigated, the monoprotonated form of DMPD is predominant.

Table 3. Equilibrium constant of the PhZ and $DMPD^{+\cdot}$ system

HCl/M	K_{ap}	$K_{ap}[H^+]^{-1}/M^{-1}$
6.3×10^{-4}	6.4×10^{-2}	1.0×10^2
$12\ \times10^{-4}$	$12\ \times10^{-2}$	1.0×10^2
$19\ \times10^{-4}$	$21\ \times10^{-2}$	1.1×10^2
$27\ \times10^{-4}$	$54\ \times10^{-2}$	2.0×10^2
		av. 1.0×10^2

$$\mathrm{DMPD}+\mathrm{H^+} \rightleftarrows \mathrm{DMPDH^+}\ ;\ K_{a1}$$

K_{ap} is related to K, the true equilibrium constant of the reaction, as follows.

$$\mathrm{PhZ} + \mathrm{DMPD^{+\cdot}} \rightleftarrows \mathrm{PhZ^{+\cdot}} + \mathrm{DMPD} \qquad (6)$$

$$K_{ap} = K K_{a1}[H^+]$$

where $K_{a1}[H^+]\gg1$ is assumed. Using $K_{a1}=(3.3\pm0.3)\times10^6$ which is determined by the pH titration, K is calculated to be

$$K = (3\pm1) \times 10^{-5}$$

$$\Delta F^\circ = 5.9\ \mathrm{kcal\,mol^{-1}}.$$

The rate of reaction (6) was studied with a temperature-jump apparatus. The pseudo first order rate constant defined by

$$\mathrm{d}\Delta[\mathrm{DMPD^{+\cdot}}]/\mathrm{d}t = -k_{obsd}\Delta[\mathrm{DMPD^{+\cdot}}]$$

is given as a function of $[H^+]$ (Fig. 2). Under the assumption that $DMPDH^+$ is inert in electron-transfer, k_{obsd} is expressed as

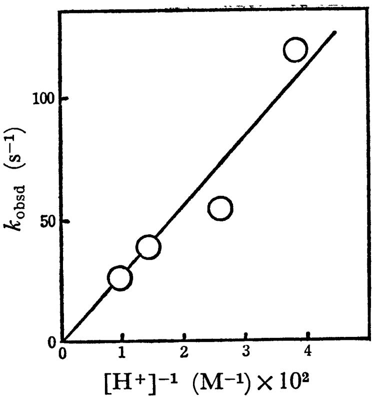

Fig. 2. The dependence of k_{obsd} on $[H^+]^{-1}$ in the reaction between PhZ and $DMPD^{+\cdot}$ in 1 : 3 ethanol–water. $[DMPDH^+]_e$ 2.5×10^{-4} M, $[PhZ]_e$ 3.1×10^{-5} M, $[DMPD^{+\cdot}]_e$ 8.9×10^{-5} M and $[PhZ^{+\cdot}]_e$ 8.9×10^{-5} M.

$$k_{obsd} = \overrightarrow{k}\{[\mathrm{PhZ}]_e+[\mathrm{DMPD^{+\cdot}}]_e\} + \overleftarrow{k}/(K_{a1}[\mathrm{H^+}]) \times \{[\mathrm{DMPDH^+}]_e+[\mathrm{PhZ^{+\cdot}}]_e\}_c \qquad (7)$$

where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the forward and backward rate constants, respectively, of reaction (6) and $[\ ]_e$ denotes the equilibrium concentration of each species at the elevated temperature. Fig. 2 shows the linear dependence of k_{obsd} on $1/[H^+]$, the second term in Eq. (7) being taken to be predominant. From the results and the relation $K=\overrightarrow{k}/\overleftarrow{k}$, we get

$$\overrightarrow{k} = (1.0\pm0.5) \times 15^5\ \mathrm{M^{-1}\,s^{-1}}$$

$$\overleftarrow{k} = (2.8\pm1) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}.$$

C. N,N-*Dimethyl*-p-*Phenylenediamine (DMPD) and* N,N,N′,N′,-*Tetramethyl*-p-*Phenylenediamine (TMPD) Cation Radical System.* A study of the TMPD/$DMPD^{+\cdot}$ system in water was reported previously.[7]

$$\mathrm{DMPD} + \mathrm{TMPD^{+\cdot}} \rightleftarrows \mathrm{DMPD^{+\cdot}} + \mathrm{TMPD} \qquad (8)$$

The forward and backward rate constants obtained are

$$\overrightarrow{k} = (4.2\pm2) \times 10^5\ \mathrm{M^{-1}\,s^{-1}},$$

$$\overleftarrow{k} = (1.5\pm0.2) \times 10^8\ \mathrm{M^{-1}\,s^{-1}}.$$

Since $\overleftarrow{k}$ which corresponds to the negative free energy change of reaction is apparently below a diffusion controlled limit in contrast to $\overleftarrow{k}$ in Reactions (1) and (6), the same system was studied in acetonitrile in order to clarify the role of solute-solvent interaction in electron-transfer.

