

The investigation of pyrocatechol electrochemical mechanism in presence of nitrite ion on platinum electrode

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Abstract

In this study, the electrochemical mechanism of catechol in presence and absence of nitrite ion, is investigated in phosphate buffer medium (pH=7) using platinum electrode through cyclic voltammetry method in various scan rates. Electrochemical oxidation of catechol showed how quinone has changed to o-benzoquinone and also how o-benzoquinone has reacted with nitrite ion and potential scan rate has effected on.

Keywords: pyrocatechol, nitrite ion, electrochemical mechanism, cyclic voltammetry

1. Introduction

Catechol electrochemical mechanism has been studied using electrodes such as gold, graphite, copper, and silver which provides us with information about electron transfer on the electrode surface [1,2]. Catechol is one of important phenolic compounds in biology and medicine and also has excellent electrochemical activity which can be worked on by different electrochemical methods[3].

One of the used methods to study the catechol electrochemical mechanism is cyclic voltammetry that effect of different ions on the catechol can be analyzed[4]. The effect of pH on the electrochemical mechanism of catechol is one of the most important influencing parameters that during previous research pH = 7 is the best

Chemical environment to study the electrochemical behavior of catechol[5]. In this study, electrochemical mechanism of catechol and the effect of nitrite that is one of the ions of interest in the environment and impacts on human health, is studied using cyclic voltammetry.

2. Experimental

2.1. Materials and Equipment

Pyrocatechol ($C_6H_6O_2$), disodium hydrogen phosphate, sodium dihydrogen phosphate, Sodium Nitrite (Merck, Germany)

Cyclic voltammetry was performed using a potentiostat-galvanostat (Ivium, model: Compact State, Poland)

2.2. Procedure

Cyclic voltammetry method is used to obtain catechol voltammogram in potential range of 0.4 V to 1 V that in three scan rates 5, 10 and 200 mVs^{-1} is studied, also, a three-electrode system in which the platinum (Pt) electrode is the working electrode and Ag / AgCl is reference electrode, and another platinum (Pt) is used as auxiliary electrode that all are put in a solution containing phosphate buffer (pH = 7) which plays the role of medium, is applied and after adding the catechol (0.1 M) and nitrite ions (0.9 M) into the solution proposed cycles are obtained. To prepare the phosphate buffer at pH = 7 sodium dihydrogen phosphate (0.2 M) and disodium hydrogen phosphate (0.2 M) were used by a pH meter.

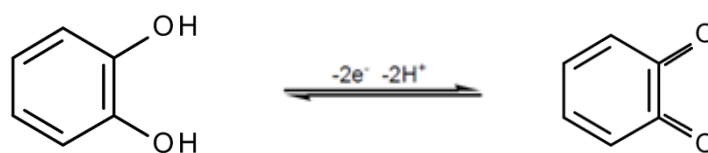
3. Results and discussion

Platinum electrode has superior characteristics such as resistance to high temperatures and chemical reactions and stable electrical properties, and also shows good electrocatalytic activity

3.1. Study on catechol electrochemical mechanism using a platinum electrode

Cyclic voltammetry method with platinum electrode were applied to survey electrochemical mechanism of catechol[6] at a scan rates of potential along with simulation (circles) according to the Quasi-reversible reaction (Eq) mechanism is shown in Figure 1 shows a cycle which contains 1.0 mg catechol in phosphate buffer at pH = 7. Catechol is known as a polyphenol in which two hydroxyl groups are substituted into the benzene ring.

Presence of leaving or recipient groups affect electrochemical reaction condition of o-benzoquinone pairing and prevent or slow the chemical reaction. Because of the high reactivity properties in o-benzoquinone most substitution chemical reactions have nucleophilic attacks, so the nucleophilic nucleus plays an important role in the reaction. These nucleophilic attacks lead to formation of catechol derivatives in high and low oxidation potentials, that are performed by E step and finally by Quasi-reversible (E_{qr}) mechanism (Scheme 1).



Scheme 1

The Scheme 1 has an electron transfer step by chemical reaction, catechol(a) in changed into two oxidized O electron and oxidation to *o*-quinone(b) leads to reversible reaction.

