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# Electrochemical Study of Catechol Derivatives in the Presence of β-diketones: Synthesis of Benzofuran Derivatives

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The electrochemical oxidation of 4-(1,3-dithiolan-2-yl)benzene-1,2-diol was studied in the presence and absence of acetylacetone (**2a**), dimedone (**2b**) and 4-hydroxycoumarin (**2c**) as nucleophiles in aqueous solution by means of cyclic voltammetry and controlled-potential coulometry. The results indicate that these nucleophiles participate in Michael addition reaction with the oxidized form of catechol derivatives, and then convert it to the corresponding new benzofuran derivatives. The electrochemical synthesis of compounds has been successfully performed at a carbon rod electrode and in two-compartment cell. The observed homogeneous rate constants ($k_{obs}$) of the reaction of oxidized form of catechol derivatives with **2a-c** as nucleophiles were estimated by comparing the experimental cyclic voltammograms with the digital simulated results. The calculated $k_{obs}$ was found to vary in the order 4-hydroxycoumarin (**2c**) < dimedone (**2b**) < acetylacetone (**2a**).
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Electrochemical methods are more and more widely used for the study of electroactive compounds in pharmaceutical forms and physiological fluids due to their simple, rapid, and economical properties.[1] Catechol derivatives play an important role in mammalian metabolism, and many compounds of this type are known to be secondary metabolites of higher plants. Moreover, 2 over 1800 examined antibiotics of microbial origin contain a catechol sub-structure. Therefore, the catechol derivatives are a promising group of compounds worthwhile for further investigation, which may lead to the discovery of selective acting biodegradable agrochemicals having high human, animal and plant compatibility.[2] Biologically active heterocyclics, benzofuran derivatives constitute a major group.[3–6] They are usually an important constituent of plant extracts used in medicinal chemistry for their various biological activities, including insecticidal, traditional medicine, antimicrobial, and antioxidant properties.[7,8] Thus, development of efficient methods to functionalize heterocyles is critical for synthetic chemistry and synthesis of organic compounds with both structures of catechol and benzofuran would be of interest from the point of view of pharmaceutical properties. This idea prompted us to investigate electrochemical oxidation of 4-(1,3-dithiolan-2-yl)benzene-1,2-diol (DITHBD; **1** in Scheme 1) in the presence of acetylacetone (**2a**), dimedone (**2b**) and 4-hydroxycoumarin (**2c**) as nucleophiles and report a facile electrochemical method for the synthesis of some new benzofuran compounds. An additional purpose of this work is to estimate the observed homogeneous rate constants ($k_{obs}$) of reaction of electrochemically generated *o*-benzoquinone with nucleophiles by digital simulation of cyclic voltammograms.

## Experimental

*Apparatus and chemicals.*— Cyclic voltammetry and preparative electrolysis were performed using a potentiostat/galvanostat (SAMA 500, electroanalyzer system, Iran). The working electrode used was a glassy carbon disk (1.8 mm diameter; purchased from AZAR, Iran) and a platinum wire was used as the counter electrode. The working electrode used in controlled-potential coulometry and macroscale electrolysis was an assembly of four carbon rods (total surface area of the four electrodes: 35 $cm^2$), while a large stainless steel gauze constituted the counter electrode. The working electrode potentials were measured versus a saturated calomel electrode (SCE; AZAR, Iran). All electrochemical oxidations were performed under controlled-potential conditions in a cell with two compartments separated by a porous fritted-glass diaphragm and equipped with a magnetic stirrer. A Metrohm 691 pH/Ion Meter was used for pH measurements. All solutions were freshly prepared using double-distilled water. Homogeneous rate constants were estimated by analyzing the cyclic voltammetric responses, using simulation software.[9] 3,4-Dihydroxybenzaldehyde, 1,2-ethanedithiol, acetylacetone, dimedone and 4-hydroxycoumarin were reagent-grade from Aldrich. Phosphate salt, sodium hydroxide, solvents and reagents were of pro-analysis grade from E. Merck. These chemicals were used without further purification. The peak current ratios (*I*pC1/*I*pA1) were determined using the following equation given in Ref. 10.

$$[I_{pc}/I_{pa} = (I_{pc})_0/I_{pa} + 0.485(I_{sp})_0/I_{pa} + 0.086]$$

where $(I_{pc})0$ and $(I_{sp})0$ are cathodic peak current and "switching potential" current with respect to the zero current, respectively, while $I_{pc}$ corresponds to the cathodic peak current and $I_{pa}$ the anodic peak current.

