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How Active *p*-Quinone Dianions Are as Proton Acceptors!

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Formation constants of two-point hydrogen-bonded complexes of *p*-quinone dianions with CH_3OH (1:2) have been successfully determined to be of the order of 10^4 dm^6 mol^{-2}. The origin of high reactivity of the dianions toward proton donors has been clarified experimentally and theoretically.

The chemistry of two-electron reduced dianions of organic molecules has received increased attention in recent years from both theoreticians and experimentalists.$^{1-5)}$ Organic dianions are usually so unstable even in aprotic solvents that direct observations on the physicochemical properties have been quite limited in number.$^{2-5)}$ Two-electron reduced products of quinones are, however, subject to a reversible electron transfer both in aprotic and protic solvents. This can inspire the reseach into characterization of organic dianions. The purpose of this paper is to get a deeper insight into the problem how active dianion species are as electron donors (proton acceptors), with the aid of both determining the formation constants of hydrogen-bonded complexes of *p*-quinone dianions ($PQ^{=}$) and investigating their electronic states.

The two-point hydrogen-bonding model is reasonable for the *p*-quinone (PQ) complexes with CH_3OH.$^{6,7)}$ UV spectra of PQ in CH_3CN systematically changed with isosbestic points on the addition of various concentrations of CH_3OH, indicating a 1:2 complex formation. Detail analysis$^{8)}$ of this spectral behavior yielded the formation constants (K) of the $PQ—(CH_3OH)_2$ complexes as summarized in Table 1. On the other hand, the sequential electroreduction of PQ as well as usual organic compounds$^{9)}$ in CH_3CN generates the corresponding anion radicals and dianions, as is seen from the reversible waves shown in Fig. 1. With increasing the concentration of CH_3OH ($[CH_3OH]_0$) both of the first and second half-wave reduction potentials ($E_{1/2,app}$) show a positive shift. The above pronounced propensity is observed for the second waves corresponding to the $PQ^{=}$ generation. When considered are an equilibrium involving a sequential two-step one-electron redox reaction of PQ, and the 1:2 complex formation of PQ and its reduced products with CH_3OH, the $[CH_3OH]_0$ dependence of $\Delta E_{1/2}$ (= $E_{1/2,app}$ - $E_{1/2}$, $E_{1/2}$ being the half-wave reduction potentials in the absence of CH_3OH) can be established as$^{10)}$

$$\Delta E_{1/2,1} = -\frac{RT}{F}\ln\frac{1 + K[CH_3OH]_0^2}{1 + K^{-}[CH_3OH]_0^2} \qquad (1)$$

$$\Delta E_{1/2,1} + \Delta E_{1/2,2} = -\frac{RT}{F}\ln\frac{1 + K[CH_3OH]_0^2}{1 + K^{=}[CH_3OH]_0^2} \qquad (2)$$

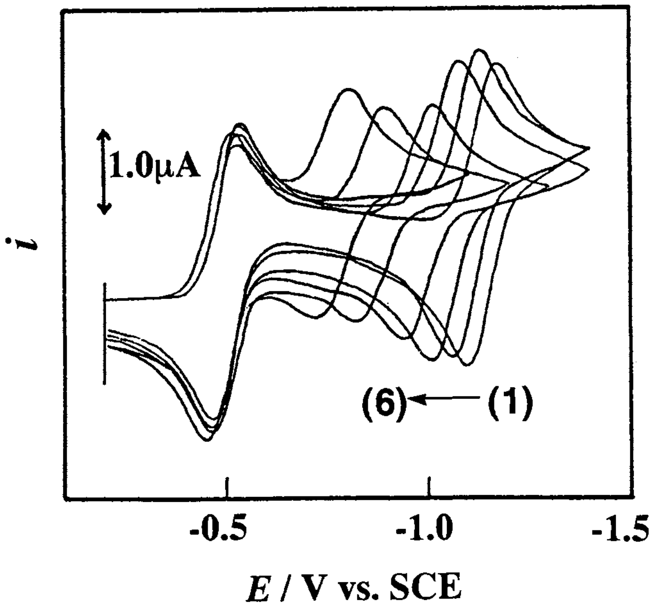

Fig. 1. Cyclic voltammograms of 2.49 X 10^{-4} mol dm^{-3} *p*-benzoquinone in the absence (1), and in the presence of 1.17 (2), 2.73 (3), 7.49 (4), 24.9 (5) and 49.9 X 10^{-2} mol dm^{-3} CH_3OH (6) in CH_3CN containing 0.1 mol dm^{-3} tetrapropylammonium perchlorate, recorded with a hanging mercury drop electrode at a scan rate of 100 mV s^{-1}.

where K^- and $K^=$ are the hydrogen-bonded complex formation constants of PQ^- and $PQ^=$ with CH_3OH, respectively. The subscripts 1 and 2 of $\Delta E_{1/2}$ denote the values for the first and second waves respectively. Non-linear regression analyses[10)] based on Eqs. 1 and 2 have made it possible to evaluate the K^- and $K^=$ values in low $[CH_3OH]_0$ region as shown in Fig. 2. The results are collected in Table 1. High $[CH_3OH]_0$ beyond 10^{-1} mol dm^{-3} allowed the $(\Delta E_{1/2,1} + \Delta E_{1/2,2})$ values to increase linearly against the $\log[CH_3OH]_0$ values without conformity to Eq. 2 (Fig. 2), which would be due to a proton-transfer reaction or a characteristic solvation of $PQ^=$ with CH_3OH. In the following, we will restrict our discussion within the scope of the hydrogen bonding. The quite large values of $K^=$ indicate that $PQ^=$ strongly attracts the weak proton-donors such as alcohols, compared to PQ, PQ^- and other organic molecules. Postulating that the *p*-benzoquinone dianion (*p*-$BQ^=$) is a closed-shell singlet species,[4)] the energy gradient method was adopted to partial geometry optimization of the hydrogen-bonded complexes within the framework of the HF calculation

