Electron-Transfer Reactions from Hydroquinone Dianions to 10-Methylacridinium Ion and a Cobalt(III) Porphyrin

Shunichi FUKUZUMI* and Tomohiro YORISUE
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565
(Received September 17, 1991)

Electron transfer from various hydroquinone dianions ($X\text{-}Q^{2-}$) to 10-methylacridinium ion ($AcrH^+$) and $[Co(tpp)]^+$ (H_2tpp=tetraphenylporphyrin) occurs efficiently in deaerated MeCN to yield 10,10′-dimethyl-9,9′-biacridine [$(AcrH)_2$] and [Co(tpp)], respectively. The electron transfer results in the one-electron or two-electron oxidation of $X\text{-}Q^{2-}$, depending on the one-electron oxidation potentials of $X\text{-}Q^{2-}$ and $X\text{-}Q^{-\cdot}$.

The important role of quinones and hydroquinones in the electron-transport systems has stimulated many chemical and biochemical studies into their redox properties.[1] Perchloric acid ($HClO_4$) is a stronger acid in an aprotic solvent (MeCN) than in H_2O and it has been reported to enhance the reactivities of quinones as electron acceptors.[2,3] On the other hand, hydroxide ion, being a stronger base in MeCN than in H_2O,[4,5] may enhance the reactivity of hydroquinones ($X\text{-}QH_2$) as electron donors. However, there has so far been no report on electron transfer from hydroquinones to oxidants in the presence of OH^- in an aprotic solvent. In this study we have found that hydroquinone dianions ($X\text{-}Q^{2-}$) which are strong reductants are formed by the deprotonation of $X\text{-}QH_2$ with OH^- in MeCN. Then, we report herein that electron transfer from $X\text{-}Q^{2-}$ to 10-methylacridinium ion ($AcrH^+$) and $[Co(tpp)]^+$ (H_2tpp=tetraphenylporphyrin) occurs efficiently, accompanied by the one-electron or two-electron oxidation of $X\text{-}Q^{2-}$. The factors to control the occurrence of such electron transfer are examined based on the one-electron oxidation potentials of $X\text{-}Q^{2-}$ and $X\text{-}Q^{-\cdot}$.

Experimental

Hydroquinones used in this study were obtained commercially and purified by the standard methods. Cobalt(II) tetraphenylporphyrin ([Co(tpp)]) was prepared as reported in the literature.[6] The [Co(tpp)] was oxidized by dioxygen in the presence of HCl in methanol to obtain [Co(tpp)]Cl, which was purified by recrystallization from methanol.[7] The perchlorate salt ([Co(tpp)]ClO_4) was obtained by the metathesis of the chloride salt with $AgClO_4$ and recrystallized from toluene.[8] Tetramethylammonium hydroxide pentahydrate ($NMe_4OH\cdot 5H_2O$) was obtained from Sigma. A $NMe_4^+OH^-$ stock aqueous solution (0.10 mol dm^{-3}) was used for the preparation of various concentrations of $NMe_4^+OH^-$ acetonitrile solutions. Reagent grade acetonitrile was purified by the successive distillation (four times) over P_2O_5.

Since some semiquinone radical anions were readily oxidized by dioxygen, the reactions were carried out under strictly deaerated conditions. A continuous flow of Ar gas was bubbled through the MeCN solution containing hydroquinone (1.0×10^{-4} mol dm^{-3}) in a square quartz cuvette for 10 min. Then, the neck of the cuvette was sealed with a rubber septum and parafilm under Ar in order to ensure that air would not leak into the system. A microsyringe was used to inject 1—40 μL of a stock solution of $NMe_4^+OH^-$ (0.10 mol dm^{-3}), which was also deaerated, into the cuvette, and the neck of the cuvette was resealed with parafilm. Electronic absorption spectra were recorded by using a Union SM-401 spectrophotometer with a quartz cell (1-mm or 1-cm i.d.), which was placed in a thermostated compartment at 298 K. The yields of semiquinone radical anions produced in the reactions were determined from the absorbance at λ_{max} of semiquinone radical anions.[9-11] The conversion in the electron-transfer reactions with $AcrH^+$ were determined by the decrease of the absorption band due to $AcrH^+$ in MeCN (λ_{max}=358 nm, $\varepsilon_{max}=1.8\times10^4$ dm^3 mol^{-1} cm^{-1}). The formation of 10,10′-dimethyl-9,9′-biacridine [$(AcrH)_2$] in CD_3CN was identified by comparing the ^1H NMR spectrum with that of an authentic sample.[12] The NMR measurements were carried out by using a JEOL JNM-GSX-400 spectrometer (400 MHz). The reduction of $[Co(tpp)]^+$ to [Co(tpp)] was monitored by the decrease and increase of the absorption bands at 432 and 412 nm due to $[Co(tpp)]^+$ and [Co(tpp)] in MeCN, respectively.[13] The rates of electron-transfer reactions were measured by using a Union RA-103 stopped-flow spectrophotometer.

