

Short Communication

Electrochemical Synthesis of Benzimidazole Derivative Using Carbon Electrode in Aqueous Medium

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Electrochemical oxidation of catechol in the presence of carbohydrazide in aqueous solution has been studied on a carbon electrode by cyclic voltammetry and controlled-potential coulometry techniques. A direct electron transfer (DET) mechanism occurred during the process on the surface of carbon anode. The results indicate that the catechol derivative is converted to benzimidazole derivative. The electrochemical oxidation of catechol in the presence of carbohydrazide leads to the formation of 1,3-diamino-5,6-dihydroxy-1*H*-benzo[*d*]imidazole-2(3*H*)-one as final product.

Keywords: Catechol, Benzimidazole, Michael reaction, Carbohydrazide, Carbon electrode

1. INTRODUCTION

Several studies have been carried out by many authors to investigate the degradation of oxidizable substrates at graphite and other carbon anodes electrodes in aqueous solution [1,2]. Catechols and their quinone derivatives have drawn considerable attention due to their abundance in nature and important roles in many biological systems. Moreover, most of the compounds incorporating to catechol moiety have been reportedly exhibit as antioxidant [3] and antibacterial activities [4,5]. *O*- and *p*-dihydroxybenzenes are well known in biological systems. Investigation on electrooxidation processes of catechols is critical in attaining a better understanding of the *o*-quinones electrogeneration [6,7]. In addition, the electrochemical process is very often parallels to the oxidation of catecholamines in mammalian central nervous system and this process occurs in the human body [8]. Benzimidazole derivatives have found applications as corrosion inhibitor [9-11] and antibacterial [12]. These compounds are also widely used in dye [13]. In the course of a wide program aimed at the

electrochemical synthesis of new *o*-dihydroxybenzenes and benzimidazole derivatives, we have studied the electrochemical behavior of catechol in the presence of carbohydrazide.

2. EXPERIMENTAL PART

2.1. General Procedure

The Catechol were reagent-grade materials from Aldrich. The KH_2PO_4 , K_2HPO_4 and other acids and bases were of pro-analysis grade from E. Merck. Carbohydrazide 98% were purchased from Aldrich. These chemicals were used without further purification. Cyclic voltammetry and controlled-potential coulometry were performed using an Autolab model PGSTAT 302N potentiostat/galvanostat.

2.2. Preparation of the cell

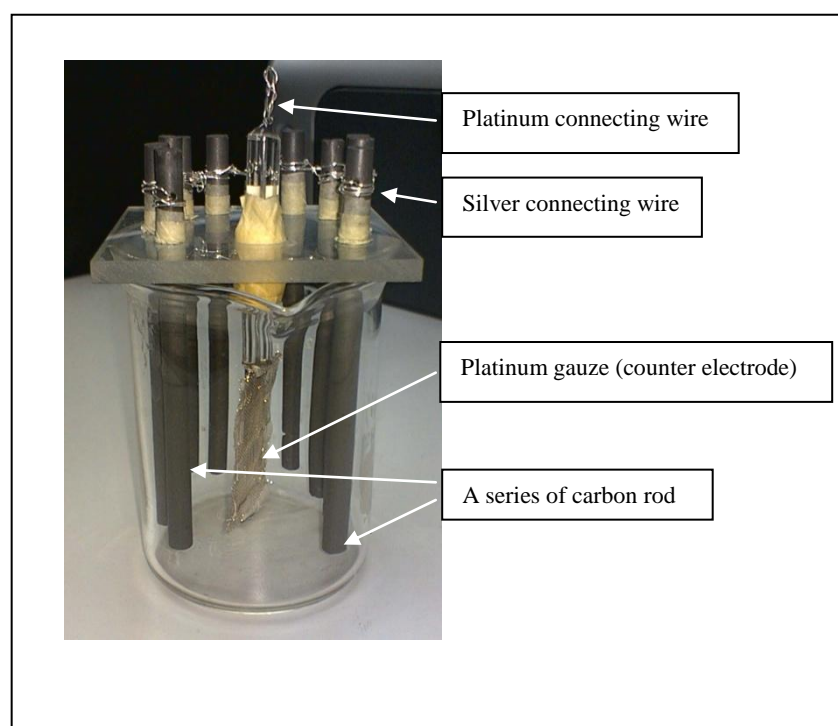


Figure 1. The photo of applied undivided cell. An assembly of 12 carbon rods 6 mm diameter and 110 mm length) as the working electrode (WE) and a large platinum gauze (25 mm width and 50 mm length) constituted the counter electrode (CE).

