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Diversity in electrochemical oxidation of dihydroxybenzenes in the presence of 1-methylindole

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Abstract. Electrochemical oxidation of some catechol derivatives (**1a–e**) have been studied in water/acetonitrile solution containing 1-methylindole (**3**) as a nucleophile, using cyclic voltammetry and controlled-potential coulometry. An interesting diversity in the mechanisms has been observed in electrochemical oxidation of catechol derivatives (**1a–e**) in the presence of **3**. In this work, we have proposed reaction schemes *ECEC*, *ECECE* and *ECECECE* for oxidation of **1a–e** in the presence of **3**.

Keywords. 1-Methylindole; catechol; Michael addition reaction; cyclic voltammetry; electrochemical oxidation.

1. Introduction

Indole is a powerful antioxidant and it appears to be especially effective against breast and cervical cancer because of its ability to increase the breakdown of estrogen in the human body.[1,2] Also, the indole structure can be found in many organic compounds like the amino acid tryptophan and in tryptophan-containing protein, in pigments, and in alkaloids.[1,2] In addition, many pharmaceutical drugs are included of specifically substituted indoles.[1,2] On the other hand, catechol derivatives play an important role in mammalian metabolism. Many compounds of this type are known to be secondary metabolites of higher plants.[3] Catechol itself and mono-substituted catechols are active in part against *Pseudomonas* and *Bacillus* species.[4] It was thought that synthesis of compounds with both structures of catechols and indoles would be useful from the point of view of pharmaceutical properties. In this direction, we have recently synthesized some derivatives of 4-(1*H*-indol-3-yl)benzene-1,2-diol using electrochemical oxidation of catechols in the presence of indole as nucleophile in acetate buffer (pH = 5.0) via *EC* mechanism.[5] In continuation of interest in compounds containing catechol and indole, in this work, we study electrochemical oxidation of catechols in the presence of 1-methylindole in water/acetonitrile (50/50, v/v) mixture and proposed a reaction mechanism (*ECEC*) and final products (figure 1, compound **I**) for it.

Furthermore, our literature survey shows that compounds with both structures of benzoquinones and indoles have pharmaceutical properties. In this direction, it is recognized that, the 3-indolylbenzoquinone fragment is a core structure in a number of biologically active natural products such as asterriquinones.[6,7] The asterriquinones (figure 1, compound **II**) and demethylasterriquinones (figure 1, compound **III**) exhibit a wide spectrum of biological activities including antitumor properties and are inhibitors of HIV reverse transcriptase.[8–10] The importance of these compounds has motivated us and many workers to synthesize a number of indolylquinone and numerous methods have been developed for their preparation.[11–19] Following our experience in electrochemical oxidation of catechols in the presence of nucleophiles[20] we envisaged that the attachment of two indoles group to an *o*-quinone ring might cause an enhancement of pharmaceutical properties and medicinal activities. This idea prompted us to investigate the electrochemical oxidation of 2,3-dihydroxybenzoic acid and 3,4-dihydroxybenzoic acid in the presence of 1-methylindole and we have proposed reaction mechanisms *ECECE* and *ECECECE* and final products **IV** and **V**, respectively (figure 1).

*For correspondence

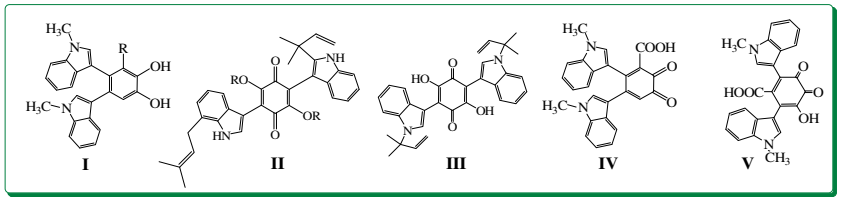


Figure 1. The structure of compounds reported here (**I**, **IV** and **V**), asterriquinone (**II**) and demethylasterriquinone (**III**).

2. Experimental

2.1 *General*

Cyclic voltammetry, controlled-potential coulometry and preparative electrolysis were performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in voltammetry experiment was a glassy carbon disc (1.8 mm diameter) which was polished sequentially with alumina powder and a platinum wire was used as counter electrode. 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 a large stainless steele plate constitute the counter electrode (for more details, see ref.[5]). For activation of carbon electrodes, the electrolysis was interrupted during the electrolysis and the carbon anode was washed in acetone. The working electrode potentials were measured versus SCE (all electrodes from AZAR Electrode). All catechols were reagent-grade materials from Aldrich and phosphate salts were of pro-analysis grade from E. Merck. These chemicals were used without further purification. All experiment was carried out at a temperature of 25 ± 1°C. Melting points of all synthesized compounds were determined in open capillary tubes and are uncorrected. IR spectra (KBr) were recorded on IFS66 Bruker FT-IR spectrometer. ^{1}H NMR spectra (DMSO-*d*6) were recorded on BRUKER DRX-400 AVANCE spectrometer operating at 400 MHz, respectively Mass spectra were recorded on a QP-1100EX Shimadzu Mass spectrometer operating at an ionization potential of 70 eV. Because of insolubility of the 1-methylindole (**3**) in water, a water/acetonitrile (50:50 v/v) mixture was used. This percentage of acetonitrile (50%) is minimum amount for dissolution of 1-methylindole (**3**) in mixture.