*Synthesis of 4-(1,3-dithiolan-2-yl)benzene-1,2-diol (1).*— A mixture of 3,4-dihydroxybenzaldehyde, (1 mmol), 1,2-ethanedithiol (1.2 mmol) and 37% $BF_3 \cdot SiO_2$ (0.3 g) was ground in a pestel at an ambient temperature. The progress of reaction was monitored by thin layer chromatography. After completion of the reaction, the product was dissolved in ethanol, filtered, and the solvent was evaporated. The obtained solid was recrystalized in chloroform.

*Electroorganic synthesis of benzofuran derivatives.*— In a typical procedure, 80 mL of 0.15 M phosphate buffer (pH 7.0) in water/acetonitrile (85/15 volume ratio), containing 0.7 mmol of DITHBD and 0.7 mmol acetylacetone (**2a**) or dimedone (**2b**) or 4-hydroxycoumarin (**2c**), was electrolyzed at controlled-potential in a two compartment cell. The applied potential used in electrosynthesis was optimized to obtain each product (0.35 vs. SCE). The electrolysis was terminated when the current decayed to 5% of its original value. The process was interrupted seven times during the electrolysis and the carbon anode was washed in acetone in order to reactivate it. The precipitated solid was collected by filtration and was washed several times with water. After washing, products were characterized by IR, $^1$H NMR, $^{13}$C NMR.

*Characteristics of products–1-(4-(1,3-dithiolan-2-yl)-6,7-dihydroxy-2-methylbenzofuran-3-yl)ethanone(5a) ($C_{14}H_{16}O_4S_2$).*— Applied potential: 0.35 vs. SCE. Mp = 268-270°C. IR (KBr) ν($cm^{-1}$): 3420, 3120, 1622, 1570, 1505, 1440, 1390, 1342, 1282, 1234, 1222, 1130, 982, 847, 764. $^1$H NMR, δ (ppm) (500 MHz, DMSO): 2.30 (s, 3H, methyl), 2.56 (m, 5H), 2.86 (t, 4H, $J$ = 11 Hz), 5.28 (s, 1H), 6.68 (s, 1H aromatic); 8.42 (broad, 1H hydroxy), 9.10 (broad, 1H hydroxy). $^{13}$C NMR, δ (ppm) (DMSO): 18.6, 30.1, 43.3, 52.2, 111.52, 118.2, 122.3, 125.0, 138.7, 140.4, 145.3, 152.0, 185.2.

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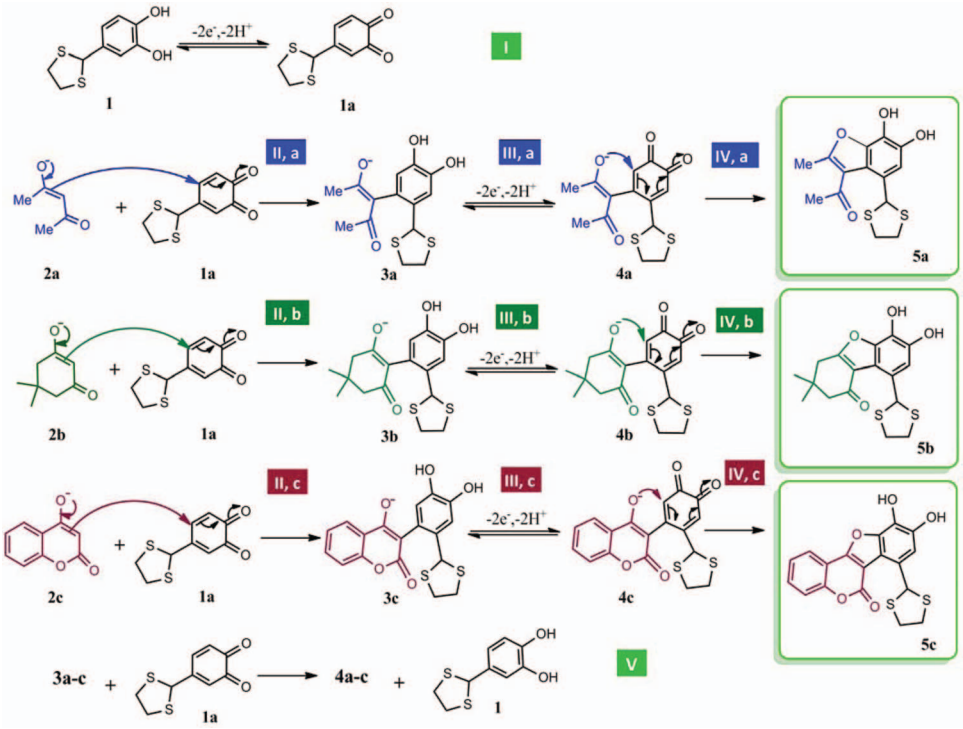

**Scheme 1.** Proposed mechanism for the electrochemical oxidation of DITHBD (**1**) in the presence of acetylacetone (**2a**), dimedone (**2b**) and 4-hydroxycoumarin (**2c**).

