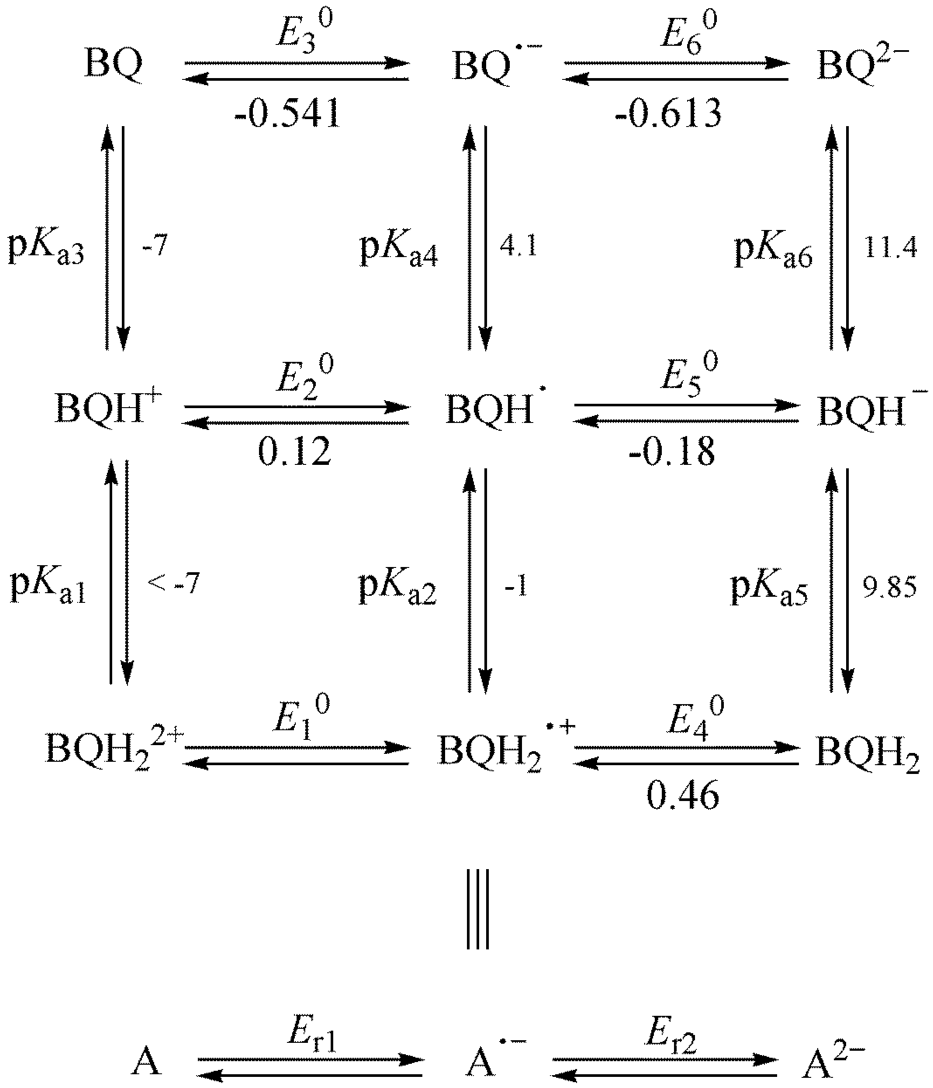
Supporting information

Enhanced electrochemical reactions of 1,4-benzoquinone at nanoporous electrodes

Je Hyun Bae, Yang-Rae Kim, R. Soyoung Kim and Taek Dong Chung*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea



Scheme S1 Laviron's analysis using a nine-membered square scheme describing 1,4-benzoquinone (BQ) reduction in buffered aqueous solutions.[1] This description consists of two ladder schemes, which involve three different protonation states for each redox state represented by A, $A^{\cdot -}$ and A^{2-}. Each ladder scheme is shown to be equivalent to a simple one-electron reaction having apparent standard potentials E_{r1} and E_{r2} by assuming that proton transfer reactions are at full equilibrium. All potentials taken from the literature[2] are given relative to mercury sulfate electrode (+ 0.64 V vs. NHE).