One-electron redox potentials of quinones (1.0×10^{-3} mol dm^{-3}) were determined by cyclic voltammetry (CV). The CV measurements were performed on a Hokuto Denko model HA-301 potentiostat-galvanostat at 298 K in deaerated MeCN containing 0.10 M $Bu_4N^+ClO_4^-$ as a supporting electrolyte using a platinum microelectrode and a saturated calomel electrode (SCE) as a reference.

In order to confirm the formation of radicals, the electron spin resonance (ESR) measurements were carried out by using a JEOL JES-SM-1 rapid mixing flow apparatus and a capirally cell. A deaerated MeCN solution containing tetrachlorohydroquinone (1.0×10^{-4} mol dm^{-3}) and $NMe_4^+OH^-$ (2.0×10^{-4} mol dm^{-3}) was mixed with a deaerated solution containing $AcrH^+$ (1.0×10^{-4} mol dm^{-3}). The ESR spectra were recorded with a JEOL X-band spectrometer (JES-ME-1X). The g values and hyperfine splitting constants were calibrated by using an Mn^{2+} ESR marker.

Results and Discussion

Various hydroquinone derivatives ($X\text{-}QH_2$) are readily deprotonated in the presence of $NMe_4^+OH^-$ in MeCN.

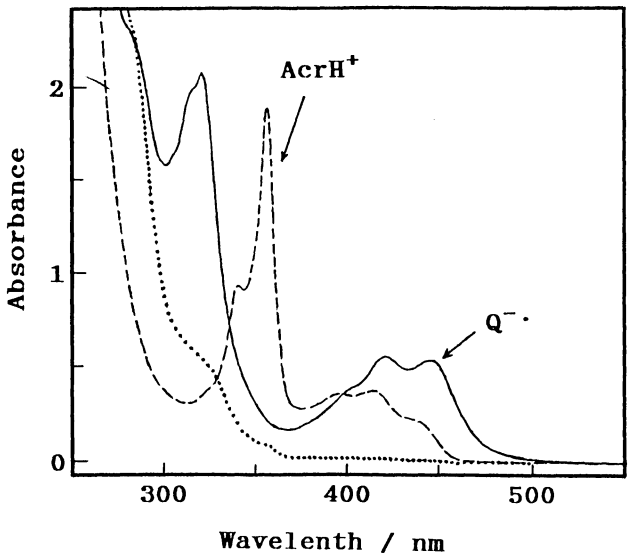


Fig. 1. Electronic spectra observed in the reaction of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}) with dfferent concentrations of hydroquinone (QH_2) in the presence of $NMe_4^+OH^-$ ($[NMe_4^+OH^-]=2[QH_2]$) in deaerated MeCN; $[QH_2]=0$ (---), 5.0×10^{-5} (·····), 1.0×10^{-4} mol dm^{-3} (—).