*9-(1, 3-dithiolan-2-yl) -6, 7- dihydroxy-3, 3-dimethyl-3, 4-dihydrodibenzo[b,d]furan-1(2H)-one(5b)($C_{17}H_{18}O_4S_2$).*— Applied potential: 0.35 vs. SCE. Mp = 286-288°C. IR (KBr) $cm^{-1}$: 3270, 3140, 2950, 2910, 1630, 1588, 1473, 1448, 1372, 1292, 1248, 1138, 1112, 1087, 983, 823, 776. $^1$H NMR, δ (ppm) (500 MHz, DMSO): 1.03 (s, 6H), 2.22 (s, 2H); 2.56 (s, 2H); 2.86 (t, 4H, $J$ = 11 Hz), 5.58 (s, 1H), 6.48 (s, 1H aromatic), 8.69 (broad, 1H, hydroxy), 9.18 (broad, 1H, hydroxy). $^{13}$C NMR, δ (ppm) (DMSO): 22.1, 29.1, 32.0, 45.2, 52.2, 57.1, 110.3, 114.2, 122.1, 127.3, 143.1, 144.4, 146.3, 161.4, 177.2.

*7-(1, 3-dithiolan-2-yl)-9, 10-dihydroxy-6H-benzofuro[3, 2-c]chromen-6-one(5c)($C_{18}H_{12}O_5S_2$).*— Applied potential: 0.35 vs. SCE. Mp = 308-310°C. IR (KBr) $cm^{-1}$: 3380, 3290, 2984, 2880, 1730, 1628, 1610, 1514, 1356, 1325, 1280, 1265, 1232, 1050, 980, 872. $^1$H NMR, δ (ppm) (500 MHz, DMSO): 2.42 (2 H, t, $J$ = 11 Hz), 2.66 (2 H, t, $J$ = 11 Hz), 5.23 (s, 1H), 6.12 (s, 1H, aromatic), 7.24 (m, 4H), 8.91 (broad, 1H, hydroxy), 9.26 (broad, 1H, hydroxy). $^{13}$C NMR, δ (ppm) (DMSO): 30.1, 52.2, 109.1, 113.2, 115.4, 122.3, 123.6, 125.2, 126.4, 127.2, 129.5, 146.2, 149.1, 153.2, 159.6, 160.2.

## Results and Discussion

*Electrochemical study.*— As DITHBD is produced using 3,4-dihydroxybenzaldehyde (DIBZ), the electrochemical behavior of these two compounds are compared. Cyclic voltammetry was used to study the effect of the change from an aldehyde group to 1,2-ethanediothiol in DIBZ. Cyclic voltammogram of a 1.0 mM aqueous solution of DIBZ in 0.15 M phosphate buffer (pH 7.0) is shown in Fig. 1 curve a. As can be seen, one anodic ($A_1$) and two cathodic peaks $C_1$ and $C_2$ were obtained. Fig. 1 curve b, shows the cyclic voltammogram of 1.0 mM DITHBD in conditions similar to those used to obtain curve a. This compound is a catechol derivative, which can be electrochemically oxidized to quinone ($A_1$ in Figure 1a and Figure 1b). The change from two cathodic peaks in curve a to one cathodic peak in curve b can be explained as follows: The electron withdrawing character of an aldehyde group is stronger than that of an ethanedithol group, leading to the formation of more reactive quinone. Then, the rate reaction in reaction side such as hydroxylation,[11,12] dimerization[13–15] or oxidative ring cleavage[16] is increased.

Comparison of the two cyclic voltammograms in Figure 1 appears to indicate that the peak current ratio $I_{pC1}/I_{pA1}$ is dependent on the

