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SHORT COMMUNICATION

Electrochemical oxidation of catechol in the presence of an aromatic amine in aqueous media

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Abstract The electrochemical oxidation of catechol has been studied in the presence of *p*-nitroaniline as a nucleophile in aqueous media at the surface of glassy carbon electrode, using cyclic voltammetry. The products of electrosynthesis have been purified and characterized by Fourier-transform infrared (FT-IR), ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, and distortionless enhancement by polarization transfer (DEPT), and the mechanism of anodic oxidation was deduced from voltammetric and spectroscopic data.

Keywords Cyclic voltammetry · Electrochemical synthesis · Catechol · Aromatic amine

1 Introduction

A vast number of quinones with great structural divergence are provided by nature and play a major role in the redox electron-transport chains of living system [1–3]; for example, vitamin K is known in blood coagulation mechanism and photosynthesis, and ubiquinone and vitamin E are important factors in electron transport and oxidative phosphorylation. More complex quinonoic compounds are used extensively in medicine, especially as anticancer agents, and their activity stems from their special ability to undergo one-electron transfer reaction to form reactive radicals [4, 5].

During recent years a number of methods have been developed to propose the mechanism of reaction between quinones and some nucleophiles, and many quinones, substituted quinones, bisquinones, and polyquinones have been synthesized [6].

Cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique for the study of electroactive species. It has been shown that *o*- and *p*-diphenols are oxidized electrochemically to *o*- and *p*-quinones, respectively [7, 8]. The quinones are quite reactive and can be attacked by suitable nucleophiles via a 1,4-Michael addition reaction [9]. As part of our ongoing program to investigate the electrochemical behavior of catechols with nitrogen nucleophiles [10], and because of importance of aminoquinones as biologically active compounds, the electrochemical oxidation of catechol was studied in the presence of *p*-nitroaniline as an aromatic nucleophile in aqueous media, and a facile electrochemical method for synthesis of new aminoquinone derivatives was developed.

2 Experimental

2.1 Apparatus

Cyclic voltammetry, controlled-potential coulometry, and preparative electrolysis were performed using EG&G Potentiostat and Galvanostat model 263A coupled with a Pentium IV personal computer with a three-electrode configuration. The working electrode used in the voltammetry experiments was a glassy carbon disc (diameter 1.8 mm, from Metrohm), and platinum wire and Ag|AgCl|KCl$_{3M}$ (from Metrohm) were used as the counter and reference

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electrodes, respectively. The working electrode used in controlled-potential coulometry and macroscale electrolysis was an assembly of four carbon rods (6 mm diameter and 4 cm length), and platinum wire constituted the counter-electrode. The glassy carbon electrode was polished between each set of experiments with aluminum oxide powder on a polishing cloth.

2.2 Reagents

All chemicals (catechol, *p*-nitroaniline, and phosphate salts) were reagent-grade materials from Fluka and were used without further purification. All solutions and subsequent dilutions were prepared using double-distilled water. All experiments were carried out in phosphate buffer solution (0.2 M) in different pH values.

2.3 Electroorganic synthesis of 3-(4-nitrophenyl amino)cyclohexa-3,5-diene-1,2-dione (**3a**) and 2,4-bis(4-nitrophenyl amino)phenol (**4a**)

According to a particular procedure, 100 ml phosphate buffer solution (pH 6.0, 0.20 M) was pre-electrolyzed at the chosen potential (1 V versus Ag|AgCl|KCl_{3M}) in a divided cell and then catechol (0.5 mmol) and *p*-nitroaniline (1.0 mmol) were added to the cell. The electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted several times during the electrolysis (due to formation of a film of product at the surface of the electrode) and we reactivated the graphite working electrode with acetone. At the end of electrolysis, a few drops of acetic acid were added to the solution and the cell was placed in a refrigerator overnight. The precipitated solid was collected by filtration and washed thoroughly with water–acetonitrile (1:1) and dried to give a yellowish solid. The crude product was purified in a silica gel column with ethyl acetate:hexane (1:5) as eluent to afford **3a** (1.281 g, 70%) and **4a** (0.245 g, 20%), which were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and DEPT.

2.4 Characteristics of products

*2.4.1 3-(4-Nitrophenyl amino)cyclohexa-3,5-diene-1,2-dione (**3a**)*

$C_{12}H_8N_2O_4$: FT-$IR_{(KBr)}$; 3400, 1692, 1591, 1516, 1342, 1185, 1111, 1038, 850, 749, 665. ^{1}H NMR, δ (ppm) (300 MHz, $CDCl_3$): 4.37 (br s, 1H–NH), 6.62 (d, $J = 9$ Hz, 2H, aromatic), 7.22 (d, $J = 8$ Hz, 1H, quinone), 7.50 (s, 1H, quinone), 8.07 (d, $J = 9$ Hz, 2H, aromatic), 8.34 (d, $J = 8$ Hz, 1H, aromatic). ^{13}C NMR, δ (ppm) (75 MHz, $CDCl_3$): 103.2, 112.8, 121.2, 124.4, 127.6, 137.7, 139.1, 157.5, 186.6, 188.7.

