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Density Functional Theoretical Study on the Reduction Potentials of Catechols in Water

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Recently, the green chemical synthesis of Au nanoparticles, in which phytochemicals were used to reduce $AuCl_4$, was reported.[1] Gallic acid (3,4,5-trihydroxy benzoic acid; GA) is the one of these nonnutritive components in a plant-based diet. The standard reduction potential, E^0, is the one of the physicochemical properties used to understand the reducing ability and antioxidant behavior of GA. In this study, a computational scheme to evaluate the E^0 value of substituted benzene diol species is described and the change in E^0 upon a change in the substitituent was discussed.

The two electron reduction of 1,2-benzoquinone into 1,2-benzenediol, as shown in Scheme 1, was considered.

The calculation scheme used to evaluate the reduction potential is similar to that reported previously to determine the pK_a.[2-6] The Gibbs energy of the reduction of benzoquinone (BQ) to its oxidation product, benzene-1,2-diols (CAT), is given as follows:

$$\Delta G^0_{\mathrm{R,aq}} = \Delta G^0_{\mathrm{aq}}(\mathrm{CAT}) - \Delta G^0_{\mathrm{aq}}(\mathrm{BQ}) - 2\Delta G^0_{\mathrm{aq}}(\mathrm{H}^+) - 2\Delta G^0_{\mathrm{aq}}(\mathrm{e}^-) \quad (1)$$

The corresponding reduction potential, E^0, is given by the following equation:

$$E^0 = \Delta G^0_{\mathrm{R,aq}}/(-2F), \quad (2)$$

where F is the Faraday constant and the factor of 2 signifies a two electron process.

The standard free energy of each species (BQ and CAT) in an aqueous solution, ΔG^0_{aq}, can be expressed as the sum of the gas-phase standard free energy, ΔG^0_{g}, and the standard free energy of solvation in water, $\Delta G^0_{\mathrm{solv}}$:

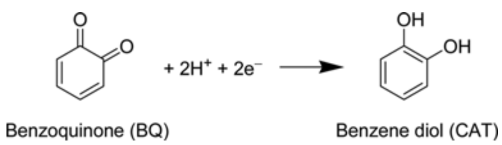
$$\Delta G^0_{\mathrm{aq}} = \Delta G^0_{\mathrm{g}} + \Delta G^0_{\mathrm{solv}}. \quad (3)$$

The standard free energy of each species in the gas phase, ΔG^0_{g}, was obtained using the following equation:

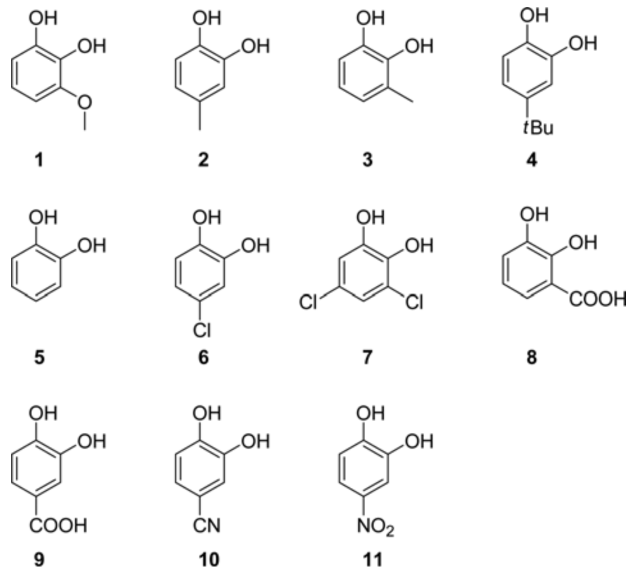
$$\Delta G^0_{\mathrm{g}} = E_{0\,\mathrm{K}} + \mathrm{ZPE} + \Delta\Delta G_{0\rightarrow 298\mathrm{K}}. \quad (4)$$

The total energy of the molecule at 0 K ($E_{0\,\mathrm{K}}$) was calculated at the geometry optimized with quantum mechanics (QM). A harmonic oscillator-rigid rotor approximation was used for the calculation. The zero-point energy (ZPE) and vibrational contribution to the change in Gibbs energy at temperatures from 0 K to 298 K ($\Delta\Delta G_{0\rightarrow 298\,\mathrm{K}}$) were calculated from the frequencies obtained from the QM calculations. The translational and rotational free energy contribution was also calculated as an ideal gas approximation. The sum of the contribution of the Gibbs energy from proton and electron, $2\Delta G^0_{\mathrm{aq}}(\mathrm{H}^+)+2\Delta G^0_{\mathrm{aq}}(\mathrm{e}^-)$, was used as a fitting parameter to ensure the best fit to the experimental data, as reported in previous pK_a calculations.