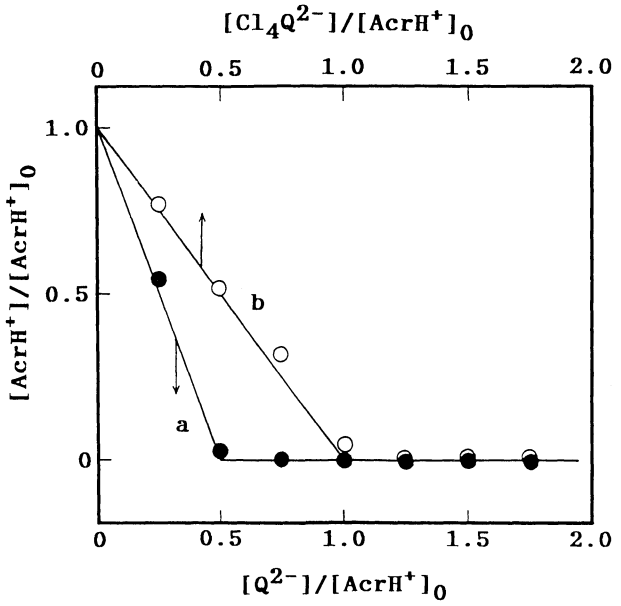
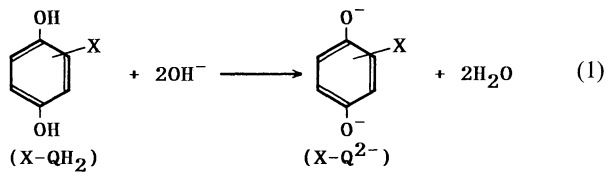


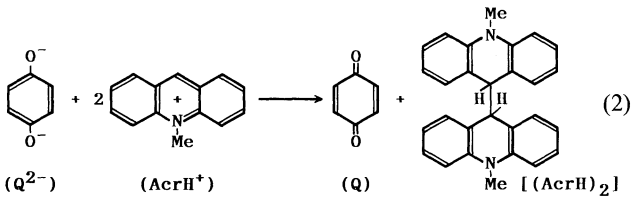
Fig. 2. Plots of the ratio of the $AcrH^+$ concentration after the reduction by (a) Q^{2-} (●) and (b) Cl_4Q^{2-} (○) in deaerated MeCN to the initial concentration of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}), $[AcrH^+]/[AcrH^+]_0$ vs. $[Cl_4Q^{2-}]/[AcrH^+]_0$ and $[Q^{2-}]/[AcrH^+]_0$, respectively.

No hydroquinone monoanion ($X\text{-}QH^-$) is formed when the OH^- concentration is smaller than the $X\text{-}QH_2$ concentration. The stoichiometry of the reaction of a hydroquinone derivative ($X\text{-}QH_2$) with OH^- is thus given by Eq. 1. The hydroquinone dianion ($X\text{-}Q^{2-}$) thus formed in deaerated MeCN is a much stronger reductant than the parent hydroquinone ($X\text{-}QH_2$) as demonstrated below.



(1)

Hydroquinone dianion (Q^{2-}), formed by the deprotonation of hydroquinone (QH_2) with OH^- in deaerated MeCN, can reduce $AcrH^+$ to yield *p*-benzoquinone (Q) and 10,10′-dimethyl-9,9′-biacridine [$(AcrH)_2$] as shown in Fig. 1.[14] The formation of the dimer [$(AcrH)_2$] was confirmed by the ^1H NMR spectra.[12] It should be noted that no reduction of $AcrH^+$ by Cl_4QH_2 has occurred in the absence of OH^-. The stoichiometry of the reaction is given by Eq. 2 as demonstrated in Fig. 2a, where one Q^{2-} reacts with two



(2)

$AcrH^+$ to yield the two-electron oxidized product, Q. When the amount of Q^{2-} is larger than the stoichiometric amount (more than one-half of $AcrH^+$), however, the formation of semiquinone radical anion ($Q^{-\cdot}$) is observed as shown in Fig. 1. The formation of $Q^{-\cdot}$ was also confirmed by the ESR spectrum (see Experimental).[11] No further increase in the absorbance of $Q^{-\cdot}$ (λ_{max} 422 nm) was observed by the addition of the excess amount of Q^{2-} to $AcrH^+$. The formation of $Q^{-\cdot}$ may be ascribed to the comproportionation reaction of Q^{2-} and Q (Eq. 3).

$$Q^{2-} + Q \longrightarrow 2Q^{-\cdot} \quad (3)$$

In contrast with the case of Q^{2-}, only one-electron oxidation of tetrachlorohydroquinone dianion (Cl_4Q^{2-}) to $Cl_4Q^{-\cdot}$ by $AcrH^+$ takes place as shown in Fig. 3, where the decrease in the absorbance due to $AcrH^+$ ($\lambda_{max}=358$ nm) is accompanied by the concomitant increase in the absorbance of the semiquinone radical anion $Cl_4Q^{-\cdot}$ ($\lambda_{max}=318$ and 447 nm). The stoichiometry (Eq. 4) is confirmed as shown in Fig. 2b, where one Cl_4Q^{2-} reacts with one $AcrH^+$ to yield $Cl_4Q^{-\cdot}$ and (1/2) $(AcrH)_2$.