*2.4.2 2,4-Bis(4-nitrophenyl amino)phenol (**4a**)*

$C_{18}H_{14}N_4O_5$: FT-$IR_{(KBr)}$; 3426 (br and s), 1645, 1593, 1518, 1344, 1111, 1025, 767. ^{1}H NMR, δ (ppm) (300 MHz, acetone-d^6): 6.35(s, 1H, quinone), 6.73(s, 1H–NH), 6.77(d, $J = 7$ Hz, 2H, aromatic), 6.91(s, 1H-NH), 7.49 (d, $J = 9$ Hz, 1H, quinone), 7.93 (d, $J = 9.5$ Hz, 2H, aromatic), 8.01 (d, $J = 7$ Hz, 2H, aromatic), 8.20 (d, $J = 9.5$ Hz, 2H, aromatic), 8.38 (d, $J = 9$ Hz, 1H, quinone), 9.54 (br s, 1H-OH), ^{13}C NMR, δ (ppm) (75 MHz, acetone-d^6): 98.7, 112.1, 112.7, 119.8, 120.7, 124.0, 124.7, 125.3, 125.7, 126.1, 128.3, 139.7, 146.8, 153.4, DEPT 135, δ (ppm) (acetone-d^6): 98.7, 112.1, 112.7, 119.8, 120.7, 124.0, 124.7.

3 Results and discussion

Cyclic voltammetry of 2.0 mM catechol in water/acetonitrile (80/20) solution containing 0.20 M phosphate buffer as the supporting electrolyte shows one anodic (*A*) and corresponding cathodic peak (*C*), which is related to the transformation of catechol (**1**) to *o*-benzoquinone (**1a**) and vice versa within a quasireversible two-electron process (Fig. 1, curve a).

A peak current ratio (I_{pC}/I_{pA}) of nearly unity, particularly during repetitive cycling of potential, can be considered as a criterion for the stability of *o*-quinone produced at the surface of the electrode under the experimental conditions. It is also reported that any hydroxylation or dimerization reactions are too slow to be observed on the time scale of cyclic voltammetry [11, 12]. The electrochemical oxidation of catechol in the presence of *p*-nitroaniline (**2**) was studied at pH 6.0 as optimum pH for the reaction between *o*-benzoquinone and *p*-nitroaniline. Figure 1 (curve b) shows the

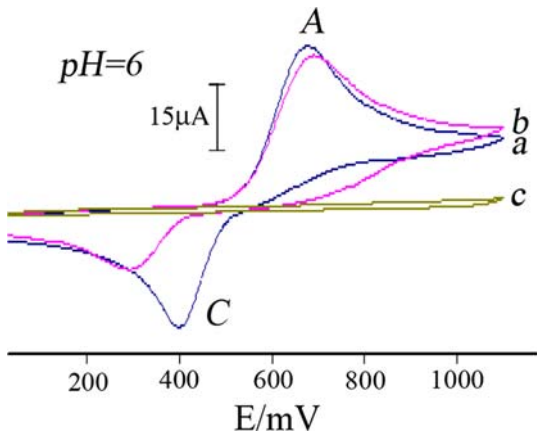


Fig. 1 Cyclic voltammograms of 2.0 mM catechol: (a) in the absence, (b) in the presence of 2.0 mM *p*-nitroaniline, and (c) 2.0 mM *p*-nitroaniline in the absence of catechol, at a glassy carbon electrode, in buffer solution pH 6.0 and 0.20 M. Scan rate: 50 mV s^{-1}; $T = 25 \pm 1$°C

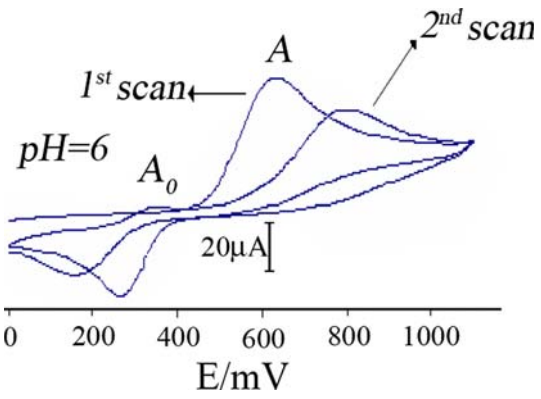


Fig. 2 Multicyclic voltammograms of 2.0 mM catechol in the presence of 2.0 mM *p*-nitroaniline, at a glassy carbon electrode, in phosphate buffer solution (pH 6.0, 0.20 M); scan rate: 50 mV s^{-1}; $T = 25 \pm 1°C$

cyclic voltammogram obtained for 2.0 mM solution of catechol in the presence of 2.0 mM *p*-nitroaniline. Under these conditions, the cathodic counterpart of the anodic peak (*A*) greatly decreases. The effect of subsequent cycles on the cyclic voltammogram of an aqueous solution containing 2.0 mM catechol and 2.0 mM *p*-nitroaniline is shown in Fig. 2.