All QM calculations were performed using Jaguar v5.5 quantum chemistry software.[7] The B3LYP[8-11] variation of DFT was used for geometry optimization and to calculate the energies of the molecules. Calculations of the vibration frequencies are generally time-consuming. Therefore, a small basis set of the 6-31G** basis set was used to optimize the geometry and calculate the vibration frequencies. The number of imaginary frequencies was monitored to determine if the optimized structure of each chemical species corresponds to the true minimum. The Poison-Boltzmann continuum model[12,13] was used to describe the solvent (water) at the B3LYP/6-31** level.



Scheme 1



Scheme 2

Table 1. Experimental and calculated E^0 of the benzene diols examined in this study

	Standard reduction potential, E^0			
	exp[a]	calc (sol)[b]	fitted[c]	calc (gas)[d]
1	0.730	0.925	0.736	0.739
2	0.739	0.921	0.733	0.684
3	0.749	0.952	0.757	0.694
4	0.750	0.930	0.739	0.690
5	0.792	0.969	0.770	0.747
6	0.792	1.026	0.816	0.742
7	0.821	1.032	0.820	0.796
8	0.870	1.111	0.884	0.933
9	0.885	1.111	0.884	0.828
10	0.924	1.160	0.923	0.853
11	0.950	1.188	0.944	0.883

[a]reference.[15] [b]from the calculated results using B3LYP/6-31G** including the solvation energy calculations. [c]fitted with the correlation result. [d]from the calculated results using B3LYP/6-31G** with gas phase calculations

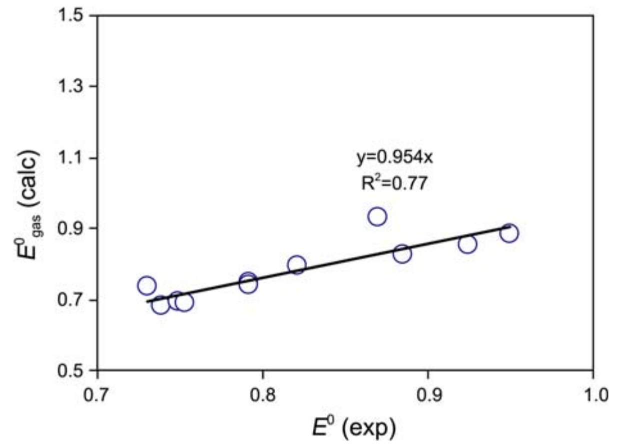


Figure 1. Standard reduction potential of the benzene diols from gas-phase calculations.

The following 11 benzenediol derivatives (Scheme 2) were used to develop the computational method.

First, the E^0 values of the benzene diols were compared with the theoretical estimation based on the Gibbs energy for the reduction reaction in the gas phase, $\Delta G^0_{\rm R,gas}$. Figure 1 shows the E^0 values of the 11 molecules as a function of the theoretical values listed in Table 1. Gas phase dissociation showed a correlation with the experimental data ($R^2 = 0.77$) with a slope of 0.954. A much better correlation ($R^2 = 0.97$) with a slope of 1.2577 was obtained by considering the solvation energy, as shown in Figure 2. As in the case of the pK_a evaluation in an aqueous solution,[14] the results showed that a solvation energy calculation is essential for making an accurate E^0 evaluation.

From a fit of the same level of calculation, the standard reduction potential E^0 of GA was estimated to be 0.863 V, which shows that GA is more effective in reducing Au nanoparticles than 3,4-dihydroxy benzoic acid (**9**) with E^0 = 0.884 V. This is in good agreement with the experimental findings from previous work on gold nanoparticles.[1]

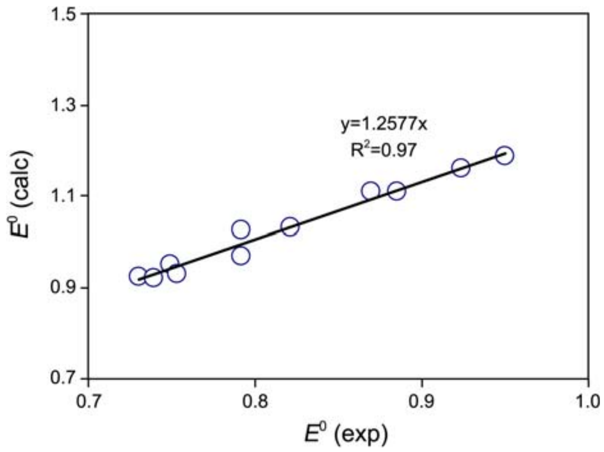


Figure 2. Standard reduction potential of the benzene diols with the solvation energy calculations.

In summary, B3LYP variation of DFT calculation coupled with a Poisson-Boltzmann continuum solvent model was performed to calculate the standard reduction potentials of benzene diols in water. The computation scheme was similar to the scheme used to calculate the pK_a. The gas phase thermodynamics results did not show a strong correlation with the experimental values. On the other hand, inclusion of the solvation energy term resulted in a good correlation with the experimental data.

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