2.2 *General procedure for the synthesis of **6a–c**, **7d** and **9e***

A solution of phosphate buffer (ca. 80 ml; c_{H2PO4^-} = 0.188 M and c = $c_{HPO4^{2-}}$ = 0.012 M, pH = 6.0) in water/acetonitrile (50:50; 80 mL) solution containing catechol (**1a–e**; 1 mmol) and 1-methylindole (**3**) (2 mmol) was electrolyzed in a two-compartment cell separated by a sintered glass membrane, at 0.35 V vs. SCE in the case of **1a–c** and 0.40 V in the case of **1d** and **1e**. The electrolysis was terminated when the current decreased by more than 95%. The process was interrupted during the electrolysis and the carbon anode was washed in acetone in order to reactivate it. After electrolysis, the precipitated solid was collected by filtration and was washed several times with water. After washing, products were characterized by: IR, ^{1}H NMR and MS. The isolated yields of **6a–c**, **7d** and **9e** obtained after washing are 41, 45, 43, 46 and 41%, respectively.

2.2a *4,5-Bis(1-methyl-1H-indol-3-yl)benzene-1,2-diol (**6a**)*: m.p.: >300°C (dec.). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.78 (s, 6H, methyl), 6.42 (s, 2H, aromatic in five-ring cycle), 7.02–7.56 (m, 10H, aromatic) 9 (broad, OH). IR (KBr/cm^{-1}): 3441, 1576, 1469, 1417, 1384, 1129, 741. MS (m/z) (%): 368 (M^+), for more detail see Supporting Information.

2.2b *3-Methyl-4,5-bis(1-methyl-1H-indol-3-yl)benzene-1,2-diol (**6b**)*: m.p.: >300°C (dec.). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.1 (s, 3H, methyl), 3.70, 3.78 (s,s 6H, methyl), 6.33 (s, 1H, aromatic in five-ring cycle), 6.88–7.61 (m, 10H, aromatic), 9 (broad, OH). IR (KBr/cm^{-1}): 3414, 1714, 1612, 1473, 1373, 1250, 1084, 743. MS (m/z) (%) 382 (2.2) [$M^{+\cdot}$], 280 (16.8), 253 (25.2), 131 (100).

2.2c *3-Methoxy-4,5-bis(1-methyl-1H-indol-3-yl)benzene-1,2-diol (**6c**)*: m.p.: >245°C (dec.). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.51 (s, 3H, methyl), 3.59 (s, 3H, methyl), 3.70 (s, 3H, methyl), 6.40–7.70 (m, 11H, aromatic), 8.2 (broad, OH). IR (KBr/cm^{-1}): 3210, 3035, 2942, 1614, 1544, 1464, 1373, 1324, 1220, 1090, 743. MS (m/z) (%): 398 (8.9) [$M^{+\cdot}$], 380 (100), 269 (100), 226 (58.8), 190 (27.3), 130 (65.1).

2.2d *2,3-Bis(1-methyl-1H-indol-3-yl)-5,6-dioxocyclohexa-1,3-dienecarboxylic acid (**7d**)*: m.p.: >300°C (dec.). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.49 (s, 3H, methyl), 3.57 (s, 3H, methyl), 6.4–7.8 (m, 11H, aromatic). IR (KBr/cm^{-1}): 3464, 2925, 1561, 1411, 1384, 740. MS (m/z) (%): 410 [M$^{+\cdot}$], for more detail see Supporting Information.

2.2e *5-Hydroxy-2,6-bis(1-methyl-1H-indol-3-yl)-3,4-dioxocyclohexa-1,5-dienecarboxylic acid (**9e**)*: m.p.: >300°C (dec.). IR (KBr/cm^{-1}): 3434, 1720, 1610, 1469, 1371, 744. MS (m/z) (%): 426 [M$^{+\cdot}$], for more detail see Supporting Information.

3. Results and discussion

3.1 *Electrochemical oxidation of 3-substituted catechols in the presence of 1-methylindole*

Figure 2, curve a, shows the voltammetric curve obtained for the oxidation of catechol (**1a**) (1 mM) in water (containing phosphate buffer, c_{H2PO4^-} = 0.188 M and $c_{HPO4^{2-}}$ = 0.012 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture at a glassy carbon electrode. This percent of acetonitrile is minimum amount for dissolution of 1-methylindole (**3**) in water/acetonitrile mixture. In the studied potential range, a well-defined voltammetric curve is obtained that has an anodic (A_1) and the corresponding cathodic (C_1) peaks. These peaks correspond to the oxidation of catechol (**1a**)