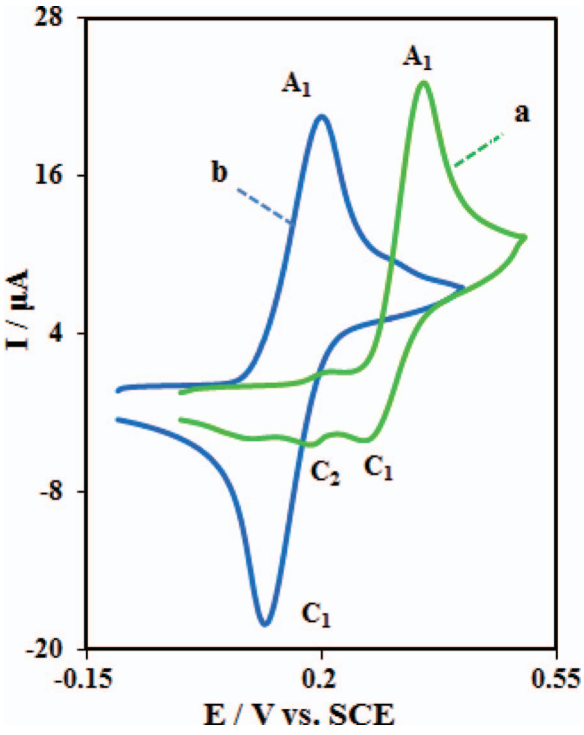


**Figure 1.** Cyclic voltammograms of 1.0 mM 3,4-dihydroxybenzaldehyde (a), 1.0 mM DITHBD (b) at glassy carbon electrode, in phosphate buffer solution (pH = 7.0, $c$ = 0.15 M). Scan rate: 100 mV $s^{-1}$.t = 25 ± 1°C.

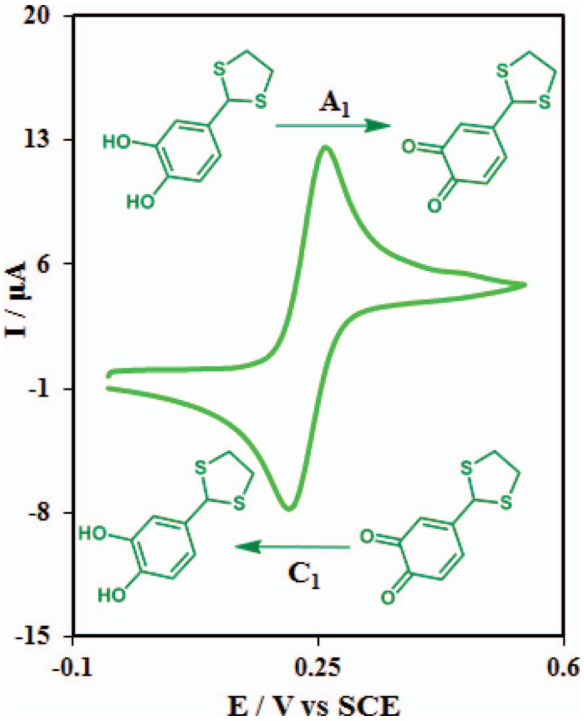


**Figure 2.** Cyclic voltammograms of 1.0 mM DITHBD (1) at glassy carbon electrode, in phosphate buffer solution (pH = 7.0, $c$ = 0.15 M). Scan rate: 50 mV $s^{-1}$. t = 25 ± 1°C.

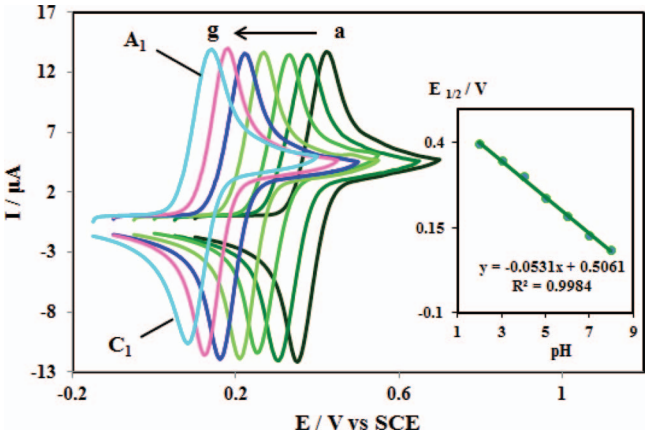


**Figure 3.** Cyclic voltammograms of 1.0 mM DITHBD (**1**), at glassy carbon electrode, in water (buffered solutions with various pHs and same ionic strength)/acetonitrile (85/15 v/v). pH values from (a) to (h) are 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 respectively. Scan rate: 50 mV $s^{-1}$. Inset: Variation of half-wave potential ($E_{1/2}$) of DITHBD (**1**) as a function of pH. t = 25 ± 1°C.

electron-withdrawing character. In the presence of the aldehyde group with more electron-withdrawing character in the structure of DIBZ, the peak current ratio, $I_{pC1}/I_{pA1}$, of DIBZ is smaller than peak current ratio in DITHBD. Also, in the presence of the ethanedithiol group, the potential of peak $A_1$ in curve b has shifted negatively by 170 mV compared to that in curve a.

Next, cyclic voltammetry of 1.0 mM DITHBD (1) in water/acetonitrile (85/15 volume ratio) was conducted in 0.15 M phosphate buffer (pH 7.0) and the result is show in Fig. 2.

