



Substituent effects on the redox potentials of dihydroxybenzenes: theoretical and experimental study



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ABSTRACT

The redox reactions of *p*-hydroquinone and pyrocatechol undergo a two-proton-two-electron process in aqueous solution. We calculated their redox potentials at the B3LYP/6-311+G(d,p) level, and verified the values by employing cyclic voltammetry experiments. Then we selected seven substituent groups (–F, –Cl, –OH, –COOH, –CN, –NH₂, and –NO₂ groups) to systematically investigate the substituent effect, including the sort, position, and number of the substituent, on the redox potentials of *p*-hydroquinone and pyrocatechol. The calculated results show that –NH₂ and –OH groups can decrease the redox potentials, while –F, –Cl, –COOH, –CN, and –NO₂ groups increase the potential values of *p*-hydroquinone and pyrocatechol. The calculations can accurately predict the substituent effects on the redox potentials of pyrocatechol and *p*-hydroquinone. We would expect that the accurate calculation results for the model systems could be applied in the prediction of electrode potentials of other molecules.

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1. Introduction

Phenolic compounds are important chemical materials and intermediates with high toxicity in industrial chemistry.¹ They can be easily oxidized to electroactive organic compounds, quinones, when in contact with oxygen. Quinones are the most important pigments occurring naturally and further studied as antibiotics and anticancer agents in chemistry, biochemistry, and electrochemistry.^{2–4} The standard electrode potential (E°) can be used to rank the stability of a molecule, in other word, its potential to donate or accept an electron. The biological activities of dihydroxybenzene compounds are closely related to their standard redox potentials, E° , so it is important to obtain their accurate E° values.⁵ Dihydroxybenzene derivatives that have been used as bioreductive agents are selective for tumor cells by exploiting the known difference in the availability of oxygen between normal and transformed cells. In the redox process of dihydroxybenzene systems, the electron density of the system undergoes important changes,

which varies depending on the involved substituent. To evaluate the primary stages of the reduction process and how they are affected by a given substituent, it is essential to predict E° values and prepare compounds with optimum E° values by chemical modifications.

Cyclic voltammetry (CV) is the most popular experimental method for measuring E° , which reveals a great deal of information about electrochemical systems and processes.^{6–8} However, for irreversible processes the experimental situation is complicated, and accurate E° values can only be obtained through some sophisticated techniques such as pulse radiolysis.^{6–8} Therefore, it is quite inconvenient to obtain reliable experimental E° data in some cases.⁵ Given the limitation of the experimental methods, chemists have developed theoretical approaches calculating E° values for various materials including phenols^{9–11} in solution. Such calculated results suggest that density functional theory (DFT) method can correctly predicate E° values of molecules.

In the present work, we studied the substituent effects on the redox potentials of dihydroxybenzene by employing DFT method. Dihydroxybenzene includes three isomers, *p*-hydroquinone, pyrocatechol, and resorcinol. Pyrocatechol and *p*-hydroquinone have similar physical and chemical properties, while resorcinol is different from the others in terms of oxidation properties because the

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conjugated structure will be destroyed upon the oxidation of the two –OH groups. Therefore, we only selected pyrocatechol and *p*-hydroquinone as model molecules to investigate the substituent effect. We first calculated the E° values of pyrocatechol and *p*-hydroquinone at B3LYP/6-311+g(d,p) level. To verify the theoretical level we used to calculate E° values, we carried out the CV experiments. The experimental E° values of *p*-hydroquinone and pyrocatechol were obtained from the relationship between the conditional potentials ($E^{\circ'}$) and pH. Then we chose seven substituent groups (–F, –Cl, –OH, –COOH, –CN, –NH₂, and –NO₂ groups) to investigate the substituent effects on the E° values of pyrocatechol and *p*-hydroquinone. At last, the correlations between the calculated energies of HOMO, LUMO, and E° values were investigated to facilitate further prediction on the E° values of unknown electroactive materials.

2. Computational details

The appropriate theoretical level can accurately predict the redox potentials of electroactive materials according to many previous reports.^{9–13} In the present work, all computations for the calculations of E° were carried out at B3LYP/6-311+G(d,p) theoretical level with Gaussian 09 package.¹⁴ In aqueous solution, both continuum model of solvation and conductor-like polarizable continuum model (CPCM) with the UAHF radii were used to obtain the optimized geometries at the same level. In search of the relationships between orbital energies and E° , both HOMO and LUMO energies of the studied phenols were calculated at the theoretical level of MP2/6-311+g(d,p) in aqueous solution. To guarantee the rationality of calculations for E° and the orbital energies of HOMO and LUMO, the stable molecular geometries of all species we studied were fully optimized at B3LYP/6-311+g(d,p) level in gas phase. Harmonic vibrational frequencies were also calculated at the same level of theory to identify all stationary points as minima.