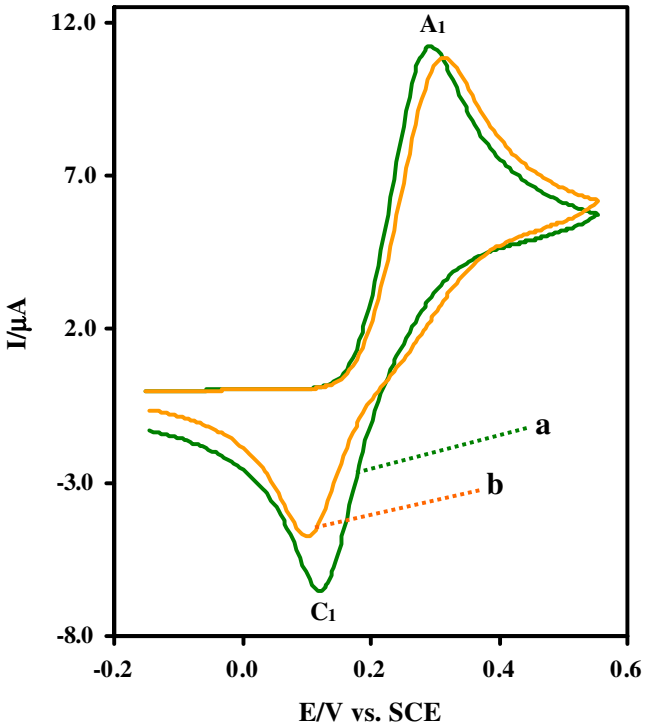


Figure 2. Cyclic voltammograms of 1 mM catechol (**1a**): (a) in the absence, (b) in the presence of 20 mM of 1-methylindole (**3**) in water (containing phosphate buffer, c = 0.2 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture at glassy carbon electrode. Scan rate: 25 mV s^{-1}; t = 25 ± 1°C.

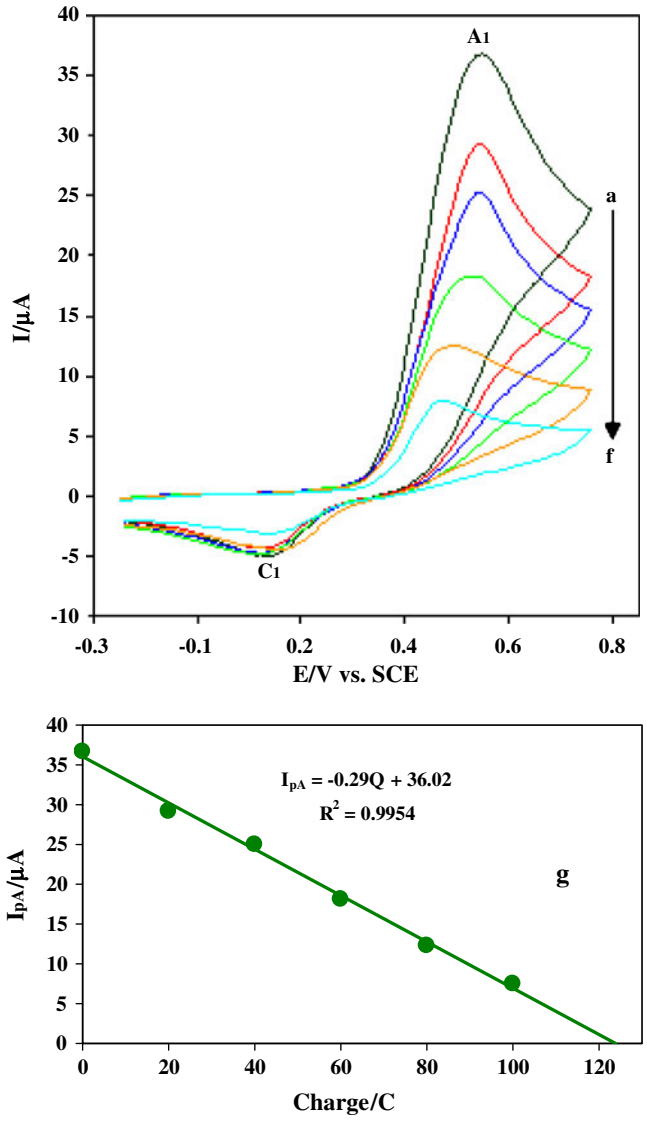
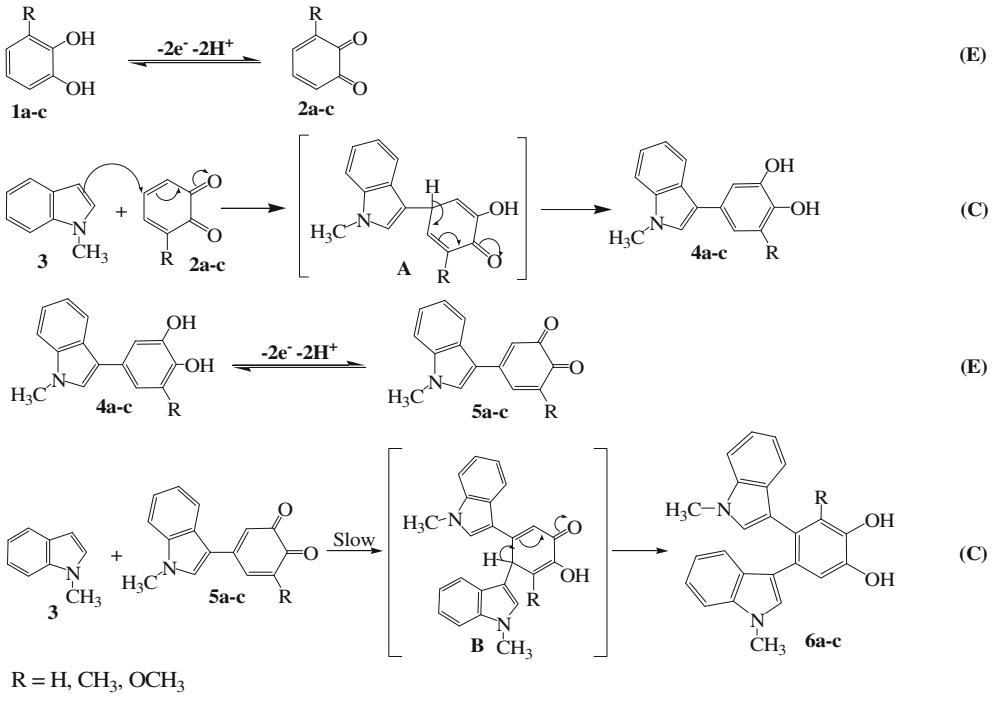


