

Correlation of electronic transitions and redox potentials measured for pyrocatechol, resorcinol, hydroquinone, pyrogallol, and gallic acid with results of semi-empirical molecular orbital computations – A useful interpretation tool

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Abstract

Cyclic voltammogram (CV) electrochemical measurements for pyrocatechol, resorcinol, hydroquinone, pyrogallol, and gallic acid in strong alkaline solution produced observable oxidation–reduction potentials for each hydroxy group present except for resorcinol. UV absorption spectra were also observed for the diluted solutions. Semi-empirical molecular orbital computations were conducted for these molecules of C_{2v} point group symmetry to determine the character and energies to aid interpretation of the experimental results. CV oxidation removed a π -electron by a radiationless π – π^* transition followed by an electron shift from a negative oxygen to the positive aromatic π -system indicated by an observable σ – π^* transition. Simple semi-empirical computations correlated with measured excited electronic states during electron transfer.

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1. Introduction

Pyrocatechol, resorcinol, hydroquinone, pyrogallol, and gallic acid exhibited the characteristics of reducing agents but their reduction potentials and their ability to remove copper oxide from copper metal were not known. A cyclic voltammogram (CV) for pyrocatechol in acetonitrile was reported [1] but CVs for the title compounds in aqueous solution were not found except for a minimal concentration of pyrocatechol [2] at neutral pH. Since UV absorption bands have been reported [3] for most of these compounds it was hoped that spectral data recorded immediately following CV measurements might reveal band correlations. The two sets of experimental data were correlated with the aid of semi-empirical quantum chemical

computations indicating a unique path for electron transfer and an unexpected requirement for reduction of copper oxide.

2. Experimental

Electrochemical sample solutions were prepared under nitrogen gas by dissolving 1 g each of reagent grade pyrocatechol, resorcinol, hydroquinone, pyrogallol or gallic acid with warming in strong base consisting of 16.34 g of electronic grade 45% potassium hydroxide solution into which was dissolved 2.66 g of solid reagent grade sodium hydroxide granules.

Reagent grade pyrocatechol and pyrogallol were both recrystallized to reduce impurity concentrations detected during initial electrochemical measurements. Pyrogallol, 5.5 g, was dissolved in 100 mL of hot reagent grade toluene and the solution allowed to cool. A first crop of thin

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rectangular shaped crystal platelets formed on the bottom of the beaker. The remaining liquid solution was decanted into a second clean dry beaker and allowed to continue to cool. A second crop of the same type of crystals formed while the solution cooled and the remaining liquid solution was decanted to a third beaker. As the toluene evaporated to a low volume of liquid a third crop of crystals, 0.10 g of collections of long needles, formed. Product crystals were dried in air at 45 °C. Cyclic voltammograms (CV) were run for each batch of dry crystals, 1 g dissolved in strong base, showing the first two to be pyrogallol and the third batch to be an impurity producing a CV with four redox potentials.

Pyrocatechol was recrystallized from a minimal volume of ethanol and dried in air at 45 °C.

Pyrocatechol, resorcinol, hydroquinone, pyrogallol, and gallic acid solutions prepared in a pH range of 3–13 were applied to thin copper oxide layers formed on copper following cleaning in dilute citric acid. The thin, visible copper oxide layer that formed on exposure of freshly cleaned copper to ambient air was not removed by pyrocatechol, resorcinol or hydroquinone. It was stained a blue–gray color by pyrogallol and removed by gallic acid at a pH of 8.8–14.

A pair of flat platinum electrodes, 6 mm by 6 mm, separated by 1.0 cm, were cleaned by repeatedly immersing in hot nitric acid, rinsing in pure water and electrochemically testing until a zero potential difference was attained. CVs were recorded by immersing the platinum electrodes into a beaker, exposed to air, containing a prepared solution of each sample. The platinum counter electrode functioned as a quasi-reference electrode. Three cycle scans were recorded at a scan rate of 10 mV/s, using a computer controlled Solartron 1287 Electrochemical Interface with Scribner software, and the potentials were measured for the second scan cycle. Refer to the cyclic voltammograms in Fig. 1 and data Table 1.