$TMPD^{+\cdot}ClO_4^-$ is stable in acetonitrile. K for Reaction (8) in acetonitrile was, therefore, obtained spectrophotometrically by adding DMPD to the $TMPD^{+\cdot}ClO_4^-$ acetonitrile solution. The gradual decomposition of $DMPD^{+\cdot}$ causes about 40% error in K.

$$K = (3.8\pm1.5) \times 10^{-2}$$

$$\Delta F^\circ = 1.8\ \mathrm{kcal\,mol^{-1}}$$

The rate was measured with a temperature-jump apparatus. k_{obsd} values at various concentrations are iven in Table 4. Here k_{obsd} is defined by the relation

TABLE 4. k_{obsd} OF THE TMPD AND DMPD^{+} SYSTEM IN ACETONITRILE

$C^{a)}$/M	k_{obsd}/s^{-1}	k_{obsd} C^{-1}/M^{-1} s^{-1}
1.2×10^{-5}	7.0×10^{4}	6.0×10^{9}
2.5×10^{-5}	$12\ \times10^{4}$	5.0×10^{9}
6.4×10^{-5}	$19\ \times10^{4}$	3.0×10^{9}
$26\ \times10^{-5}$	$35\ \times10^{4}$	1.3×10^{9}
		av. $4\pm2\times10^{9}$

a) C is defined as $K([\mathrm{TMPD}^{+}]_e+[\mathrm{DMPD}]_e)+[\mathrm{TMPD}]_e+[\mathrm{DMPD}^{+}]_e$. $[\mathrm{TMPD}]_e$ $4.0-40\times10^{-5}$ M, $[\mathrm{DMPD}]_e$ $8-25\times10^{-3}$ M, $[\mathrm{DMPD}^{+}]_e$ $4.0-40\times10^{-5}$ M and $[\mathrm{TMPD}^{+}]_e$ $9-25\times10^{-6}$.

$$-\mathrm{d}\Delta[\mathrm{TMPD}^{+}]/\mathrm{d}t = k_{obsd}\Delta[\mathrm{TMPD}^{+}],$$

and expressed by

$$k_{obsd} = \overrightarrow{k}\{[\mathrm{TMPD}^{+}]_e+[\mathrm{DMPD}]_e\} + \overleftarrow{k}\{[\mathrm{TMPD}]_e+[\mathrm{DMPD}^{+}]_e\},$$

or

$$= \overleftarrow{k}[K\{[\mathrm{TMPD}^{+}]_e+[\mathrm{DMPD}]_e\} + \{[\mathrm{TMPD}]_e+[\mathrm{DMPD}^{+}]_e\}],$$

where $K=\overrightarrow{k}/\overleftarrow{k}$. $\overrightarrow{k}$ and $\overleftarrow{k}$ are determined to be

$$\overrightarrow{k} = (1.5\pm1)\times10^{8}\ \mathrm{M^{-1}\,s^{-1}},$$

$$\overleftarrow{k} = (4\pm2)\times10^{9}\ \mathrm{M^{-1}\,s^{-1}}.$$

$\overleftarrow{k}$ is almost a diffusion controlled rate constant (*ca.* 10^{10} M^{-1} s^{-1}) in acetonitrile. It is, therefore, concluded that the low value of $\overleftarrow{k}$ in water arises from the water-solute interaction, or most likely from the hydrogen-bonding of water on the nitrogen atoms of the amino groups in TMPD and DMPD.