Figure 3. Cyclic voltammograms of 0.30 mmol catechol (**1a**) in the presence of 0.60 mmol 1-methylindole (**3**), in water (phosphate buffer, c = 0.2 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture during controlled-potential coulometry at 0.35 V vs. SCE after the consumption of (a) 0, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 100 C. (g) Variation of peak current (I_{pA1}) vs. charge consumed. Scan rate: 100 mV s^{-1}. Other conditions are the same as reported in figure 2.

to *o*-benzoquinone **2a** and vice versa within a two-electron process.[20] The oxidation of catechol (**1a**) in the presence of 1-methylindole (**3**) as a nucleophile was studied in some detail. In figure 2, curve b shows the cyclic voltammogram obtained for a 1 mM solution of **1a** in the presence of 1 mM of 1-methylindole (**3**). Under these conditions, the voltammogram exhibits anodic and cathodic peaks A_1 and C_1, respectively. The comparison of peak C_1 in the absence and presence of **3** shows a decrease in peak C_1 current. The existence of a subsequent chemical reaction between *o*-benzoquinone **2a** and 1-methylindole (**3**) is supported by the following evidence: (i) Decreasing of I_{pC1} during the reverse scan (figure 2), this could be indicative of the fact that electrochemically generated *o*-benzoquinone **2a** is removed partially by chemical reaction with 1-methylindole (**3**). (ii) Dependency of peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ on potential sweep rate. In this case, for the highest sweep rate employed a well-defined cathodic peak C_1 is observed. For lower sweep rates, the peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ is less than one and increases with increasing sweep rate. This is indicative of departure from intermediate and arrival to diffusion region with increasing sweep rate.[21] (iii) Dependency of peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ on concentration of 1-methylindole (**3**). This is related to the increase of the homogeneous reaction rate of following chemical reaction between *o*-benzoquinone **2a** and 1-methylindole (**3**) with increasing of concentration of 1-methylindole (**3**).

The observed shift of the A_1 peak potential (E_{pA1}) in curve b, relative to curve a, is due to the formation of a thin film of product at the surface of the electrode, inhibiting to a certain extent the performance of the electrode process.[22]

Our previous works illustrate that in acidic and neutral media, cyclic voltammograms of catechol (**1a**) shows one anodic and a corresponding cathodic peak, which corresponds to the transformation of catechol (**1a**) to *o*-benzoquinone (**2a**) and vice versa within a two-electron process.[20,22,23] Under these conditions, peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ of nearly unity, can be considered as a criterion for the stability of *o*-benzoquinone under the experimental conditions. But, in basic solutions, the peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ is less than unity and decreases with increasing pH.[22] This behaviour is related to the coupling of the anionic or dianionic forms of catechol with *o*-benzoquinone (dimerization reaction).[22] On the other hand, it is shown that indole and its derivatives such as 1-methylindole (**3**) form dimer or trimer on acid-catalysed conditions.[24] Consequently in this work, because of the



Scheme 1. Electrochemical oxidation mechanism of catechol, 3-methyl catechol and 3-methoxycatechol in the presence of 1-methylindole.

decrease in the rate of the polymerization of catechol on the one hand and prevention of dimerization of 1-methylindole (**3**) on the other hand, a solution containing phosphate buffer (c = 0.2 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture has been selected as a suitable medium for the electrochemical study and synthesis.

Controlled-potential coulometry was performed in water (containing phosphate buffer, c = 0.2 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture containing 0.30 mmol of **1a** and 0.60 mmol of 1-methylindole (**3**) at 0.35 V versus SCE. The electrolysis was monitored by cyclic voltammetry. It was observed that anodic peak A_1 decreases proportionally to the advancement of coulometry. All anodic and cathodic peaks disappear when the charge consumption becomes about $4e^-$ per molecule of **1a** (figure 3).