CV scans of hydroquinone in a strong base solution presented two current maxima for the oxidative branch and two current maxima for the reductive branch of each cycle, refer to Fig. 1. Measured data is presented in Table 1 showing potentials representing oxidation of 1.39 V and 1.54 V with potentials representing reduction of –1.42 V and –1.69 V as measured for the second of three scan cycles. CV scans for resorcinol produced measured potentials of 1.61 V and –1.63 V on the second scan. CV scans for pyrocatechol produced measured oxidation potentials of 1.15 V and 1.33 V with reduction potentials of –1.20 V and –1.36 V on the second scan. CV scans for pyrogallol produced measured potentials of 1.12 V, 1.35 V, 1.86 V, –1.21 V, –1.45 V, and –1.97 V on the second scan with a set of weak peaks at 1.61 V, and –1.70 V identified as impurity peaks since they matched the CV of the impurity needles isolated during compound recrystallization. CV scans for gallic acid produced measured potentials of 1.12 V, 1.36 V, 1.50 V, 1.79 V, –1.22 V, –1.40 V, –1.65 V, and –1.90 V. Four of these five compounds produced one oxidation potential and one reduction potential

peak for each hydroxyl group (and carboxylic acid group) present in the compound, however resorcinol produced only one set of peaks. Electrolysis of water was quite evident above ± 1.5 V causing additional current flow as observed at the extreme ends of the CV curves presented in Fig. 1.

Pyrocatechol CVs were also measured in aqueous solutions in the pH range of 3.3–14 demonstrating a shift in oxidation potential from 0.94 V to 1.34 V, respectively, refer to Table 2. Maximum current flow also increased with pH demonstrating solutions of high pH produced the strongest signals.

UV–visible spectra were observed for sample solutions in 1 cm quartz cuvettes using a Hewlett Packard UV–visible spectrophotometer model 8453 with a diode array detector. Solutions prepared for cyclic voltammogram measurements were diluted 1–1000 with pure water to concentrations of approximately 50 ppm and their UV spectra measured, as referenced to a pure water blank, following CV measurements and again after diluted samples had been sitting in air for 1½ to 2 h. Refer to spectral data presented in Table 3 with comments therein.

3. Discussion

Semi-empirical molecular orbital computations were conducted to identify the symmetry and character of each MO, and to estimate the band of energies near the highest occupied molecular orbital (HOMO) and lowest unoccupied (LUMO) levels for alkaline solutions of pyrocatechol, resorcinol, hydroquinone, pyrogallol and gallic acid. Excited state energies were computed for molecules of the same spin multiplicity and same irreducible representation of the spatial C_{2v} symmetry group as those of the electronic ground state even though in ab initio work [4] they are usually obtained from two independent computations. This data formed a basis for computing energy transitions as well as for interpretation of the measured redox potentials and UV absorption spectra. Semi-empirical quantum chemical computations were conducted using the QCPE 11 computer program [5] originally written by R. Hoffmann using averaged published bond lengths [6,7] of 0.963 Å for C–H, 1.384 Å for ring C–C, 1.371 Å for ring to phenoxy C–O, 1.084 Å for phenoxy O–H, 1.389 Å for ring to carboxylic acid C–C, 1.372 Å for carboxylic acid C–O and 1.080 Å for carboxylic acid CO₂–H with atom positions [7] for the in-plane syn-configuration (hydroxyl hydrogen atoms both on same side of aromatic ring plane) on a desktop PC, refer to Fig. 3. This molecular geometry conformed to C_{2v} a non-degenerate point group symmetry having A_1 , A_2 , B_1 , and B_2 irreducible representations. Note that hydroquinone may conform to D_{2h} symmetry only if the hydroxyl groups are linear in the plane of the ring. Molecular computations are simplified in the absence of degeneracy where molecular symmetry is present such that semi-empirical results are representative of the molecular characteristics.

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