$$Cl_4Q^{2-} + AcrH^+ \longrightarrow Cl_4Q^{-\cdot} + (1/2)(AcrH)_2 \quad (4)$$

When $AcrH^+$ is replaced by $[Co(tpp)]^+$, however, one Cl_4Q^{2-} can reduce two $[Co(tpp)]^+$ (Eq. 5) as shown in the spectral titration in Fig. 4a. When Cl_4Q^{2-} is replaced by 2,3-dicyanohydroquinone dianion ($(CN)_2Q^{2-}$) which is a

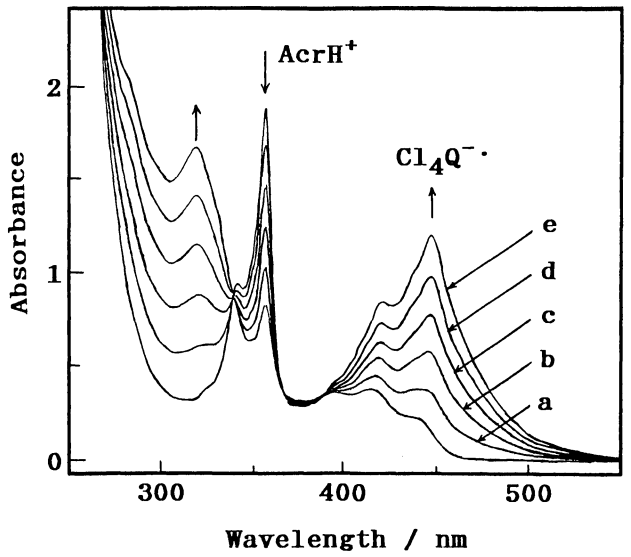


Fig. 3. Electronic spectra observed in the reaction of $AcrH^+$ (1.1×10^{-4} mol dm^{-3}) with different concentrations of tetrachlorohydroquinone (Cl_4QH_2) in the presence of $NMe_4^+OH^-$ ($[NMe_4^+OH^-]=2[Cl_4QH_2]$) in deaerated MeCN; $[Cl_4QH_2]$=(a) 1.8×10^{-5}, (b) 3.6×10^{-5}, (c) 5.4×10^{-5}, (d) 7.2×10^{-5}, (e) 9.0×10^{-5} mol dm^{-3}.

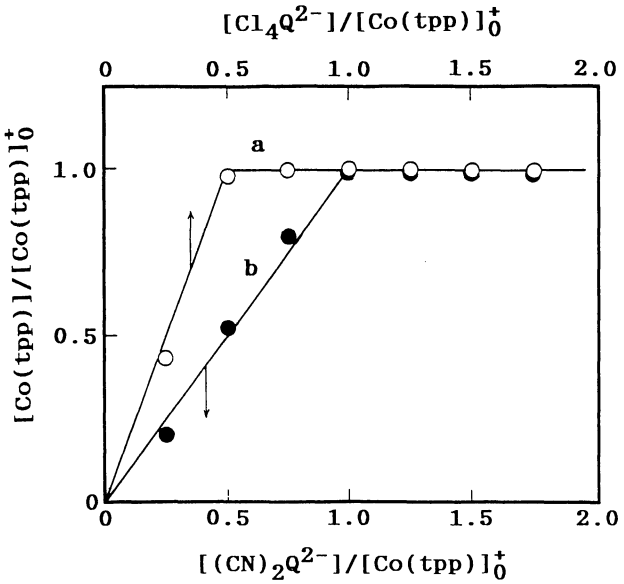


Fig. 4. Plots of the ratio of the [Co(tpp)] concentration formed in the reduction of $[Co(tpp)]^+$ by (a) tetrachlorohydroquinone dianion (Cl_4Q^{2-}, ○) and (b) 2,3-dicyanohydroquinone dianion ($(CN)_2Q^{2-}$, ●) to the initial concentration of $[Co(tpp)]^+$ (1.0×10^{-4} mol dm^{-3}) in deaerated MeCN, $[Co(tpp)]/[Co(tpp)]_0^+$ vs. $[Cl_4Q^{2-}]/[Co(tpp)]_0^+$ and $[(CN)_2Q^{2-}]/[Co(tpp)]_0^+$, respectively.