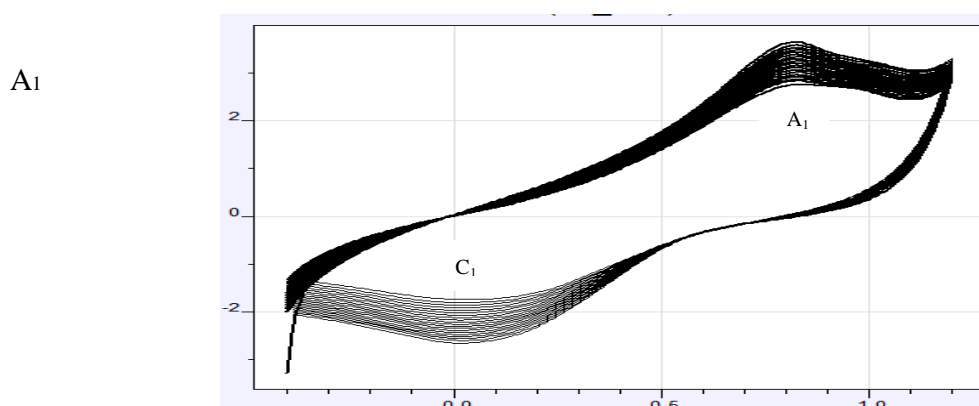
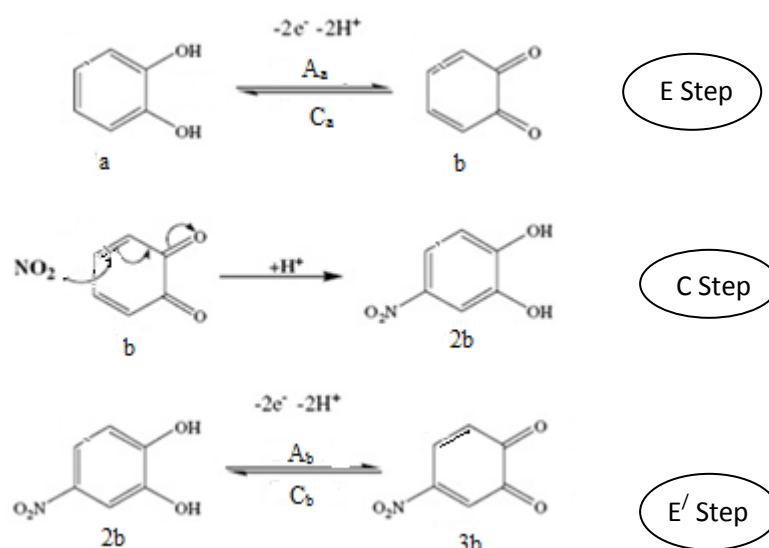


Figure 1. Cyclic voltammograms of 0.1 mM catechol in the absence of 0.9 mM nitrite ion on a platinum electrode, in a phosphate buffer solution of pH 7 at a scan rate of 100 mV s⁻¹.

All of chemical and electrochemical reactions of catechol derivatives depend on the nature of the solvent and pH [7,8]. Also catechol oxidation potential, nucleophilic reaction, quinone production reaction strongly depend on pH and solvent reaction conditions affect the final product, shown in (Fig. 1). As can be seen, there is one anodic peak (A₁) related to the oxidation of catechol to *o*-quinone and one corresponding cathodic peak (C₁) related to the reduction of *o*-quinone to catechol with a half-wave potential, E_{1/2} equal to 0.7 V vs. Ag | AgCl. The peak separation potential, ΔE_p at a scan rate of 100 mV s⁻¹ showing a quasi-reversible behavior of a two-electron, two-proton process. The simulated cyclic voltammograms based on an E_q mechanism show good agreement with those obtained experimentally [9].

3.2 Study on catechol electrochemical mechanism in presence of nitrite ion using platinum electrode

Catechol electrochemical oxidation in presence of nitrite as a nucleophil in aqueous solution obeys ECE' (Scheme 2) reaction[10]. Results shows participation of produced (b) *o*-benzoquinones in a Michael addition (2b) nitrocatechols and changing of nitrocatechol to nitro (3b) *O*-benziquinone. Due to nitrite group being electron reciving, nitrocatechol is oxidized in more positive potentials in comparison with primary catechol. Cyclic voltamograms of 1mM catechol in presence of 0.9mM nitrite ion the surface of platinum in phosphate buffer solution (pH=7). Scanning speeds of potential in this study are 5, 10, and 200 mVs⁻¹. Presence of nitrite ion as a nucleophilic nucleus in aqueous solution shows increase of Michael addition to *O*-benzoquinone and production of nitrocatechol.



Despite the basis of nitration of most of aromatic compounds is nucleophile, basis of catechol nitration is electrochemical electron receiving in production of *O*-benzoquinone. Nitrocatechol oxidation potential more strongly prevents oxidation in comparison with catechol. In nitrite ion electrolysis voltammogram, slow formation of second anode peak and concurrently disappearing of first peak can be seen[11]. In figure 2, 3 and 4 the peak(A_a) relates to changing of catechol to *O*-benzoquinone and the peak(A_b) relates to changing of nitrocatechol to nitro *O*-benziquinone that have positive potential in most positions, catechol electrolysis in presence of nitrite ion in various rates is investigated and the less the scan rate and increase speed of potential scanning the peak(A_b) and the peak(C_b) is omitted with less in speed of potential scanning and gets more similar to EC mechanism.

