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

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Electron transfer from various hydroquinone dianions (X-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-Q^{2-}, depending on the one-electron oxidation potentials of X-Q^{2-} and X-$Q^{-\cdot}$.

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-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-Q^{2-}) which are strong reductants are formed by the deprotonation of X-QH_2 with OH^- in MeCN. Then, we report herein that electron transfer from X-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-Q^{2-}. The factors to control the occurrence of such electron transfer are examined based on the one-electron oxidation potentials of X-Q^{2-} and X-$Q^{-\cdot}$.

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 ($NMe_4OH\cdot5H_2O$) 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-QH_2) are readily deprotonated in the presence of $NMe_4^+OH^-$ in MeCN.

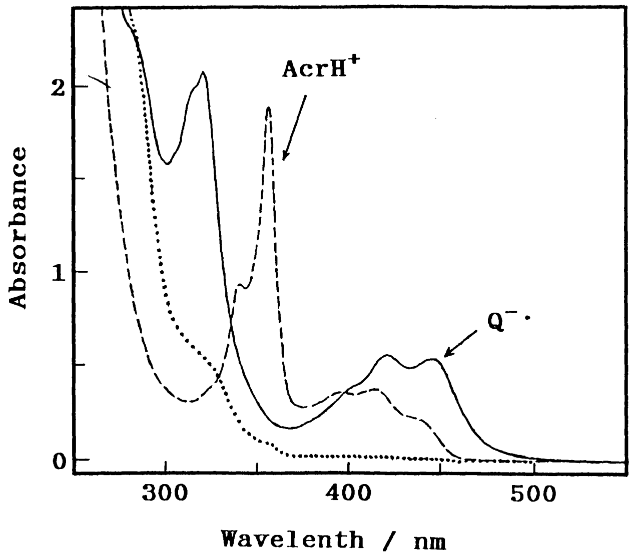


Fig. 1. Electronic spectra observed in the reaction of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}) with dfferent concentrations of hydroquinone (QH_2) in the presence of $NMe_4^+OH^-$ ($[NMe_4^+OH^-]=2[QH_2]$) in deaerated MeCN; $[QH_2]=0$ (---), 5.0×10^{-5} (······), 1.0×10^{-4} mol dm^{-3} (—).

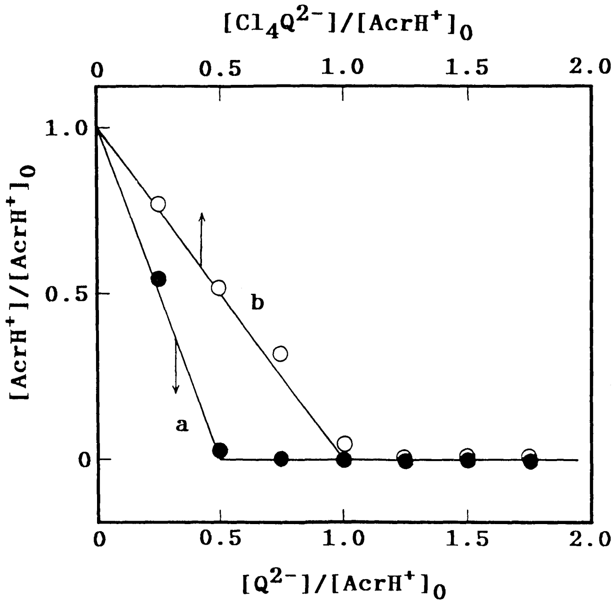
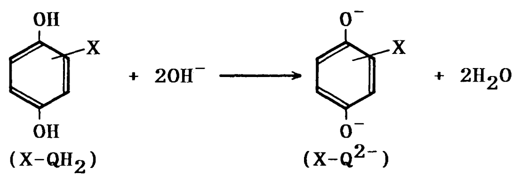


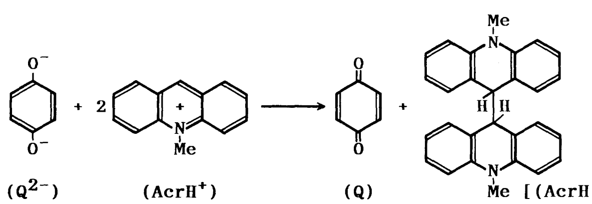
Fig. 2. Plots of the ratio of the $AcrH^+$ concentration after the reduction by (a) Q^{2-} (●) and (b) Cl_4Q^{2-} (○) in deaerated MeCN to the initial concentration of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}), $[AcrH^+]/[AcrH^+]_0$ vs. $[Cl_4Q^{2-}]/[AcrH^+]_0$ and $[Q^{2-}]/[AcrH^+]_0$, respectively.

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 $AcrH^+$ 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).