$$Cl_4Q^{2-} + 2[Co(tpp)]^+ \longrightarrow Cl_4Q + 2[Co(tpp)] \quad (5)$$

weaker oxidant than Cl_4Q^{2-}, $(CN)_2Q^{2-}$ can reduce only one $[Co(tpp)]^+$ (Eq. 6) as shown in Fig. 4b.

$$(CN)_2Q^{2-} + [Co(tpp)]^+ \longrightarrow (CN)_2Q^{-\cdot} + [Co(tpp)] \quad (6)$$

In the case of Cl_4Q^{2-}, the one-electron oxidized product, $Cl_4Q^{-\cdot}$ has no ability to reduce $AcrH^+$, but it can reduce $[Co(tpp)]^+$, resulting in the one-electron and two-electron oxidation of Cl_4Q^{2-} by $AcrH^+$ and $[Co(tpp)]^+$, respectively. In contrast, $Q^{-\cdot}$ can reduce $AcrH^+$, resulting in the two-electron oxidation of Q^{2-} by $AcrH^+$ to yield Q and $(AcrH)_2$ (Eq. 2). In any case the rates of electron transfer were too fast to be determined by using a conventional stopped-flow spectrophotometer.

Various hydroquinone dianions ($X\text{-}Q^{2-}$) undergo either the two-electron oxidation (Eq. 2) or the one-electron oxidation (Eq. 4) by $AcrH^+$ depending upon the substituent X, accompanied by the one-electron reduction of $AcrH^+$. Whether the one-electron or two-electron oxidation of $X\text{-}Q^{2-}$ takes place or not is solely determined by the Gibbs energy change of electron transfer from $X\text{-}Q^{2-}$ to $AcrH^+$ ($\Delta G^\circ_{et}/F$) and that from $X\text{-}Q^{-\cdot}$ to $AcrH^+$ ($\Delta G^\circ_{et'}/F$) being negative or positive as shown in Table 1. The $\Delta G^\circ_{et}/F$ and $\Delta G^\circ_{et'}/F$ values are obtained by Eqs. 7 and 8, where E°_{ox} and $E^\circ_{ox'}$ are the one-

Table 1. One-Electron Reduction of $AcrH^+$ by Hydroquinone Dianion Derivatives ($X\text{-}Q^{2-}$), Accompanied by the One-Electron or Two-Electron Oxidation of Hydroquinone Dianion Derivatives, and the Gibbs Energy Change of the Electron Transfer from $X\text{-}Q^{2-}$ ($\Delta G^\circ_{et}/F$) and $X\text{-}Q^{-\cdot}$ ($\Delta G^\circ_{et'}/F$) to $AcrH^+$ in MeCN at 298 K

$X\text{-}QH_2$	Reduction by $X\text{-}Q^{2-}$ [a]	$(\Delta G^\circ_{et}/F)/V$ [b]	Reduction by $X\text{-}Q^{-\cdot}$ [a]	$(\Delta G^\circ_{et'}/F)/V$ [c]
Tetramethylhydroquinone (Me_4QH_2)	Yes	−1.02	Yes	−0.41
2,6-Dimethylhydroquinone (Me_2QH_2)	Yes	−0.67	Yes	−0.15
Hydroquinone (QH_2)	Yes	−0.71	Yes	−0.08
Chlorohydroquinone ($ClQH_2$)	Yes	−0.54	Yes	0.09
Tetrachlorohydroquinone (Cl_4QH_2)	Yes	−0.28	No	0.44
2,3-Dicyanohydroquinone ($(CN)_2QH_2$)	No	0.43	No	0.71

a) Yes or no denotes whether the electron transfer takes place or not. b) Obtained by the relation, $\Delta G^\circ_{et}/F=E^\circ_{ox}-E^\circ_{red}$, where the E°_{ox} values of $X\text{-}Q^{2-}$ and the E°_{red} value of $AcrH^+$ (−0.43 V) are taken from Refs. 15 and 16, respectively. c) Obtained by the relation, $\Delta G^\circ_{et'}/F=E^\circ_{ox'}-E^\circ_{red}$, where the $E^\circ_{ox'}$ values of $X\text{-}Q^{-\cdot}$ are taken from Ref. 15.