As can be seen, one anodic ($A_1$) peak arising from the oxidation of DITHBD to its quinone and one cathodic ($C_1$) peak arising from the reduction of the quinone back to DITHBD were obtained.

Fig. 3 shows the cyclic voltammograms of DITHBD (1) in water/acetonitrile (85/15 volume ratio) obtained at different pH. Between pH 2.0 and 7.0, the cyclic voltammograms show one anodic ($A_1$) and a corresponding cathodic peak ($C_1$). Under these conditions, peak current ratio ($I_{pC1} = I_{pA1}$) of nearly unity was obtained, supporting a degree of stability of DITHBD (1) produced at the electrode surface under the specified experimental conditions. In other words, any hydroxylation,[11,12] dimerization[13–15] or oxidative ring cleavage[16] reactions are too slow to be observed on the time scale of cyclic voltammetry. When the potential sweep rate was decreased from 50 mV $s^{-1}$ ($Ip_{C1} = Ip_{A1}$) to 10 mV $s^{-1}$, A peak current ratio ($I_{pC1}/I_{pA1}$) obtained are 0.8, 0.8, 0.76, 0.7, 0.6, and 0.46 for the pH of 2.0–7.0, respectively. At pH 8.0 (scan rate: 50 mV $s^{-1}$), a peak current ratio ($I_{pC1}/I_{pA1}$) of 0.73 (<1) was obtained (Fig. 3). A peak current ratio of 0.38 was also obtained when the potential sweep rate was decreased from 50 mV $s^{-1}$ to 10 mV $s^{-1}$. With increasing pH, the peak current ratio ($I_{pC1} = I_{pA1}$) becomes less than unity as well as decreasing potential sweep rate. These changes in the peak current ratio can be related to the occurrence of side reactions such as hydroxylation, dimerization or oxidative ring cleavage under the experimental conditions. These reactions are enhanced by increasing pH. Also, it was found that the peak potential for peak $A_1$ ($E_{pA1}$) shifted negatively as a function of pH. This is expected because of the participation of proton(s) in the oxidation of DITHBD (**1**) to its quinonic form (**1a**).

$$\text{DITHBD} \rightleftharpoons \text{DITHBDQ} + \text{mH}^+ + 2\text{e}^-$$

DITHBDQ denotes the quinone of DITHBD (1a); and m is the number of proton(s) involved in the reaction. The half-wave potential ($E_{1/2}$), is given by:[17]

$$E_{1/2} = E'_{1/2} - (2.303\,\text{mRT}/2\text{F})\,\text{pH}$$

where $E'_{1/2}$ at pH = 0.0, and R, T, and F have their usual meanings. The half-wave potentials ($E_{1/2}$) were calculated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms $\{(E_{pa} + E_{pc})/2\}$.[17]

The values of $E_{1/2}$ as a function of solution pH are plotted in the inset of Fig. 3. As can be seen, $E_{1/2}$ shifted to negative potentials with the slope of 53 mV/pH, which is in agreement with the theoretical slope (2.303 mRT/2F) of 59 mV/pH when m = 1.8 ≈ 2. This is expected because DITHBD has a catechol ring with two-electron two-proton redox behavior.[18] Extrapolation of the plot to pH = 0 yields the $E'_{1/2}$ = 0.51 V versus SCE.

The oxidation of DITHBD (1) was also studied in the presence of β-diketones (acetylacetone (**2a**), dimedone (**2b**)) and β-ketoester (4-hydroxycoumarin (**2c**)) as nucleophiles. In Fig. 4, the cyclic voltammograms of 1 mM DITHBD (**1**) obtained in the presence of 1 mM acetylacetone (**2a**), 1 mM dimedone (**2b**) and 1 mM 4- hydroxycourmarin (**2c**) are shown in I, II and III, respectively. In each study, the first cyclic voltammetric scan is represented by trace b. These voltammograms exhibit an anodic peak ($A_1$) and a cathodic peak ($C_1$).

The voltammograms exhibit one anodic peak, and the cathodic ($C_1$) decreases. This could be indicative of the fact that electrochemically generated **1a** is removed by chemical reaction with nucleophiles (**2a-c**). The observed shift (<10 mV) of the $A_1$ and $C_1$ peaks in curve b (Fig. 4), relative to curve a (Fig. 4) are probably 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.[19,20]

In the second cycle, parallel to the shift of the peak $A_1$ in a positive direction, a new peak ($A_0$) appears (Fig. 4 curve b, 2nd scan). This new peak is related to electrochemical oxidation of intermediate (**3a-c**). It is seen that, proportionally to the augmentation of the potential sweep rate, the peak current ratio ($I_{pC1}/I_{pA1}$) increases (Fig. 5). A similar situation is observed when the concentration ratio of nucleophiles (**2a-c**) to DITHBD (**1**) decreased.