Diagnostic criteria of cyclic voltammetry and controlled potential coulometry accompanied by a molecular mass of 368 of the final product (**6a**), obtained during macroscale electrolysis, (see Supporting Information), indicates that the reaction mechanism of electrooxidation of catechol (**1a**) in the presence of 1-methylindole (**3**), in water (phosphate buffer, c = 0.2 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture is *ECEC* (scheme 1).[25–30]

Generation of *o*-benzoquinone **2a** is followed by a Michael addition of **3** to the benzoquinone **2a**, producing the compound **4a**. In applied potential (0.35 V vs. SCE), **4a** is converted to *o*-benzoquinone **5a**. In final stage, the 'slow' next Michael addition reaction, converts **5a** to catechol derivative **6a** as a final product. The oxidation of **6a** was circumvented during the preparative reaction because of the insolubility of it in water

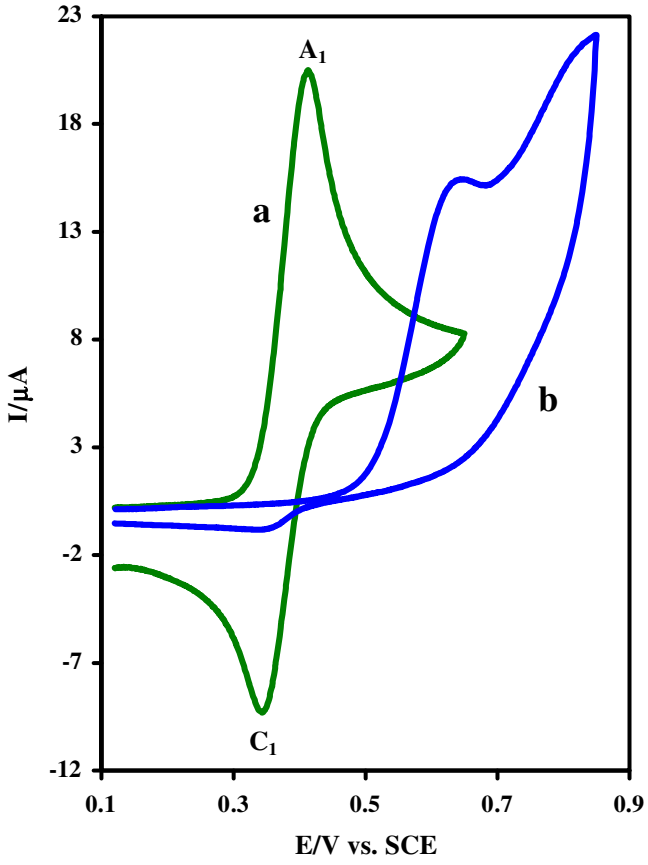


Figure 4. Cyclic voltammograms of (a) 1 mM 2,3-dihydroxybenzoic acid (**1d**), (b) 3 mM of 1-methylindole (**3**) in water (containing phosphate buffer, c_{H2PO4^-} = 0.188 M and $c_{HPO4^{2-}}$ = 0.012 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture at glassy carbon electrode. Scan rate: 100 mV s^{-1}; t = 25 ± 1°C.

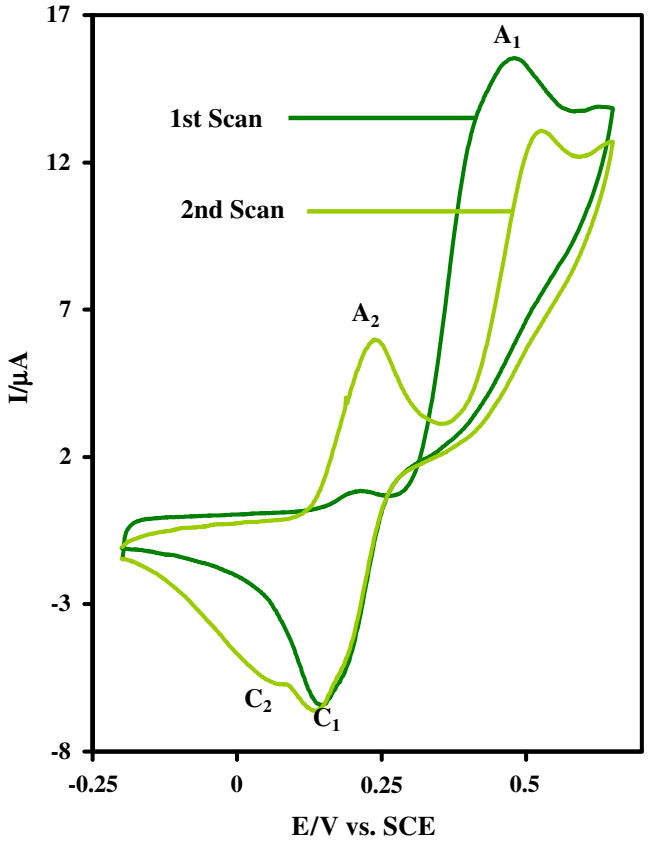


Figure 5. First and second cycle of cyclic voltammograms of 1 mM 2,3-dihydroxybenzoic acid (**1d**) in the presence of 1 mM 1-methylindole (**3**) at glassy carbon electrode, in water (containing phosphate buffer, c_{H2PO4^-} = 0.188 M and $c_{HPO4^{2-}}$ = 0.012 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture. Scan rate: 50 mV s^{-1}; t = 25 ± 1°C.