The working electrode (WE) used in the voltammetry experiments was a glassy carbon disc (1.8 mm diameter). Glassy carbon was polished with polishing cloth before each measurement. The platinum wire was used as a counter electrode (CE) and the reference was an Ag/AgCl. All electrodes for CV experiments were from Radiometer analytical. An undivided cell was used for controlled-potential coulometry (CPC). An assembly of 12 carbon rods (6 mm diameter and 110 mm length),

whose upper rims were wrapped by a silver wire, was employed as the working electrode (WE) in controlled-potential coulometry and a large platinum gauze (25 mm width and 50 mm length) constituted as the counter electrode (CE) (Figure 1). The working electrode potentials were measured versus Ag/AgCl. The Ag/AgCl references and carbon rods were put together and their distance from the counter electrode was about 20 mm. The applied potential throughout CPC was 0.5 V vs. Ag/AgCl and controlled by the potentiostat. During electrolysis, a magnetic stirrer was used. The cell used was a simple and undivided cell.

2.3. Electroorganic synthesis of benzimidazole derivative

Table 1. Electroanalytical and preparative data.

Conversion	Purification (Extraction)	Applied potential (V) (Ag/AgCl)	Product yield (%)
1 → 6	Chloroform	0.5	58.4
1 → 6	Chloroform	0.4	49.6
1 → 6	Dichloromethane	0.5	44.5
1 → 6	Dichloromethane	0.4	36.8

In a typical procedure, an aqueous solution containing phosphate buffer (pH 7.0, 0.15 M) was pre-electrolyzed at the chosen potential (see Table 1), in an undivided cell equipped with carbon rods anode and a large platinum gauze cathode at room temperature under constant-current density of 2 mA/cm²; then, 2 mmol of catechol (**1**) and carbohydrazide (**3**) (2 mmol) were added to the cell. The electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted during the electrolysis, and the carbon rods anode was washed in acetone for reactivation. At the end of electrolysis, the solution was extracted by the chosen solvent in Table 1, the solution was dried by sodium sulfate. After purification, the electrolysis product obtained was characterized by IR, ¹H NMR and ¹³C NMR spectroscopy.

2.4. Spectroscopic data of the product

Name: 1,3-diamino-5,6-dihydroxy-1H-benzo[d]imidazole-2(3H)-one

Molecular formula: (C₇H₈N₄O₃)

Isolated yield = 58.4%, IR_(KBr): 3413, 3175, 2314, 1588, 1356, 1234, 806, 732 and 647 cm⁻¹. ¹H NMR, δ ppm (200 MHz DMSO-d₆): 2.13 (s, 2H, amine protons), 2.46 (s, 2H, amine protons), 5.08 (s, 2H, hydroxy protons), 7.10 (s, 2H aromatic protons). ¹³C NMR, δ ppm (150 MHz DMSO-d₆): 102.3, 119.8, 138.2, 157.6.

3. RESULTS AND DISCUSSION

3.1. Electrochemical oxidation of catechol (1) in the presence of carbohydrazide (3)

In this experiment, the electrochemical behavior of catechol and carbohydrazide was studied by cyclic voltammetry. The cyclic voltammogram of 1.0 mM catechol in aqueous solution containing 0.15 M phosphate buffer (pH 7.0) as supporting electrolyte was as recorded in Figure 2 (curve a).

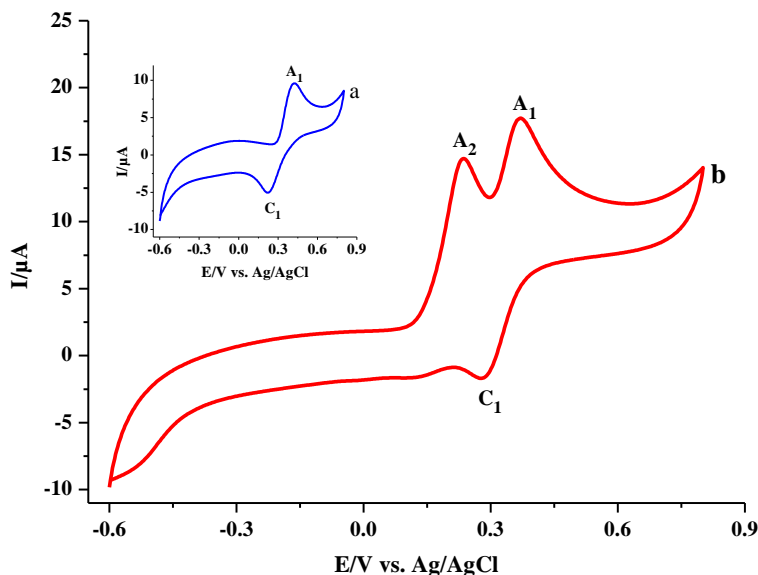


Figure 2. Cyclic voltammograms of 1.0 mM catechol (1): (a) in the absence; (b) in the presence of 1.0 mM carbohydrazide (3) at a glassy carbon electrode (1.8 mm diameter) in the 0.15 M phosphate buffer solution ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$) pH=7; at scan rate: 10mVs^{-1} ; $T = 25 \pm 1^\circ\text{C}$.