D. N,N-*Dimethyl*-p-*Phenylenediamine (DMPD) and* N,N,N′,N′-*Tetramethylbenzidine (TMBZ) Cation Radical System.* Electrolytically generated TMBZ^{+} is stable in acetonitrile. Thus the equilibrium constant of reaction (9) is determined by adding DMPD to the solution containing TMBZ^{+} and excess TMBZ (Fig. 3).

$$\mathrm{DMPD} + \mathrm{TMBZ}^{+} \rightleftarrows \mathrm{DMPD}^{+} + \mathrm{TMBZ} \qquad (9)$$

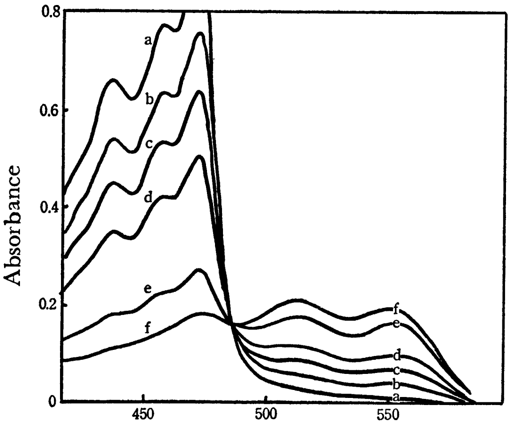

Fig. 3. The variation of the electronic spectrum of TMBZ^{+} with the addition of DMPD in acetonitrile. a) TMBZ^{+} only b)—e) DMPD added to the amount of 2.4×10^{-5} M f) no TMBZ^{+} left when 3.3×10^{-5} M DMPD added.

The isosbestic point at 486 nm confirms the occurrence of the one-electron-transfer from DMPD to TMBZ^{+}. The equilibrium constant is determined to be

$$K = (3\pm1)\times10^{3}$$

and

$$\Delta F^{\circ} = -4.6\ \mathrm{kcal\,mol^{-1}}$$

The molar extinction coefficient of TMBZ^{+} $\varepsilon_{472}=2.5\times10^{4}$ is also obtained from the result in Fig. 3. At a large excess of DMPD over TMBZ^{+}, the isosbestic point at 472 nm disappears, showing the decomposition of cation radicals. When the temperature-jump measurements were performed, only an increase of the transmittance was observed in the time range of 50 μs at 470—550 nm, corresponding to the decrease of DMPD^{+} at the temperature rise, no increase of TMBZ^{+} being observed at 400—470 nm. It is not certain whether the signal obtained actually corresponds to the electron-transfer reaction (9).

We have tried to obtain the forward rate of reaction (9) with a stopped-flow apparatus, using a 1 : 3 : 0.4 ethanol–water–acetonitrile solvent. TMBZ^{+} is stable in this solvent for $[\mathrm{H}^{+}]<10^{-3}$ M. In more acidic media, the fine structure in the electronic spectra of TMBZ^{+} in 430—480 nm is smoothed out, indicating the conversion of TMBZ^{+} into another species. Thus the rate was measured by mixing the TMBZ^{+} solution with the solution containing DMPD and HCl less than 10^{-3} M. The pseudo first-order rate constant of the decrease of TMBZ^{+} depends linearly on $1/[\mathrm{H}^{+}]$ (Fig. 4). Assuming that DMPDH^{+} is inert in donating an electron, the forward rate constant of reaction (9), $\overrightarrow{k}$, is obtained from the relation

$$k_{obsd} = \overrightarrow{k}/(K_{a1}[\mathrm{H}^{+}])\cdot[\mathrm{DMPDH}^{+}].$$

This leads to

$$\overrightarrow{k} = (6\pm2)\times10^{8}\ \mathrm{M^{-1}\,s^{-1}},$$

where K_{a1} is assumed to be equal to the one obtained

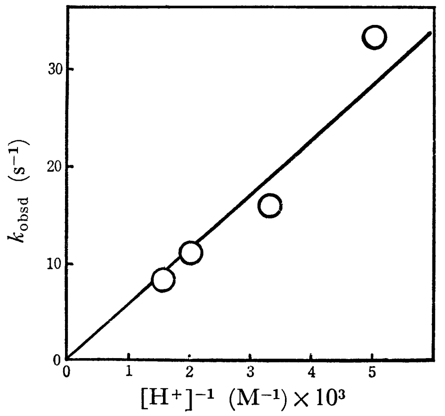

Fig. 4. The dependence of k_{obsd} on $[\mathrm{H}^{+}]^{-1}$ in the reaction between TMBZ^{+} and DMPD in 1 : 3 : 0.4 ethanol-water-acetonitrile. $[\mathrm{DMPD}]=2.0\times10^{-5}$ M. $[\mathrm{TMBZ}^{+}]_0=2.0\times10^{-6}$ M.

in 1 : 3 ethanol–water solvent. $\overrightarrow{k}$ is apparently below a diffusion controlled limit, which is analogous to the DMPD/TMPD$^{\dot{+}}$ system in water.