The current function for the peak $A_1$ ($I_P{}^{Al}/\nu^{1/2}$) decreases with an increasing scan rate and such behavior is adopted as indicative of an *ECEC* mechanism.[19–22]

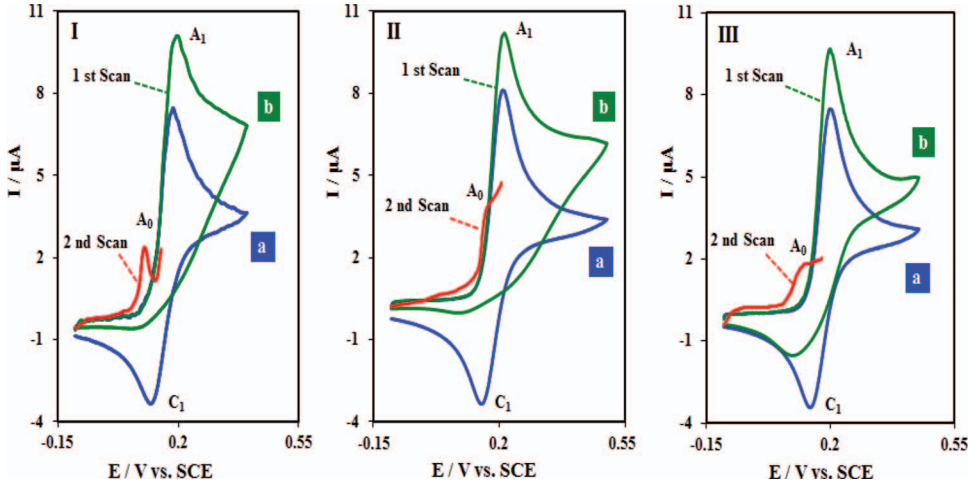


**Figure 4.** (a) Cyclic voltammograms of 1.0 mM DITHBD (**1**) in the absence of nucleophiles. (b) Cyclic voltammograms of 1.0 mM DITHBD (**1**) in the presence of 1 mM **2a** (curve I); 1 mM **2b** (curve II) and 1 mM **2c** (curve III), at glassy carbon electrode, in aqueous solution containing phosphate buffer (pH = 7.0, $c = 0.15$ M). Scan rate: 25 mV $s^{-1}$. t = 25 ± 1°C.

Controlled-potential coulometry was performed in aqueous solution containing 0.7 mmol of **1** and 0.7 mmol of nucleophiles (**2a-c**) at the chosen potential (see section 2.4.). The electrolysis progress was monitored using cyclic voltammetry (Fig. 6). It is shown that, as coulometry progresses, the anodic peak $A_1$ decreases and disappears when the charge consumption reaches approximately $4e^-$ per molecule of DITHBD (**1**), and the new anodic peak ($A_0$) which is related to the transformation of intermediate (**3a**) to the corresponding quinonic form (**4a**) (Scheme 1, Eq. (III, a), appears. These observations allow us to propose the pathway in Scheme 1 for the electrochemical oxidation of DITHBD (**1**) in the presence of **2a-c** as nucleophiles.

According to our results, it seems that the Michael addition reaction of the enolate anion of nucleophiles (**2a-c**) to electrochemically generated **1a** is faster than the other secondary reactions, leading to the intermediate **3a-c**. The oxidation of these compounds (**3a-c**) is easier than the oxidation of the DITHBD (**1**) by virtue of the presence of an electron-donating group. The intramolecular reaction (Scheme 1, reaction (IV, a-c)), occurring via a 1,6-addition reaction, because of the existence of the ethanedithiol group at the C-4 position of the *o*-quinone ring, leads to the formation of the final products (**5a-c**).[21] It can be seen from the mechanism shown in Scheme 1 that, as the chemical reaction (Eq. (III, a-c) occurs, quinone **1a** is regenerated through homogeneous oxidation (Eq. (V) and hence, can be reoxidized at the electrode surface. Thus, as the chemical reaction takes place, the apparent number of electrons transferred increases from n = 2 to n = 4 electrons per molecule. The reaction products (**5a-c**) can also be oxidized at a lower potential than the starting compound (DITHBD). However, the oxidation of products **5a-c** was circumvented during the preparative reaction because of the insolubility of the product in mixture of water–acetonitrile (85:15) containing phosphates as the buffer and supporting electrolyte (pH = 7.0, $c = 0.15$ M).

