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Electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline in aqueous solutions

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ABSTRACT

Electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (**1**) has been studied at various pH values using cyclic voltammetry and controlled-potential coulometry. The results indicate that electrochemically generated *p*-benzoquinonediimine (**1ox**) is unstable and participates in the two types of reactions based on solution's pH. The results also show that in the acidic media, electrochemically generated **1ox** via two successive hydrolysis reactions is converted to 2,5-diethoxy-*p*-benzoquinone (**3ox**), while at intermediate pH values, the Michael addition reaction of **1**–**1ox** takes place prior to the hydrolysis reaction. Our data show that in these pH values, **1ox** via two successive Michael addition reactions followed by a hydrolysis reaction is converted to 2,5-bis(2,5-diethoxy-4-morpholinophenylamino)-3,6-diethoxy-*p*-benzoquinone (**6ox**).

1. Introduction

Electrochemistry presents very versatile means for the electrochemical synthesis of organic and inorganic compounds, kinetic and mechanistic studies of electron transfer reactions [1–7]. Electrooxidation of amines were reported by many workers at different conditions such as aqueous and non aqueous solvents or at various pH values [8–11]. It was reported that electrooxidation of aromatic amines is not simple and leading to the various products depending on their structure and electrolysis conditions [10,11]. Results of the investigations indicated that depending on the solution's pH, the electrochemical oxidation of amines leads to the dimerization, trimerization, hydrolysis and hydroxylation reactions [12–14]. The hydrolysis and formation of Schiff bases is important due to its relevance to the transformation of >C=O to >C=N [15] and vice versa in biochemical processes [16–19]. It should be noted that, in the formation of the imine derivatives (Schiff bases), primary amines, undergo nucleophilic addition with aldehydes or ketones to give carbinolamines which then dehydrate to give substituted imines [20]. Electrochemical evidence for the formation of carbinolamines as intermediate in the reaction of hydrazine with various carbonyl compounds has been reported recently by Zuman and Baymak [21]. Formation and hydrolysis of imines have also studied by several workers [22,23]. It was reported that the rate of hydrolysis for some amines increases with increasing pH, while it was decreased for some others in the same condition [13]. In this work electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline using cyclic voltammetry (CV) and controlled-potential coulometry methods with different time scale was investigated. Since, this compound has two amine groups, its hydrolysis reaction occurs in two steps. Our results show that hydrolysis competes with dimerization. In acidic pH values, the rate of hydrolysis is high, while at intermediate pH values, trimerization reaction is predominant. Our data also show that although trimerization at intermediate pH values is predominant, hydrolysis reaction also contribute to the formation of the final product. This work also represents a facile and one-pot electrochemical method for the synthesis of new *p*-benzoquinone derivatives via electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline at different pHs under green conditions, without toxic reagents and solvents at a carbon electrode in a divided cell, using an environmentally friendly method. This mild aqueous reaction expands the repertoire of aqueous chemistries available for small molecules.

2. Experimental

2.1. Apparatus and reagents

Cyclic voltammetry (CV) and controlled potential coulometry were performed using a conventional three-electrode potentiostat. A divided cell was used for coulometry. The working electrode used in the voltammetry experiments was a glassy carbon disk (1.8 mm diameter) and a platinum wire was used as the counter electrode. The working electrode used in controlled-potential coulometry was

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an assembly of four carbon rods (31 cm^2) and a large platinum gauze was used as counter electrode. The working electrode potentials were measured vs. Ag/AgCl. More details are described in our previous paper [24].

2.2. Computational study

The geometries of all species in the gas phase were fully optimized at Density Functional Theory (DFT), B3LYP [25,26] level of theory using Gaussian 03 [27]. The standard 6-311G+ (p,d) basis set was used for all species. Vibrational frequency analysis, calculated at the same level of theory, indicates that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. Also Natural Bond Orbital (NBO) analyses [28] were carried out at the mentioned levels of theory. A starting molecular-mechanics structure for the ab initio calculations was obtained using the HyperChem 5.02 Program [29].