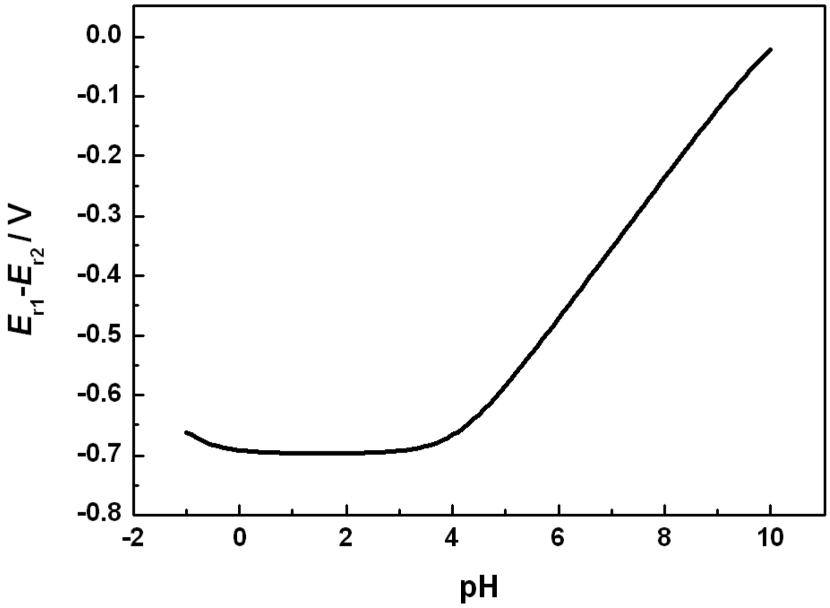


Fig. S1 E_{r1} - E_{r2} as a function of the pH. E_{r1} - E_{r2} was calculated by eqns (S1) and (S2)[1] employing E^0 and pK_a values given in Scheme S1. pK_{a1} = -7.

$$E_{r1} = E_2^0 + \frac{RT}{F}\ln\left(\frac{\frac{K_{a4}}{[\mathrm{H}^+]}+1+\frac{[\mathrm{H}^+]}{K_{a2}}}{\frac{K_{a3}}{[\mathrm{H}^+]}+1+\frac{[\mathrm{H}^+]}{K_{a1}}}\right) \quad \text{(S1)}$$

$$E_{r2} = E_5^0 + \frac{RT}{F}\ln\left(\frac{\frac{K_{a6}}{[\mathrm{H}^+]}+1+\frac{[\mathrm{H}^+]}{K_{a5}}}{\frac{K_{a4}}{[\mathrm{H}^+]}+1+\frac{[\mathrm{H}^+]}{K_{a2}}}\right) \quad \text{(S2)}$$

Simulation results of cyclic voltammograms for 5 mM BQ and BQH_2 in 1 M $HClO_4$ at 50 mV s^{-1} using flat Pt and L_2ePt

Table S1. Values for the standard potentials and electron and proton transfer rates for the simulation of BQ and BQH_2

		$E_{\text{1st step}}{}^{0}$ / V vs. MSE	$E_{\text{2nd step}}{}^{0}$ /V vs. MSE	k_{ET} / cm s^{-1}	k_{PT} or k_{dPT} / M^{-1} s^{-1}
Reduction	Flat Pt	$E_3{}^0 = -0.32$	$E_5{}^0 = 0.04$	0.1	$1\text{x}10^7$
	L_2ePt			10	$1\text{x}10^{10}$
Oxidation	Flat Pt	$E_4{}^0 = 0.29$	$E_2{}^0 = -0.05$	0.5	$1\text{x}10^7$
	L_2ePt			10	$1\text{x}10^{10}$

The reduction wave of BQ at a flat Pt was fitted based on ECEC mechanism. A variety of E^0, k_{ET}, and k_{PT} values were tried to fit the voltammogram obtained at a flat Pt. All the other parameters including pK_a values and diffusion coefficients were used as described in the Experimental section. The fitting process started with values for $E^{0'}$s taken from the literature, which were carefully varied to find the best fit. Throughout the fitting process, the value of $E_3{}^0$ - $E_5{}^0$ in the literature (see the Scheme S1), -360 mV, was kept constant since this value was critical enough to determine the shape of cyclic voltammograms. The k_{ET} value obtained, 0.1 cm s^{-1}, was confirmed to be plausible referring to the EE simulation result (Fig. S2), and k_{PT} was tuned at a relatively low but reasonable value according to the literature.[3]

However, E^0 values obtained from the fitting deviated from the literature values given by Laviron. We can find a clue to explain this by considering how the E^0 values had been obtained by Laviron. In his theory, by assuming proton transfer reactions are fast enough to be at full equilibrium, the two-electron/two-proton transfer reaction was simplified as a two-electron transfer reaction with apparent standard potentials E_{r1} and E_{r2}. These apparent standard potentials were given by solution pH, individual E^0, and pK_a values in Laviron’s scheme as seen in eqns

(S1) and (S2). The individual E^0's were calculated from the E_{r1} and E_{r2} values that were experimentally determined.

In contrast to Laviron's frame, the rate of protonation and deprotonation reactions were not deduced but explicitly addressed in our simulation study. When kinetics is slow, the apparent peak potentials for a voltammogram will appear at more negative potential for reduction and more positive potential for oxidation for the same standard potential because more overpotential is required. Thus, we can suppose that if proton transfer reactions are not fast enough in reality, Laviron would have obtained more negative and positive E^0's for reduction and oxidation, respectively, from the experimentally observed apparent standard potentials E_r's. In fact, the E^0's for reduction and oxidation obtained by fitting our voltammograms were more positive and negative than Laviron's E^0's as explained by this scenario. Moreover, the smaller the proton transfer rate constants employed for fitting were, the larger was the magnitude of difference between Laviron's E^0's and ours.