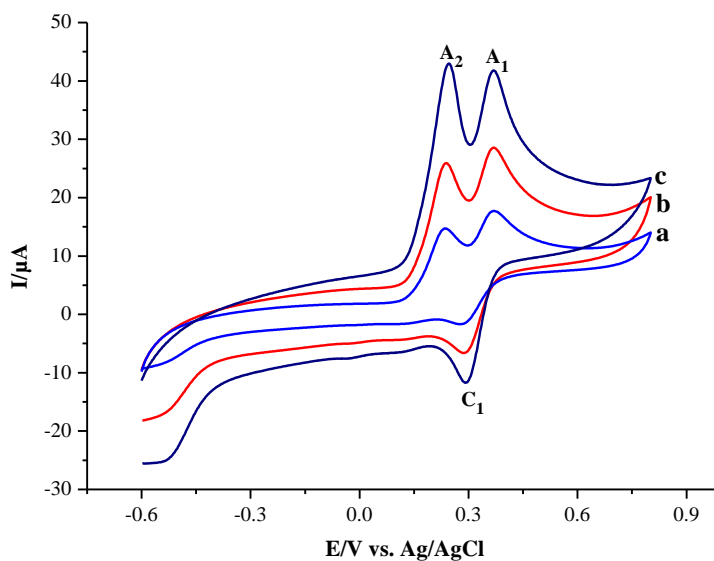
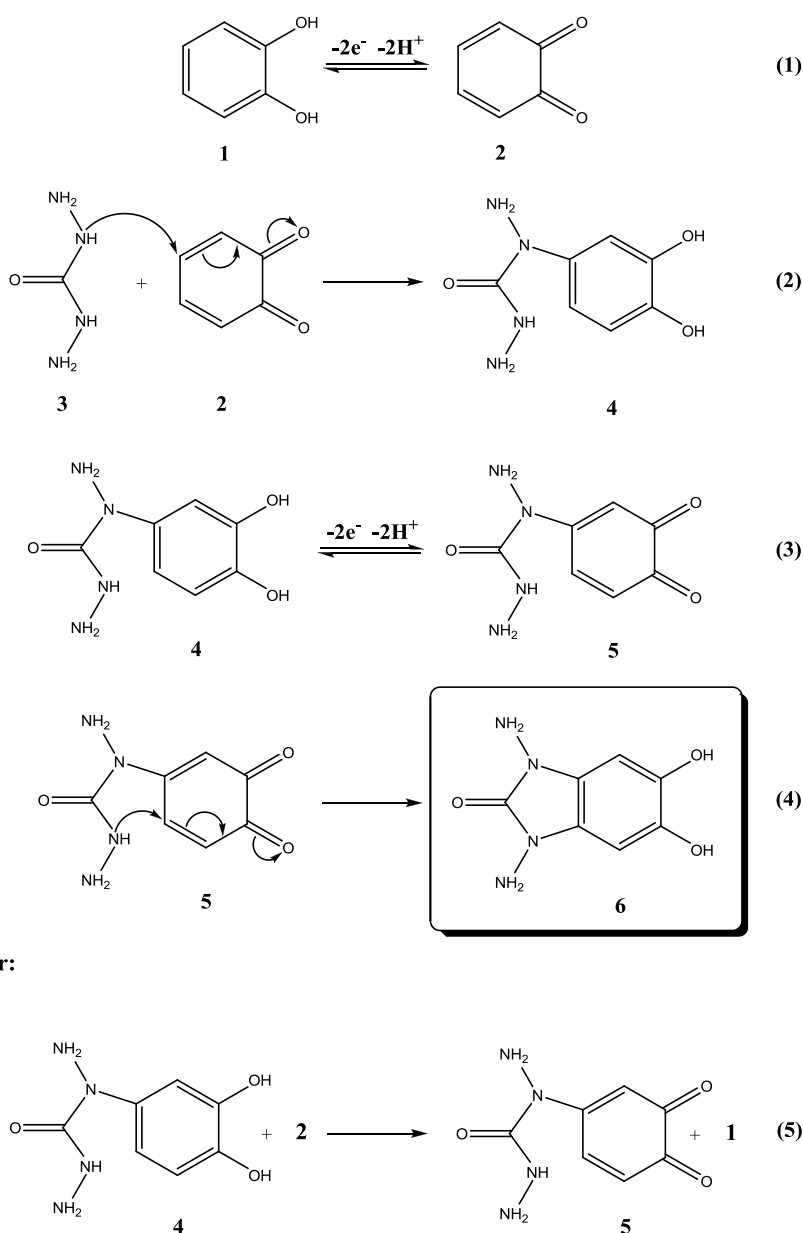