As can be seen, a new anodic peak (A_0) that is related to oxidation of intermediate **3** (catechol derivative) to 3-(4-nitrophenyl amino)cyclohexa-3,5-diene-1,2-dione (**3a**) appeared at a lower potential during second cycle. The anodic shift of *A* is probably because of a thin film of product at the surface of the electrode, inhibiting to a certain extent the performance of the electrolysis process [13, 14]. Furthermore, it shows that, proportional to the augmentation of potential sweep rate, the height of the cathodic peak (*C*) of catechol is increased (Fig. 3 curves a–h).

A similar situation is observed when the concentration ratio of *p*-nitroaniline to catechol is decreased (Fig. 4). The progress of the electrolysis was monitored by cyclic voltammetry and is presented in Fig. 5. As indicated in this figure, during the progress of electrolysis, A_0 disappears while *A* decreases. These observations and the voltammetry results allow us to suggest an ECEC mechanism for the electrooxidation of catechol in the presence of *p*-nitroaniline, as illustrated in Scheme 1.

As shown in Scheme 1, it seems that *p*-nitroaniline (**2**) attacks electrogenerated *o*-quinone via a 1,4-Michael addition reaction to form intermediate **3**, which could be oxidized to **3a**. Subsequent reaction of **3a** with *p*-nitroaniline (**2**) led to formation of 2,4-bis(4-nitrophenyl amino)phenol **4a**. When we interrupted the electrolysis at the middle of total time scale, we simply separated compound **3a** by filtration. Amines **3a** and **4a** were purified by recrystallization in chloroform and characterized by spectroscopic data.

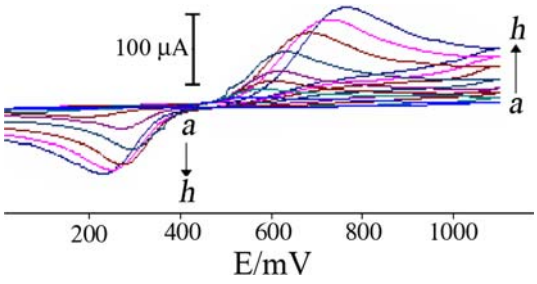


Fig. 3 Typical cyclic voltammograms of 2.0 mM catechol in the presence of 2.0 mM *p*-nitroaniline at a glassy carbon electrode, in phosphate buffer solution (pH 6.0, 0.20 M). Scan rates for (a) to (h) are: 10, 25, 50, 100, 250, 500, 750, and 1,000 mV s^{-1}, respectively. $T = 25 \pm 1°C$

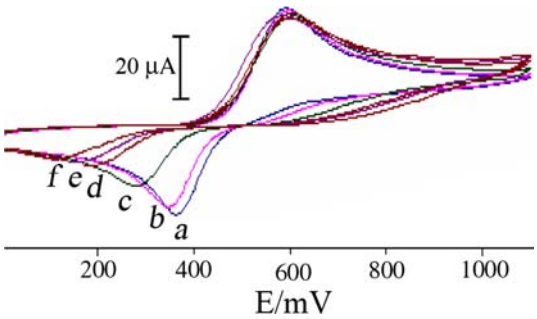


Fig. 4 Cyclic voltammograms of 2.0 mM catechol in the presence of various amounts of *p*-nitroaniline: (a) 0.5 mM, (b) 1.5 mM, (c) 2.0 mM, (d) 2.5 mM, and (e) 3.5 mM *p*-nitroaniline, at a glassy carbon electrode, in phosphate buffer solution (pH 6.0, 0.20 M); scan rate: 50 mV s^{-1}; $T = 25 \pm 1°C$