Discussion

The observed rate constants are plotted against the free energy change of reaction, ΔF° (Fig. 5). For the systems, PhZ/TMPD$^{\dot{+}}$, PhZ/DMPD$^{\dot{+}}$ in ethanol–water, and DMPD/TMPD$^{\dot{+}}$ in acetonitrile, the rate constants for $\Delta F^\circ < 0$ are nearly equal to a diffusion controlled limit. The systems are quite analogous to the reactions between tetracyanoquinodimethane anion radical and substituted *p*-benzoquinones in acetonitrile.[1] In the latter systems, too, the rate constants for $\Delta F^\circ < 0$ are in the range 10^9—10^{10} M^{-1} s^{-1} at 25±2 °C. Thus, the results may lead us to the conclusion that the electron-transfer between a free organic ion radical and a neutral molecule takes place with no activation free energy, as long as ΔF° is less than zero, unless the rigid solvation structure or ion pairing is formed around reactants. This conclusion is consistent with the results accumulated for the electron exchanges between free organic ion radicals and their parent molecules.[8]

It should be noted that the electron-transfer from TMPD to PhZ$^{\dot{+}}$ proceeds at the same rate of magnitude as from DMPD to PhZ$^{\dot{+}}$ in spite of the increased steric hindrance of TMPD due to additional methyl groups on nitrogen atoms. As far as the dimerizations of TMPD$^{\dot{+}}$ and DMPD$^{\dot{+}}$ are concerned, the interaction between two cation fragments is appreciably diminished because of the presence of methyl groups.[9] It is concluded that the electronic interaction which operates in the electron-transfer of cation radicals is of a considerably different nature from the one operating in dimerization.

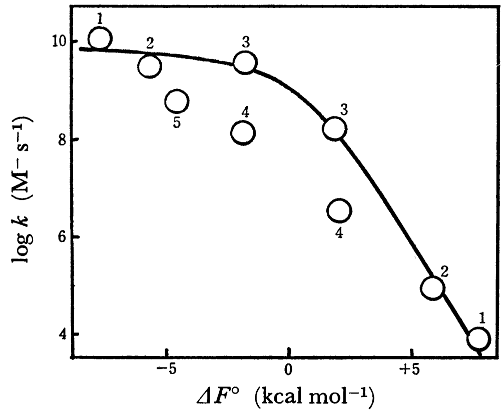

Fig. 5. The rate constants plotted against ΔF°: (1) PhZ/TMPD$^{\dot{+}}$, (2) PhZ/DMPD$^{\dot{+}}$, (3) DMPD/TMPD$^{\dot{+}}$ (in acetonitrile) (4) DMPD/TMPD$^{\dot{+}}$] (in water), (5) DMPD/TMBZ$^{\dot{+}}$.

In contrast to the above systems, the rate constants for the systems, DMPD/TMPD$^{\dot{+}}$ in water and DMPD/TMBZ$^{\dot{+}}$ in ethanol–water–acetonitrile, are about one order less than a diffusion controlled limit, even when ΔF° is negative. The origin for these slower rates is not certain. One possiblility is that the strong solvent-solute interaction causes an additional energy barrier to the electron-transfer as was reported for the electron exchange of nitrobenzene anion radical in acetonitrile/water.[10] In the systems showing slower rate constants, the nitrogen atoms on the amino groups of aromatic *p*-diamines seem to be hydrogen-bonded with water molecules. The difficulty in this interpretation lies in the fact that these hydrogen bonds do not slow down the rates of reactions between phenothiazine cation and TMPD or DMPD.

The author thanks Professor Masatoshi Fujimoto for his continuous encouragement, Dr. Mitsuyuki Soma for his valuable suggestions and Dr. Yoichi Iida for kindly supplying the materials. The work was supported by the Ministry of Education.

References

1) A. Yamagishi, *Chem. Lett.*, **1975**, 899. Parts of the results were presented at the 29th Annual Meeting of the Japan Chemical Society, Tokyo, April 1—4, 1975.

2) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

3) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", John Wiley and Sons, Inc., New York (1967), p. 454.

4) L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **68** 1747 (1943).

5) Y. Iida, This Bulletin, **44** 663 (1971).

6) L. Michaelis, M. P. Schubert, and S. Granick, *J. Amer. Chem. Soc.*, **61** 1981 (1939).

7) A. Yamagishi, *Chem. Lett.*, **1975**, 595.

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

9) S. Nakayama and K. Suzuki, This Bulletin, **46** 3694 (1973).

10) T. Layloff, T. Miller, R. N. Adams, H. Fah, A. Horsfield, and W. Proctor, *Nature*, **205**, 382 (1965).