(phosphate buffer, $c = 0.2$ M, pH = 6.0)/acetonitrile (50:50 v/v) mixture.

The same results are obtained in electrochemical oxidation of 3-methylcatechol (**1b**) and 3-methoxycatechol (**1c**).

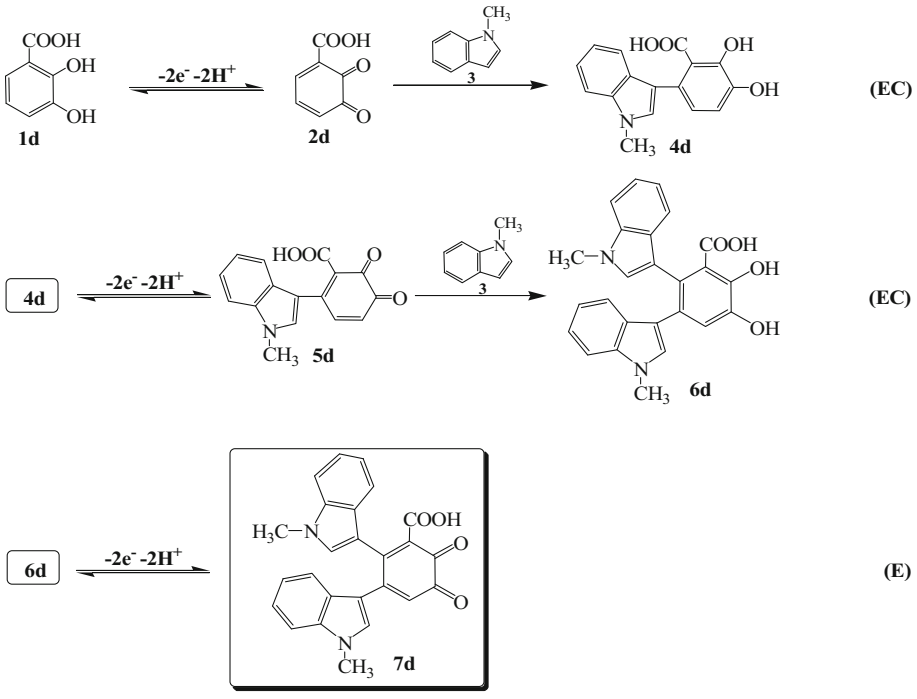
3.2 *Electrochemical oxidation of 2,3-dihydroxybenzoic acid in the presence of 1-methylindole*

The cyclic voltammogram of 2,3-dihydroxybenzoic acid (**1d**) in the absence of 1-methylindole (**3**) (figure 4, curve a) shows one anodic peak (A_1) at 0.42 V and the corresponding cathodic peak (C_1) at 0.33 V, which corresponds to the transformation of 2,3-dihydroxybenzoic acid (**1d**) into the related *o*-benzoquinone (5,6-dioxocyclohexa-1,3-dienecarboxylic acid, **2d**) and vice versa within a two-electron process.[23] As can be seen, in time scale of our experiments, the peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ which can be considered as a criterion for instability of *o*-benzoquinone **2d** is less than unity. The instability of *o*-benzoquinone **2d** can be due to the participation of it in hydroxylation or dimerization reactions.[31–35] In this figure, curve b is the voltammogram of **3**.

The oxidation of 2,3-dihydroxybenzoic acid (**1d**) in the presence of 1-methylindole (**3**) was studied in some detail (figure 5). Under these conditions, the anodic peak current A_1 increases and the cathodic counterpart of it (peak C_1) decreases. In addition, in second cycle, new anodic and cathodic peaks (A_2 and C_2) appear at less positive potential in comparison with peaks A_1 and C_1.

For more data, the influence of the potential sweep rate on the shape of cyclic voltammograms of a solution of **1d** in the presence of **3** has been studied. The results show that proportional to the increasing of the potential sweep rate, the peak current ratio $\left(I_p^{C1}/I_p^{A1}\right)$ increases. It reaches to nearly unity in higher sweep rates. Also, disappearance of peak A_2 in higher sweep rates is another aspect of increasing of sweep rate. This is indicative of departure from intermediate and arrival to diffusion region with increasing sweep rate.[21] This peak (A_2) can be related to the oxidation of intermediate **6d** (see scheme 2). A comparable condition is observed when the **3** to **1d** concentration ratio is decreased.

Controlled-potential coulometry was performed in water (phosphate buffer, $c = 0.2$ M, pH = 6.0)/acetonitrile (50:50 v/v) mixture containing 0.25 mmol of 2,3-dihydroxybenzoic acid (**1d**) and 0.50 mmol of **3** at potential of peak A_1. Cyclic voltammetric analysis carried out during the electrolysis shows the progressive formation of anodic peak A_2 and cathodic peak C_2, parallel to the disappearance of the peak A_1 (figure 6, curves I). This peak (A_1) disappears when the charge consumption becomes about $6e^-$ per molecule of **1d**.