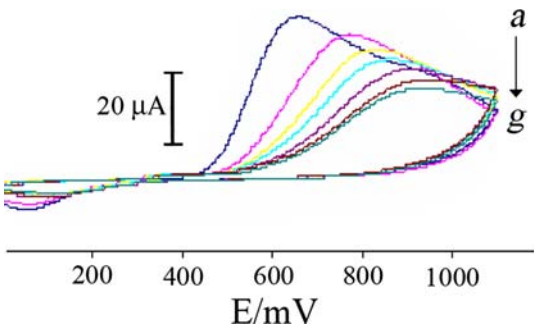
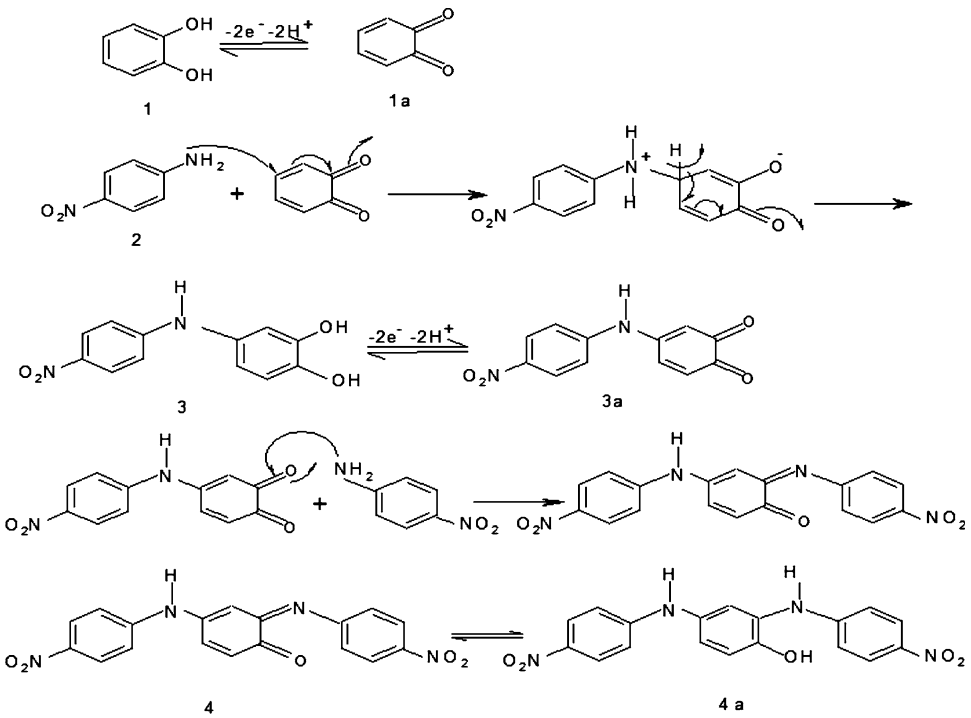


Fig. 5 Cyclic voltammograms of 0.5 mmol catechol in the presence of 0.5 mmol *p*-nitroaniline, at a glassy carbon electrode during controlled potential electrolysis at 1.0 V versus Ag|AgCl |KCl_{3M} and after termination times of: (a) 0 s, (b) 2,000 s, (c) 4,000 s, (d), 6,000 s, (e) 8,000 s, (f) 10,000 s, and (g) 12,000 s. Scan rate: 100 mV s^{-1}; $T = 25 \pm 1°C$

4 Conclusion

We have shown that electrosynthesis of new amine derivatives **3a** and **4a** can be accomplished by electrolyzing catechol to *o*-quinone in water and subsequent 1,4-Michael addition of *o*-quinone with *p*-nitroaniline as a nucleophile. In this method, amines **3a** and **4a** were prepared in high

Scheme 1 The mechanism for the electrooxidation of catechol



yield and purity. An ECEC mechanism for these amines has been suggested. The structures of **3a** and **4a** were fully characterized by spectroscopic data.

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References

1. Rich PR (1982) Faraday Discuss Chem Soc 148:54
2. Sutherland HS, Higgs KC, Taylor NJ, Rodrigo R (2001) Tetrahedron 57:309
3. Bringmam G, Tasler S (2001) Tetrahedron 57:331
4. Das MR, Conner HD, Leniart DS, Freed JH (1970) J Am Chem Soc 92:2258
5. Leary G, Porter G (1970) J Chem Soc (A) 2273
6. Patai S, Rappoport Z (1987) The chemistry of quinonoid compounds. Wiley, New York
7. Nematollahi D, Golabi SM (2000) J Electroanalysis 481:208
8. Kiani A, Raoof JB, Ojani R (2006) Bull Electrochem 22:275
9. Morrison RT, Boyd RN (1987) Organic chemistry, 5th edn. Allyn and Bacon, USA, p 1087
10. Kiani A, Raoof JB, Nematollahi D, Ojani R (2005) Electroanalysis 17:1755
11. Papouchado L, Petrie G, Adams RN (1972) J Electroanal Chem 38:389
12. Rayn MD, Yueh A, Wen-Yu C (1980) J Electrochem Soc 127:1489
13. Nematollahi D, Golabi SM (1998) Bull Electrochem 14:97
14. Nematollahi D, Goodarzi H (2001) J Electroanal Chem 510:108