*Kinetic study.*— Electrochemical oxidation of DITHBD (**1**) in the presence of **2a-c** as nucleophiles was tested by digital simulation. The simulation was carried out assuming semi-infinite one-dimensional diffusion and planar electrode geometry. The experimental parameters entered for digital simulation consisted of the following: $E_{start}$,

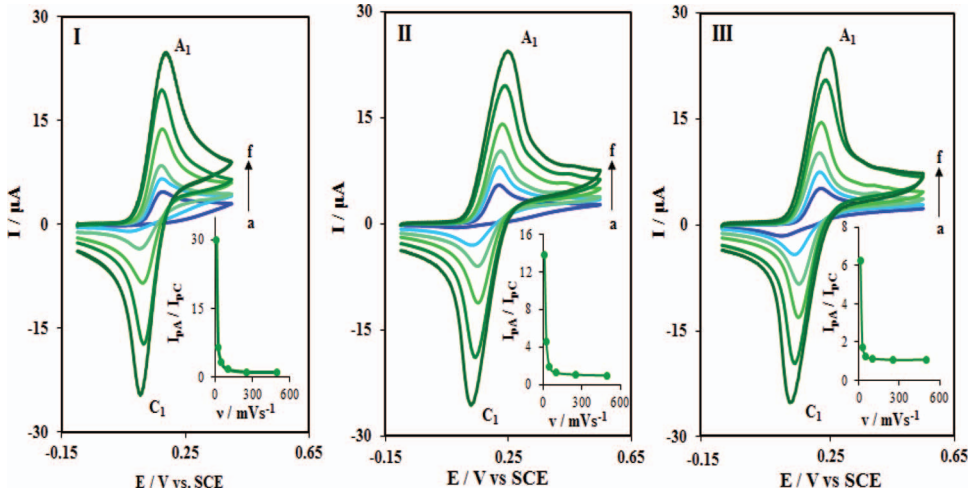


**Figure 5.** Cyclic voltammograms of 1.0 mM DITHBD (**1**) in the presence of **2a** (I), **2b** (II) and **2c** (III) at a glassy carbon electrode, in phosphate buffer solution (pH = 7.0, $c = 0.15$ M). Scan rates from (a) to (f) are: 10, 25, 50, 100, 250 and 500 mV $s^{-1}$, respectively. Inset: Variation of peak current ratio ($I_{PA1}$ /$I_{PC1}$) versus scan rate. t = 25 ± 1°C.

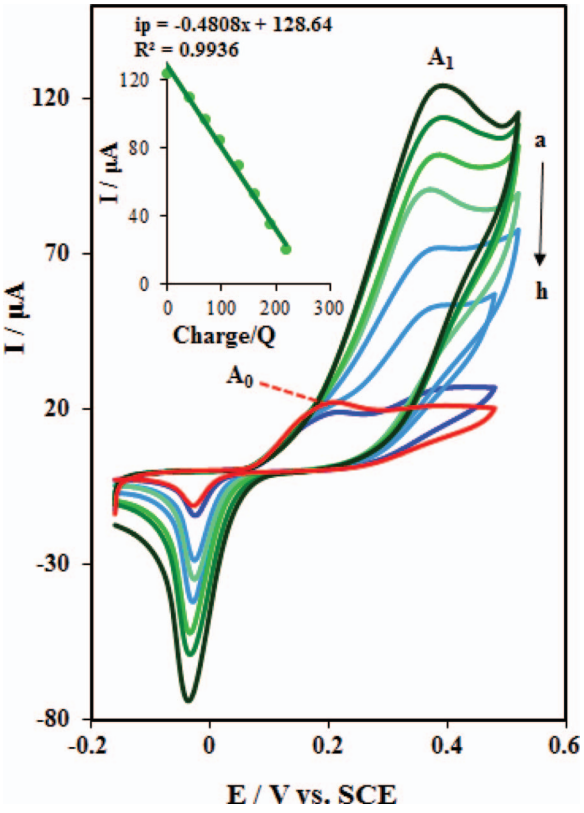


**Figure 6.** Cyclic voltammograms of 0.7 mmol DITHBD (**1**) in the presence of 0.7 mmol acetylacetone, at a glassy carbon electrode during controlled potential coulometry. After consumption of: (a) 0, (b) 40, (c) 70, (d), 95 (e), 130, (f), 160, (g) 190, and (h) 230 C. Inset: Variation of the peak $A_1$ current ($I_{pA1}$) vs. consumed charge. scan rate: 100 mV $s^{-1}$ · t = 25 ± 1°C.