Table 2. One-Electron Reduction of $[Co(tpp)]^+$ by Hydroquinone Dianion Derivatives ($X\text{-}Q^{2-}$), Accompanied by the One-Electron or Two-Electron Oxidation of Hydroquinone Dianion Derivatives, and the Gibbs Energy Change of the Electron Transfer from $X\text{-}Q^{2-}$ ($\Delta G^\circ_{et}/F$) and $X\text{-}Q^{-\cdot}$ ($\Delta G^\circ_{et'}/F$) to $[Co(tpp)]^+$ in MeCN at 298 K

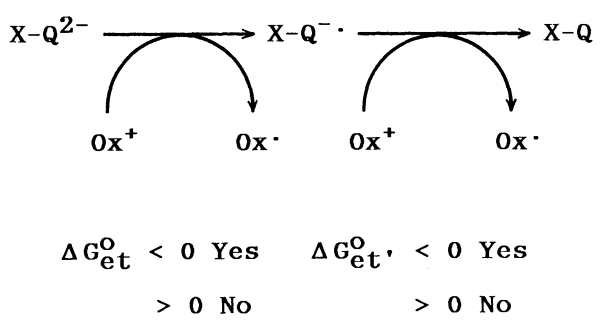
X-QH$_2$	Reduction by $X\text{-}Q^{2-}$ [a]	$(\Delta G^\circ_{et}/F)/V$ [b]	Reduction by $X\text{-}Q^{-\cdot}$ [a]	$(\Delta G^\circ_{et'}/F)/V$ [c]
Me_4QH_2	Yes	−1.80	Yes	−1.19
$MeQH_2$	Yes	−1.45	Yes	−0.93
QH_2	Yes	−1.49	Yes	−0.86
$ClQH_2$	Yes	−1.32	Yes	−0.53
Cl_4QH_2	Yes	−1.06	Yes	−0.34
$(CN)_2QH_2$	Yes	−0.35	No	−0.07

a) Yes or no denotes whether the electron transfer takes place or not. b) Obtained by the relation, $\Delta G^\circ_{et}/F = E^\circ_{ox} - E^\circ_{red}$, where the E°_{ox} values of $X\text{-}Q^{2-}$ and the E°_{red} value of $[Co(tpp)]^+$ are taken from Refs. 15 and 13, respectively. c) Obtained by the relation, $\Delta G^\circ_{et'}/F = E^\circ_{ox'} - E^\circ_{red}$, where the $E^\circ_{ox'}$ values of $X\text{-}Q^{-\cdot}$ are taken from Ref. 15.

$$\Delta G^\circ_{et}/F = E^\circ_{ox} - E^\circ_{red} \quad (7)$$

$$\Delta G^\circ_{et'}/F = E^\circ_{ox'} - E^\circ_{red} \quad (8)$$

electron oxidation potentials of $X\text{-}Q^{2-}$ and $X\text{-}Q^{-\cdot}$, respectively.[11-15] The one-electron reduction potential (E°_{red}) of $AcrH^+$ has previously been reported as −0.43 V vs. SCE.[16] Although the $\Delta G^\circ_{et}/F$ value for $ClQ^{-\cdot}$ is slightly positive (0.09 V), electron transfer from $ClQ^{-\cdot}$ to $AcrH^+$ takes place (Table 1). This is because the electron transfer is followed by the C–C bond formation of AcrH· to yield the dimer [$(AcrH)_2$]. When the $\Delta G^\circ_{et'}/F$ value is largely positive (0.44 V in the case of $Cl_4Q^{-\cdot}$), however, no electron transfer from $Cl_4Q^{-\cdot}$ to $AcrH^+$ occurs during the time scale (ca. 1 h at 298 K), since the back electron transfer from AcrH· to Cl_4Q may be much faster than the dimerization of AcrH·. This is the reason why the reduction of Cl_4Q^{2-} by $AcrH^+$ results in the formation of $Cl_4Q^{-\cdot}$ (Eq. 4) in contrast with the other cases (Eq. 2). By the same token, $X\text{-}Q^{2-}$ undergoes either the one-electron oxidation or two-electron oxidation by $[Co(tpp)]^+$ depending upon the substituent X, and signs of the ΔG°_{et} and $\Delta G^\circ_{et'}$ values being negative or positive determine whether one $X\text{-}Q^{2-}$ can reduce one or two $[Co(tpp)]^+$ or not as shown in Table 2. The one-electron oxidation or two-electron oxidation of $X\text{-}Q^{2-}$ by the oxidants (Ox^+: $AcrH^+$ and $[Co(tpp)]^+$), determined by the difference in their one-electron redox potentials is summarized in Scheme 1.