Scheme 2. Electrochemical oxidation mechanism of 2,3-dihydroxybenzoic acid in the presence of 1-methylindole.

Another important difference between voltammograms in figure 6, is related to the amounts of currents at starting potential (−0.25 V *versus* SCE) (see, figure 6, curves II). The results show that the amount of current for curve a at starting potential is nearly zero, but curves b–d show cathodic currents at starting potential. These cathodic currents increase with progress of coulometry. These currents are related to reduction of produced **7d**.

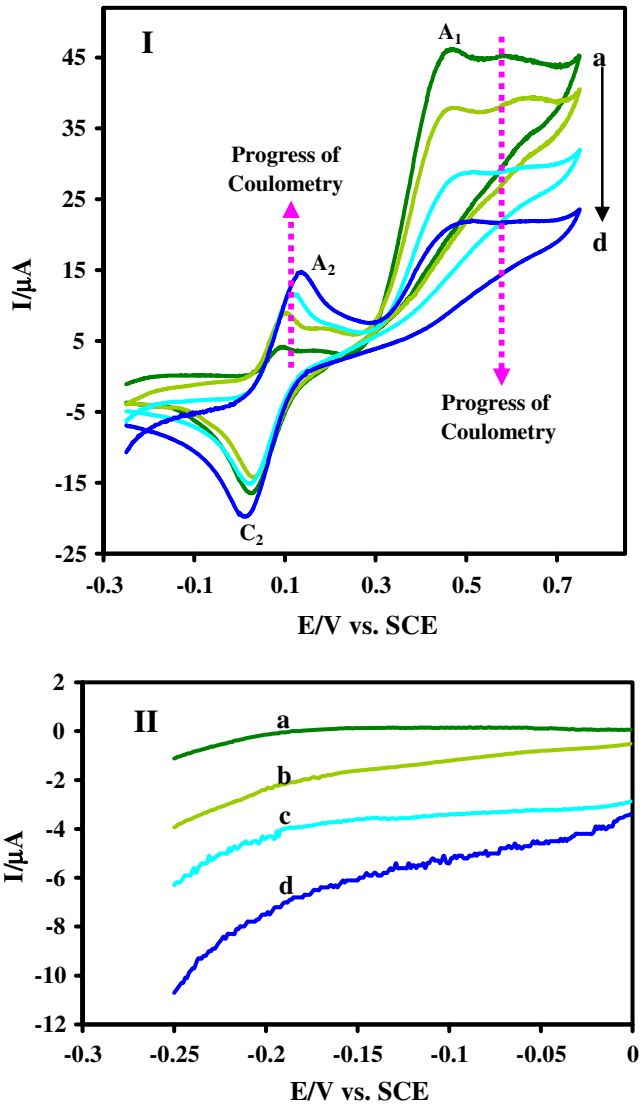


Figure 6. Cyclic voltammograms of 0.25 mmol 2,3-dihydroxybenzoic acid (**1d**) in the presence of 0.50 mmol 1-methylindole (**3**), at glassy carbon electrode in water (phosphate buffer, c = 0.2 M, pH = 6.0)/acetonitrile (50:50 v/v) mixture during controlled-potential coulometry at 0.40 V vs. SCE, after the consumption of (a) 0, (b) 30, (c) 60 and (d) 90 C. Scan rate: 100 mV s^{-1}; t = 25 ± 1°C. Curves II are as same as I, from −0.25 to 0.00 V vs. SCE.

These voltammetric and coulometric data is accompanied by a molecular mass of 410 of the final product (**7d**), obtained during macroscale electrolysis, (see Supporting Information) lead us to propose the following mechanism (*ECECE*) for electrochemical oxidation of 2,3-dihydroxybenzoic acid (**1d**) in the presence of **3** (scheme 2).[36]