Similarly, the oxidation wave of BQH_2 was first fitted for the voltammogram at a flat Pt with ECEC mechanism by varying E^0, k_{ET}, and k_{dPT}. For oxidation, the $E^{0'}$s corresponded to E_2^0 and E_4^0 in Scheme S1, and the condition E_2^0 - E_4^0 = 340 mV was kept invaiable. The k_{ET} value obtained, 0.5 cm s^{-1}, was likewise checked by comparing with the EE simulation result (Fig. S2).

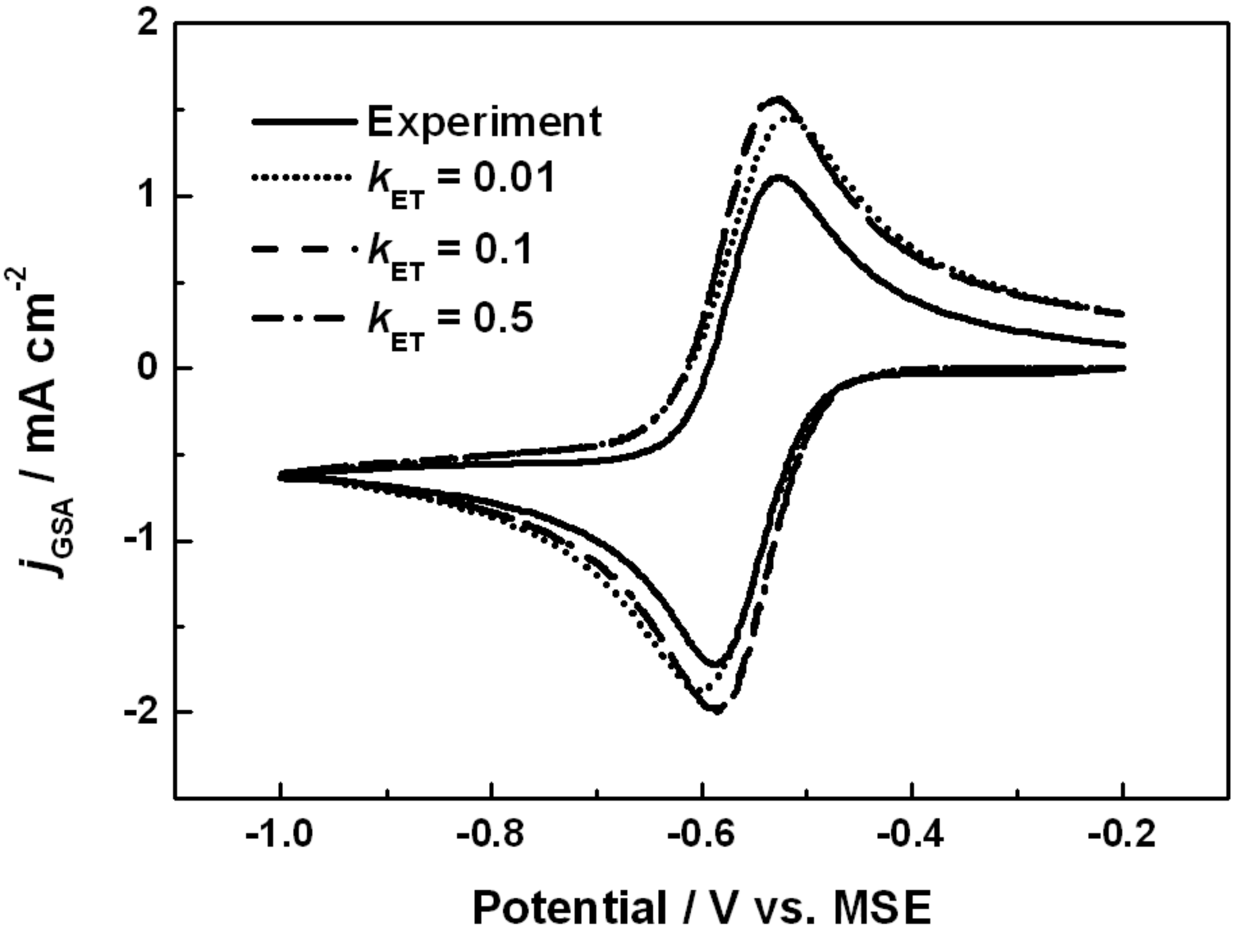


Fig. S2 Cyclic voltammograms for 5 mM BQ in 1 M $NaClO_4$ at 50 mV s^{-1}. The experimental data was fitted based on EE mechanism as a function of k_{ET}. The experimental cyclic voltammogram in 1 M $NaClO_4$ appeared to be nearly reversible electrochemical reaction. When k_{ET} was set to be 0.01 cm s^{-1}, the simulated curve deviated from experimental data. Augmenting k_{ET} up to 0.1~0.5 cm s^{-1} made the simulated voltammograms changed no more, leading to the best fit in shape.

References

1 E. Laviron, *J. Electroanal. Chem.*, 1983, **146**, 15-36.

2 E. Laviron, *J. Electroanal. Chem.*, 1984, **164**, 213-227.

3 M. Eigen, *Discuss. Faraday Soc.*, 1965, 7-15.