(2)

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

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 $Cl_4Q^{-\cdot}$ (λ_{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

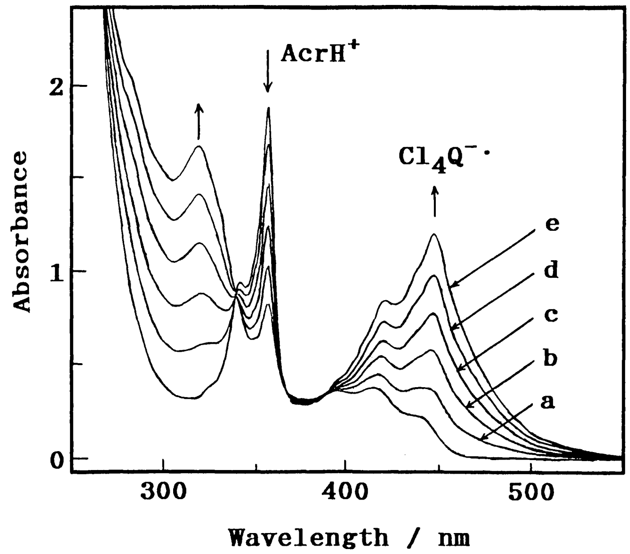


Fig. 3. Electronic spectra observed in the reaction of $AcrH^+$ (1.1×10^{-4} mol dm^{-3}) with different concentrations of tetrachlorohydroquinone (Cl_4QH_2) in the presence of $NMe_4^+OH^-$ ($[NMe_4^+OH^-]=2[Cl_4QH_2]$) in deaerated MeCN; $[Cl_4QH_2]$=(a) 1.8×10^{-5}, (b) 3.6×10^{-5}, (c) 5.4×10^{-5},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

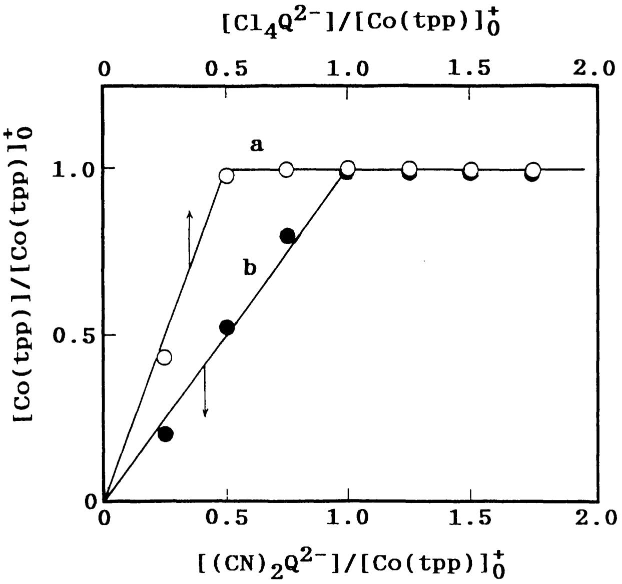


Fig. 4. Plots of the ratio of the [Co(tpp)] concentration formed in the reduction of $[Co(tpp)]^+$ by (a) tetrachlorohydroquinone dianion (Cl_4Q^{2-}, ○) and (b) 2,3-dicyanohydroquinone dianion ($(CN)_2Q^{2-}$, ●) to the initial concentration of $[Co(tpp)]^+$ (1.0×10^{-4} mol dm^{-3}) in deaerated MeCN,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

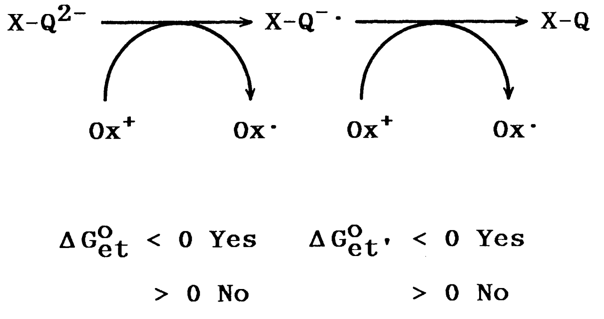
X-QH2	Reduction by $X\text{-}Q^{2-}$ [a]	$(\Delta G^\circ_{et}/F)/V$ [b]	Reduction by $X\text{-}Q^{-\cdot}$ [a]	$(\Delta G^\circ_{et'}/F)/V$ [c]
Me_4QH_2	Yes	−1.80	Yes	−1.19
$MeQH_2$	Yes	−1.45	Yes	−0.93
QH_2	Yes	−1.49	Yes	−0.86
$ClQH_2$	Yes	−1.32	Yes	−0.53
Cl_4QH_2	Yes	−1.06	Yes	−0.34
$(CN)_2QH_2$	Yes	−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.

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