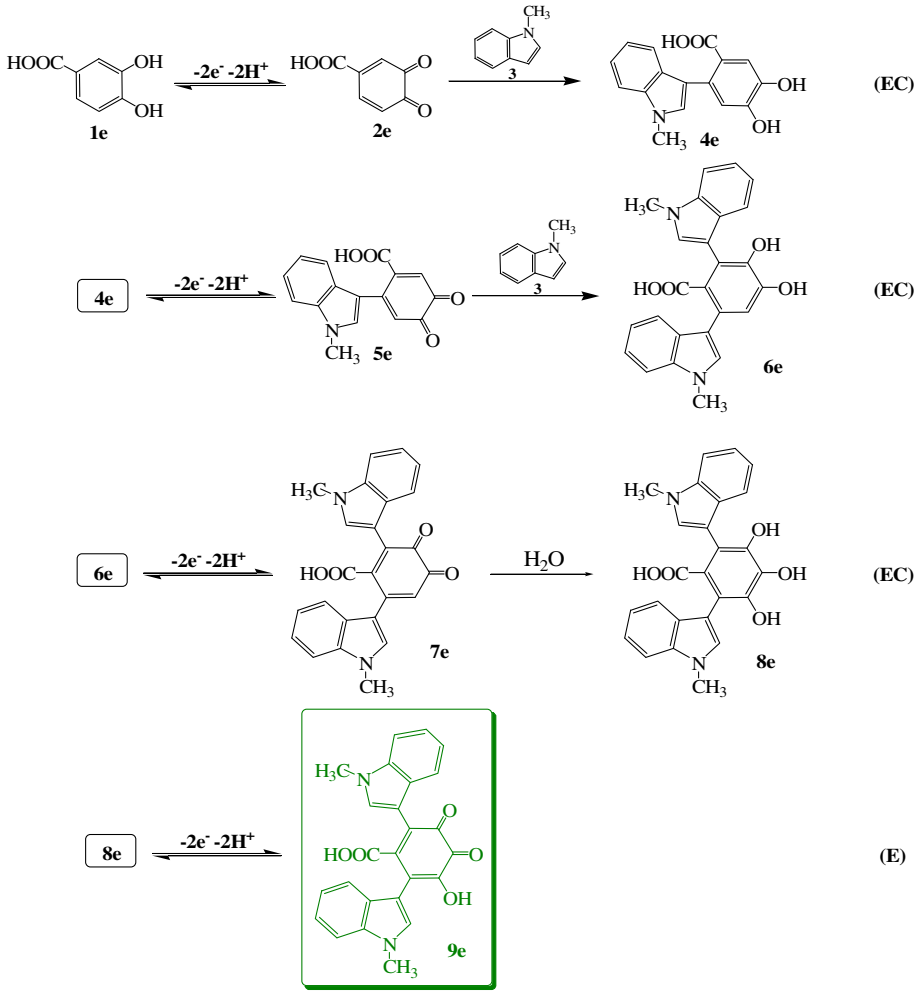
According to our results, it seems that the Michael addition reaction of the 1-methylindole (**3**) to *o*-benzoquinone **2a** is faster than other side reactions and leads to intermediate **4d**. In applied potential **4d** is converted to *o*-benzoquinone **5d**. In the next step, *o*-benzoquinone **5d**, via another intermolecular Michael reaction, is converted to intermediate **6d**. Further oxidation converts intermediate **6d** into the final product **7d**.

Accordingly, the anodic peaks A_1 and A_2 pertain to the oxidation of 2,3-dihydroxybenzoic acid (**1d**) and dihydroxybenzoic acid **6d** to the *o*-benzoquinone **2d** and **7d**, respectively. Obviously, the cathodic peaks C_1 and C_2 correspond to the reduction of *o*-benzoquinones **2d** and **7d**, respectively.

3.3 *Electrochemical oxidation of 3,4-dihydroxybenzoic acid in the presence of 1-methylindole*

Such as 2,3-dihydroxybenzoic acid (**1d**), the same voltammetric data have been obtained in the case of 3,4-dihydroxybenzoic acid (**1e**). But, contrary to the previous case, the mass spectrum of final product obtained from electrochemical oxidation of 3,4-dihydroxybenzoic acid (**1e**) in the presence of 1-methylindole (**3**) shows mass = 426 g/mol. Diagnostic criteria of voltammetry accompanied by the molecular mass of the final product, obtained during macroscale electrolysis, (see Supporting Information), indicates that the reaction mechanism of electrooxidation of **1e** in the presence of 1-methylindole (**3**) in our electrolysis condition, is *ECECECE* (scheme 3).[37]

According to scheme 3, it seems that the Michael addition reaction of **3** to *o*-benzoquinone **2e** is faster than other side reactions and leads to intermediate **4e**. The next oxidation process converts **4e** to *o*-benzoquinone **5e**. In the next step, *o*-benzoquinone **5e**, via a Michael reaction, is converted to intermediate **6e**. Another oxidation process transforms intermediate **6e** to *o*-benzoquinone **7e**. Michael addition reaction of water to *o*-benzoquinone **7e**, converts **7e** to intermediate **8e** and further oxidation converts intermediate **8e** into the final product **9e**.



Scheme 3. Electrochemical oxidation mechanism of 3,4-dihydroxybenzoic acid in the presence of 1-methylindole.

4. Conclusion

The reaction scheme for oxidation of catechol (**1a**), 3-methylcatechol (**1b**) and 3-methoxycatechol (**1c**) in the presence of 1-methylindole (**3**), in water (phosphate buffer, $c_{H2PO4^-} = 0.188$ M and $c_{HPO4^{2-}} = 0.012$ M, pH = 6.0)/acetonitrile (50:50 v/v) mixture is presented (scheme 1). In the case of these catechols, the over-oxidation of compounds **6a–c** were circumvented during the preparative reaction because of the insolubility of the final products. The reaction scheme for oxidation of 2,3-dihydroxybenzoic acid (**1d**) in the same conditions is presented (scheme 2). In this case, because of the presence of carboxyl group in structure of intermediate **6d** and solubility of it in electrolysis medium, the final product **7d** was obtained after over-oxidation of **6d**. The reaction scheme for oxidation of 3,4-dihydroxybenzoic acid (**1e**) is presented (scheme 3). The oxidation, Michael addition reaction of water and over-oxidation convert intermediate **6e** to product **9e**.

Supporting information

Mass spectra of **6a**, **7d** and **9e** are provided as supplementary material (figures S1–S3). See www.ias.ac.in/chemsci for supporting information.

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