Figure 3. Typical cyclic voltammograms of 1.0 mM catechol (1) in the presence of 1.0 mM carbohydrazide (3) in water containing of 0.15 M phosphates ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$) as the buffer and supporting electrolyte (pH=7) using a glassy carbon electrode (1.8 mm diameter) and at various scan rates. Scan rate from (a) to (c) are 10, 25 and 50mVs^{-1} , respectively. $T = 25 \pm 1^\circ\text{C}$.

At the conditions used, voltammogram exhibit one anodic peak (A_1) in the positive scan and a cathodic counterpart peak (C_1) in the negative scan which corresponds to the transformation of catechol (**1**) to *o*-benzoquinone (**2**). The oxidation of catechol (**1**) in the presence of 1.0 mM carbohydrazide (**3**) as a nucleophile was later studied in some detail (Figure 2, curve b). The voltammogram obtained exhibits two anodic peaks (A_1 and A_2) and a cathodic peak (C_1).

The A_2 peak corresponds to the electrooxidation of intermediate (**4**). In these conditions, the cathodic counterpart of the anodic peak A_2 disappears. Furthermore, it is seen that proportional to the augmentation of potential sweep rate, the height of C_1 peak of (**1**) increases (Figure 3, curves a-c). A similar situation is observed when the concentration ratio of carbohydrazide (**3**) to catechol (**1**) is decreased.



Scheme 1. The mechanism for the electrooxidation of catechol in the presence of carbohydrazide.

Controlled-potential coulometry was then performed in aqueous solution containing 0.15 M phosphate buffer (pH 7), 0.2 mmol of species (1) and 0.2 mmol of species (3) at 0.5 V versus Ag/AgCl. Papouchado et al. [14] and Nematollahi et al. [15-17] have demonstrated that the anodic oxidation of catechol and its derivatives, in the presence of different nucleophiles, follows a pattern of an *EC* or *ECEC* mechanism, depending on the nature of the nucleophile. For example, when 2-acetylcyclopentanone is the nucleophile, the initial two-electron oxidation is followed by 1,4-addition of 2-acetylcyclopentanone to generate catechol derivatives (an *EC* mechanism) [15]. However, in the presence of acetylacetone [16], or dimedone [17], it follows an *ECEC* type mechanism, to form benzofuran derivatives. It is well known [18] that the mechanism of the oxidation of catechol and its derivatives, in aprotic solvents and in the absence of proton donors, is an *ECEC* type mechanism, and a typical CV shows two-step, one-electron each process. However, in the presence of proton donors or in protic solvents, the mechanism becomes a one-step, two-electron process. Based on the above information, it is likely that, in our case, an *ECEC* type mechanism may take place to produce compound 6. These observations allow us to propose the *ECEC* pathway illustrated in Scheme 1 for the electrooxidation of catechol in the presence of carbohydrazide. According to the results obtained, it seems that the Michael addition reaction of carbohydrazide (3) to *o*-quinone (2) (Scheme 1, Eq. 2) is faster than the other secondary reactions, leading to the product adduct (4). The adduct (4) was then undergoes the abstraction of a second pair of electrons, leading to *o*-benzoquinone (5). The intramolecular addition of (4) to (5) leads to the formation of 1,3-diamino-5,6-dihydroxy-1*H*-benzo[*d*]imidazole-2(3*H*)-one (6) as final product. Besides, it is possible that the oxidation of (4) take place through a single electron transfer (SET) reaction (Scheme 1, Eq. (5)). The overall reaction mechanism for the anodic oxidation of catechol in the presence of carbohydrazide as a nucleophile is presented in Scheme 1.

4. CONCLUSIONS

According to our results, it seems that the Michael reaction of carbohydrazide to *o*-quinone formed leads to the formation of 1,3-diamino-5,6-dihydroxy-1*H*-benzo[*d*]imidazole-2(3*H*)-one (C₇H₈N₄O₃) as a final product. Catechol is oxidized in water to their respective *o*-benzoquinone. The quinone is then attacked by carbohydrazide to form benzimidazole derivative adduct. From the point of view of green chemistry, the use of electrosynthesis method has some significant benefits. The use of electricity as an energy instead of oxidative reagents, clean synthesis, one-step reaction, use of aqueous media instead of organic solvents, technical applicability, work in room temperature and pressure, and especially significantly high atom economy are of preminent green advantages.

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