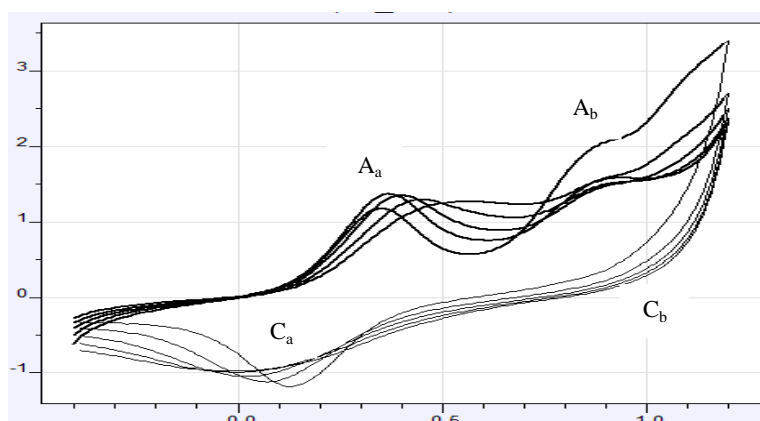


Figure2. Cyclic voltammograms of 0.1 mM catechol in the presence of 0.9mMnitrite ion on platinum electrode , in phosphate buffer solution of pH 7 at a scan rate of 5 mV s⁻¹.

in (Fig2) Couriers were separated because the scanning rate down the time required for the reaction mechanisms exist and all four peaks are visible.

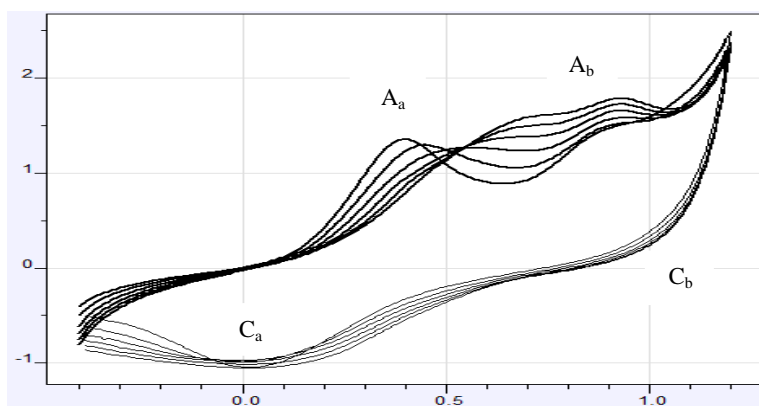


Figure3. Cyclic voltammograms of 0.1 mM catechol in the presence of 0.9mMnitrite ion on platinum electrode , in phosphate buffer solution of pH 7 at a scan rate of 10 mV s⁻¹

in (Fig3) Scan rate increased and are nearing peakA_a to peakA_b.

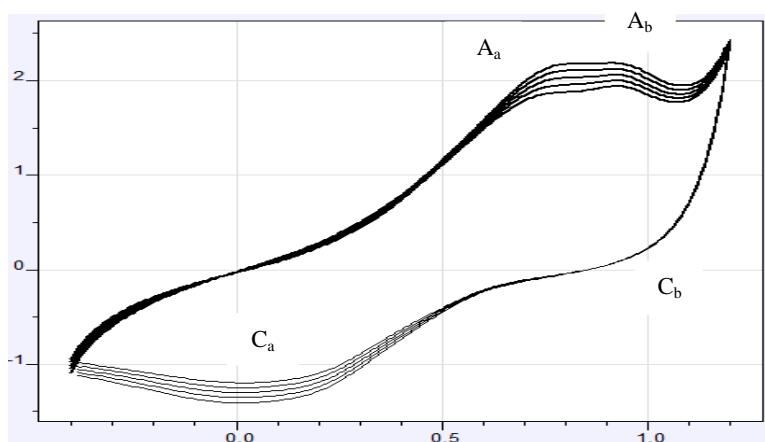


Figure4. Cyclic voltammograms of 0.1 mM catechol in the presence of 0.9mMnitrite ion on platinum electrode , in phosphate buffer solution of pH 7 at a scan rate of 200 mV s⁻¹

in (Fig4) Scanning rate is too high, so are peakA_a and A_bs almost had one. So the potential scan rate is less than the ECE mechanism will be better.

5. Conclusion:

- The conclusion of applying of platinum electrode as working electrode in order to study on catechol mechanism in presence of nitrite ion is ECE^r mechanisms and in absence of nitrite ion is E_{qr} mechanism.
- In presence of nitrite, nucleophile is added to O-quinone that depends on nitrite ion concentration, if concentration of nitrite ion gets low the reaction would not happen.
- Sensitivity of platinum electrode to catechol concentration is studied and the result is better performance of platinum electrode in higher concentration of catechol.
- Also effect of pH can not be disregarded in catechol oxidation. In low pH, catechol does not oxidize and forms no redox pair and in high pH oxidation mechanism is irreversible, so the optimized pH for oxidation is 7.

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