Scheme 1.

In conclusion, the strong basicity of OH^- in MeCN is demonstrated by the formation of hydroquinone dianions which can act as strong one-electron or two-electron donors towards $AcrH^+$ and $[Co(tpp)]^+$. Whether electron transfer from hydroquinone dianions and semiquinone radical anions to these oxidants takes place or not is mainly determined by the difference in the one-electron redox potentials of electron donors and acceptors.

The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) G. Dryhurst, K. M. Kadish, F. Scheller, and R. Renneberg, "Biological Electrochemistry," Academic Press, New York (1982), Vol. 1, p. 1; F. L. Crane, "Biological Oxidations," ed by T. P. Singer, Wiley, New York (1968), p. 533.

2) S. Fukuzumi, M. Ishikawa, and T. Tanaka, *J. Chem. Soc., Perkin Trans. 2,* **1989**, 1811.

3) S. Fukuzumi, M. Ishikawa, and T. Tanaka, *Tetrahedron,* **42**, 1021 (1986).

4) D. T. Sawyer and J. L. Roberts, Jr., *Acc. Chem. Res.,* **21**, 469 (1988).

5) S. Fukuzumi and T. Yorisue, *J. Am. Chem. Soc.,* **113**, 7764 (1991).

6) A. D. Adler, F. R. Longo, and V. Varadi, *Inorg. Synth.,* **16**, 213 (1976); A. Shirazi and H. M. Goff, *Inorg. Chem.,* **21**, 3420 (1982).

7) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakamoto, *Bull. Chem. Soc. Jpn.,* **49**, 3042 (1976).

8) C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Scheidt, K. Spartalian, and G. Lang, *J. Am. Chem. Soc.,* **101**, 2948 (1979).

9) The λ_{max} and ε_{max} values of various semiquinone radical anions in the visible region have been reported; K. B. Patel and R. L. Willson, *J. Chem. Soc., Faraday Trans. 1,* **69**, 814 (1973).

10) The electronic spectra of stable semiquinone radical anions

derived from *p*-chloranil, *p*-bromanil, 2,3-dicyano-*p*-benzoquinone, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone have been reported; Y. Iida, *Bull. Chem. Soc. Jpn.*, **43**, 2772 (1970); **44**, 1777 (1971).

11) S. Fukuzumi, N. Nishizawa, and T. Tanaka, *J. Org. Chem.*, **49**, 3571 (1984).

12) S. Fukuzumi, T. Kitano, and K. Mochida, *J. Am. Chem. Soc.*, **112**, 3246 (1990).

13) S. Fukuzumi, S. Mochizuki, and T. Tanaka, *Inorg. Chem.*, **28**, 2459 (1989).

14) The OH^- concentration was chosen as being equal or smaller than two-fold of the hydroquinone concentration in order to avoid the reaction of $AcrH^+$ with OH^-; S. Shinkai, T. Tsuno, and O. Manabe, *J. Chem. Soc., Perkin Trans. 2,* **1981**, 661.

15) D. H. Evans, "Encyclopedia of Electrochemistry of the Elements, Organic Section," ed by A. J. Bard and H. Lund, Marcel Dekker, New York (1978), Chap. XII-1. The E°_{ox} value of $(CN)_2Q^{2-}$ is determined as 0.0 V (vs. SCE) from the cyclic voltammogram of $(CN)_2Q$ in MeCN containing Bu_4NClO_4 (0.10 mol dm^{-3}) at 298 K (see Experimental).

16) S. Fukuzumi, Koumitsu, K. Hironaka, and T. Tanaka, *J. Am. Chem. Soc.*, **109**, 305 (1987).