Table 1. Formation Constants of Hydrogen-Bonded Complexes of *p*-Quinones with CH_3OH (1:2) at 25.0 ± 0.3°

Compounds	K/dm^6 mol^{-2}	$K^{-a)}$/dm^6 mol^{-2}	$K^=$/dm^6 mol^{-2}
p-Benzoquinone—$(CH_3OH)_2$	0.75	6	2.89 X 10^4
1,4-Naphthoquinone—$(CH_3OH)_2$	1.97	21	3.92 X 10^4
9,10-Anthraquinone—$(CH_3OH)_2$	1.31	15	6.57 X 10^4

a) Small values of $\Delta E_{1/2,1}$ and overlapping of the first and second waves in high $[CH_3OH]_0$ region cause somewhat low precision in estimation of K^-.

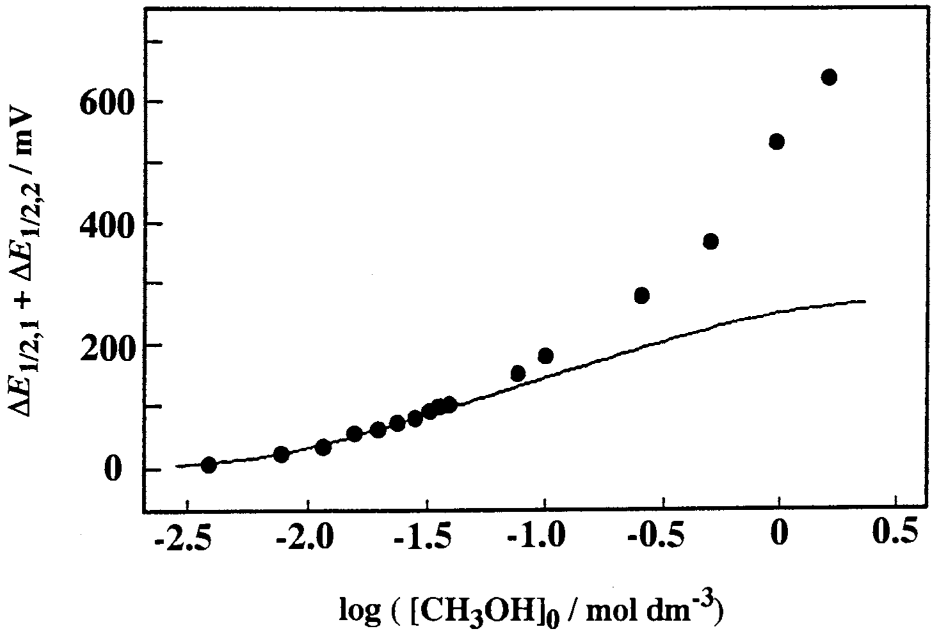

Fig. 2. Dependence of the ($\Delta E_{1/2,1} + \Delta E_{1/2,2}$) values of *p*-benzoquinone on the concentrations of CH_3OH. A curve represents the regression curve analyzed on the basis of Eq. 2.

using 4-31G basis sets (HF/4-31G). The results are listed in Table 2. The hydrogen-bond (CO····HO bond) distance in the *p*-BQ$^{=}$ complex with CH_3OH is much shorter than that in the *p*-BQ complex, and the atomic bond population is large enough to be considered as a value of a weak covalent bond. The formation energies of the hydrogen-bonded complexes have been estimated as 6.58 and 33.12 kcal mol^{-1} per hydrogen bond for the neutral and dianion species, respectively, by the use of the HF/4-31G geometries. These calculations have revealed that the bond of PQ$^{=}$ with CH_3OH is remarkably strong compared to usual

Table 2. Partially Optimized Geometries and Atomic Bond Population of the Hydrogen-Bonded Complexes of *p*-BQ and *p*-BQ$^{=}$ with CH_3OH Calculated by the HF/4-31G Energy Gradient Method

Compounds	Bond lengths/Å (Atomic bond population)			∠COH/°
	C=O	CO····HO	O-H	
p-BQ—CH_3OH	1.22 (0.431)	1.97 (0.029)	0.96 (0.240)	116.07
p-BQ$^{=}$—CH_3OH	1.34 (0.243)	1.43 (0.113)	1.05 (0.171)	128.83

hydrogen bonds involving O····H–O, and clearly explain the origin of the quite large observed $K^{=}$ values, considering enthalpy driven stabilization of a hydrogen bonding.6)

In conclusion, we have explicitly shown that $PQ^{=}$ possesses very strong proton accessibility. This might well explain that $PQ^{=}$ is easy to abstract protons *in vivo*, and further inspection of this model can give extensive insight into chemical reactions involving dianion intermediates.

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