$E_{switch}$, $E_{end}$, t = 25°C and analytical concentration of DITHBD (**1**) and **2a-c**. The transfer coefficient (α) was assumed to be 0.5 and the formal potentials were obtained experimentally as the midpoint potential between the anodic and cathodic peaks ($E_{mid}$). All these parameters were kept constant throughout the fitting of the digitally simulated voltammogram to the experimental data. The parameter homogeneous rate constants ($k_{obs}$) was allowed to change through the fitting processes. On the basis of Scheme 1, the observed homogeneous rate constants ($k_{obs}$) of reaction of DITHBD (**1**) with **2a-c** have been estimated by comparison of the simulation results (Fig. 7, curve Si) with experimental cyclic voltammograms (Fig. 7, curve Ex).

The calculated values of observed homogeneous rate constants, $k_{obs}$, for Michael addition reaction of nucleophiles (**2a-c**) with quinonic form DITHBD (**1a**) are 267 ± 6 $M^{-1}s^{-1}$, 178 ± 3 $M^{-1}s^{-1}$, 46 ± 2 $M^{-1}s^{-1}$ (standard deviation of five independent simulations) for the nucleophile of acetylacetone (**2a**), dimedone (**2b**) and 4-hydroxycoumarin (**2c**), respectively.

As can be seen, $k_{obs}$ was found to vary in the order acetylacetone (**2a**) > dimedone (**2b**) > 4-hydroxycoumarin (**2c**). This is related to the lower nucleophilicity of **2c**, which can be explained as follows. Notably, **2c** is basically a β-ketoester, and the resonance of C = O of ester with oxygen and, also resonance of keto tautomer of C-OH with aromatic ring lead to decrease of enol form, therefore the nucleophilicity of **2c** is lower than **2a** and **2b**. Acetylacetone (**2a**) is an open chain β-diketone and dimedone is a cyclic β-diketone. Hence, the nucleophilicity of **2a** is higher than **2b**.[23] To omit the effect of the side reactions on the calculation of $k_{obs}$, the homogeneous rate constant for side reactions is firstly calculated for DITHBD (**1**) in the absence of **2a-c** and then it subtracted from the data in the presence of **2a-c.**

## Conclusions

The results of this work show that DITHBD (**1**) is oxidized in aqueous solution to their respective *o*-quinone. The quinones are then attacked by the enolate anion of nucleophiles (**2a-c**) to form benzofuran derivatives (**5a-c**). The overall reaction mechanism for anodic oxidation of DITHBD (**1**) in the presence of (**2a-c**) as the nucleophiles is presented in Scheme 1. According to our results, it seems that the Michael reaction of these nucleophiles to the *o*-quinone formed leads to the formation of new benzofuran derivatives as final products. Also, we studied the kinetics of the reaction of the electrochemically generated *o*-quinone **1a** with **2a-c** by cyclic voltammetry. The simulated cyclic voltammograms show good agreement with those obtained experimentally. The maximum value of $k_{obs}$ is calculated in electrochemical oxidation of DITHBD (**1**) in the presence of acetylacetone (**2a**).

## Acknowledgments

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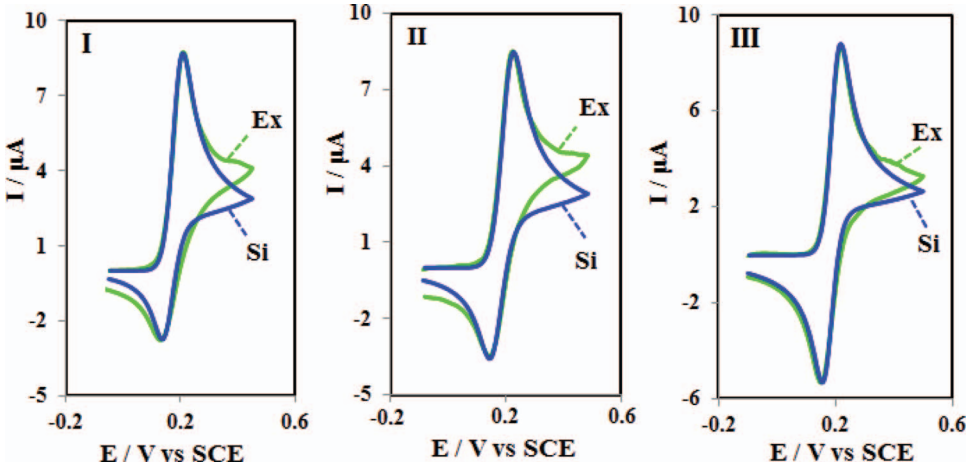


**Figure 7.** Experimental (Ex) and simulated (Si) cyclic voltammograms of 1 mM DITHBD (**1**), in the presence of 1 mM **2a** (I); in the presence of 1 mM **2b** (II) and in the presence of 1 mM **2c** (III), at a glassy carbon electrode, in aqueous solution containing phosphate buffer (pH = 7.0, *c* = 0.15 M). Scan rate: 20 mV $s^{-1}$. t = 25 ± 1°C.

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