3. Experimental section

p-Hydroquinone and pyrocatechol were purchased from Aladdin Inc in Shanghai. The buffer solutions used in the present work were prepared from 0.1 mol L^{–1} citric acid and 0.2 mol L^{–1} Na₂HPO₄ solutions. 0.1 mol L^{–1} KCl solution worked as supporting electrolyte to increase the ionic strength during the whole experiment. All solutions were prepared with doubly distilled water and analytic grade reagents without further purification.

Electrochemical measurements were carried out using a CHI 660C electrochemical station. A three-electrode electrochemical cell was employed for all electrochemical measurements. A glassy carbon electrode (GCE) with a diameter of 3.0 mm served as a working electrode, while the counter and reference electrodes were platinum wire electrode and saturated calomel electrode (SCE), respectively. All the experimental potentials measured from cyclic voltammograms were relative to SCE. The phosphate buffer solutions were prepared according to the buffer preparation table and justified by a Metrohm 691 pH/mV meter. All experiments were performed in a double-walled electrolytic tank, which was connected to a thermostatic water bath to control the reaction temperature.

The CV method was employed during the whole experiment at a scan rate of 100 mV/s. The GCE was successively polished by 0.3 and 0.05 μm alumina slurry to obtain a renewed electrode surface. Highly pure nitrogen was passed through the solution for 15 min to remove dissolved oxygen in solution prior to measurements, and all measurements were carried out under nitrogen atmosphere.

4. Results and discussion

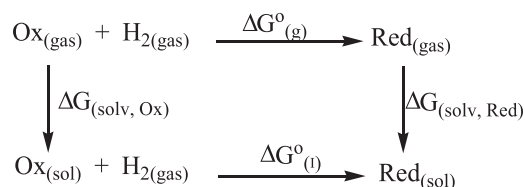
4.1. Theoretical studies on the redox potentials of *p*-hydroquinone and pyrocatechol

The reduction state (Red) of *p*-hydroquinone and pyrocatechol can be obtained from the oxidation state (Ox) of the corresponding quinones, through the following reaction:



As shown in Scheme 1, a thermodynamic cycle is established to calculate the total change of Gibbs free energy ΔG° . From this thermochemical cycle, ΔG° can be computed from its components through the following formula:

$$\Delta G^\circ = \Delta G_{(\text{g})}^\circ + \Delta G_{(\text{solv})} \quad (2)$$



Scheme 1.

In Eq. 2, $\Delta G_{(\text{g})}^\circ$ and $\Delta G_{(\text{solv})}$ are the change of standard Gibbs energy in the gas phase and the change of solvation energy in aqueous solution, respectively. $\Delta G_{(\text{g})}^\circ$ and $\Delta G_{(\text{solv})}$ are defined as follows:

$$\Delta G_{(\text{g})}^\circ = G_{(\text{gas, Red})}^\circ - G_{(\text{gas, Ox})}^\circ - G_{(\text{gas, H}_2)}^\circ \quad (3)$$

$$\Delta G_{(\text{solv})} = \Delta G_{(\text{solv, Red})} - \Delta G_{(\text{solv, Ox})} \quad (4)$$

$G_{(\text{gas, Red})}^\circ$ and $G_{(\text{gas, Ox})}^\circ$ are the Gibbs free energies of Red and Ox calculated accurately using the 6-311+G(d,p) basis set at the B3LYP level of theory in gas phase. $G_{(\text{gas, H}_2)}^\circ$ is calculated to be –1.180997 kcal mol^{–1} at the B3LYP/6-311+G(d,p) level. $\Delta G_{(\text{solv, Red})}$ and $\Delta G_{(\text{solv, Ox})}$ are the solvation free energies of Red and Ox in aqueous solution obtained using the CPCM model with UAHF radii at the B3LYP/6-311+G(d,p) level of theory.

Accordingly, the changes of the calculated free energies in gas and aqueous solution for *p*-hydroquinone are –23.30 and –8.65 kcal mol^{–1}, respectively, while the corresponding values for pyrocatechol are –32.74 and –4.44 kcal mol^{–1}. Consequently, the total changes of Gibbs free energies ΔG° are calculated to be –31.95 and –37.18 kcal mol^{–1} for *p*-hydroquinone and pyrocatechol, respectively.

The thermodynamic parameters can link to standard redox potential E° relative to the standard hydrogen electrode (SHE) via Eq. 5.

$$\Delta G^\circ = -nFE^\circ \quad (5)$$

where n is the number of transferred electrons in reaction (n is 2 in our case), and F is Faraday constant (96,485 C mol^{–1} or 23.061 kcal mol^{–1} V^{–1}).⁶ The E° value of SHE is equal to 0.00 V in SI units.

Based on Eq. 5, the corresponding E° values are calculated to be 0.693 and 0.806 V for *p*-hydroquinone and pyrocatechol, indicating that pyrocatechol is more stable than *p*-hydroquinone. In other words, pyrocatechol is harder to be oxidized than *p*-

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