2.3. Electroorganic synthesis of 2,5-diethoxy-p-benzoquinone ($C_{10}H_4O_4$) (**3ox**)

Phosphate buffer solution (80 ml, 0.2 M, pH 2.0) containing 0.05 mmol of 2,5-diethoxy 4-morpholinoaniline (**1**) was subjected to electrolysis at 0.40 V vs. Ag/AgCl, in a divided cell. The electrolysis was terminated when the current decayed to 5% of its original value. The product was extracted by ethylacetate and was washed with water. After drying, the product was characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS (isolated yield 43%). M.p = 183–184 °C. $IR_{(KBr)}$ = 497, 826, 879, 920, 1029, 1107, 1208, 1232, 1288, 1359, 1412, 1446, 1609, 1673, 2937, 2978, 3060 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): 1.40 (6H, t, methyl), 4.06 (4H, q, methylene), 5.88 (2H, s, aromatic). ^{13}C NMR (75 MHz, acetone-d_6): 14.1, 65.9, 106.5, 159.4, 182.2. MS (*m*/*e*) (relative intensity), 140 (M-C_4H_6, 100), 112 (21), 95 (8), 94 (12), 84 (30), 71(52), 70 (28), 69 (53). "*M*" is the molecular mass of **3ox**.

2.4. Electroorganic synthesis of 2,5-bis(2.5-diethoxy-4-morpholinophenylamino)-3,6-diethoxy-p-benzoquinone ($C_{38}H_{52}N_4O_4$) (**6ox**)

Phosphate buffer solution (80 ml, 0.2 M, pH 6.5) containing 0.25 mmol of 2,5-diethoxy-4-morpholinoaniline (**1**) was subjected to electrolysis at 0.23 V vs. Ag/AgCl, in a divided cell. The electrolysis was terminated when the current decayed to 5% of its original value. Oxidized product extract by ethylacetate and dried (isolated yield 36%). M.p = 168–169 °C. $IR_{(KBr)}$ = 575, 705, 765, 823, 917, 958, 1044, 1119, 1203, 1266, 1295, 1338, 1395, 1450, 1472, 1510, 1588, 1629, 1651, 2817, 2847, 2929, 2977, 3263 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6/D_2O): 1.18, 1.28, 1.34, 1.42 (18H, t, t, t, t, methyl), 3.06 (6H, t, methylene), 3.76 (10H, t, methylene), 3.98 (6H, m, methylene), 4.10 (2H, t, methylene), 5.86 (1H, s, aromatic), 5.91 (1H, s, aromatic), 6.49 (1H, s, aromatic), 6.65 (1H, s, aromatic). ^{13}C NMR (75 MHz, acetone-d_6/D_2O): 14.3, 14.4, 15.3, 15.4, 51.8, 51.9, 64.7, 65.2, 65.6, 65.7, 67.6, 100.5, 100.7, 106.6, 109.2, 134.6, 140.7, 142.6, 147.1, 154.4, 154.5, 163.0, 182.1. MS: *m*/*e* (relative intensity), 727 (M+3H, 1), 724 (M, 0.6), 699 (100), 670 (22), 625 (21), 596 (7), 450 (26), 421 (9), 376 (7), 352 (44), 271 (21), 242 (20). "*M*" is the molecular mass of **6ox**.

3. Results and discussion

3.1. Potential-pH study

The CV recorded for 0.5 mM of 2,5-diethoxy-4-morpholinoaniline (**1**) in aqueous phosphate buffer solution (pH 6.5) at scan rate = 200 mV s^{-1} is shown in Fig. 1. The voltammogram indicates an anodic peak (A_1) in the positive-going scan and a cathodic counterpart peak (C_1) in the negative-going scan which corresponds to the transformation of **1** to *p*-quinonediimine (**1ox**) and vice versa within a quasi reversible two electron process [30–34]. Under these conditions, the peak current ratio (I_{pC_1}/I_{pA_1}) is about one can be considered as a criterion for the stability of *p*-quinonediimine **1ox** produced at the surface of electrode. With increasing the concentration of **1**, or decreasing potential scan rate, the peak current ratio (I_{pC_1}/I_{pA_1}) decreases and a new cathodic peak appears at less positive potentials.

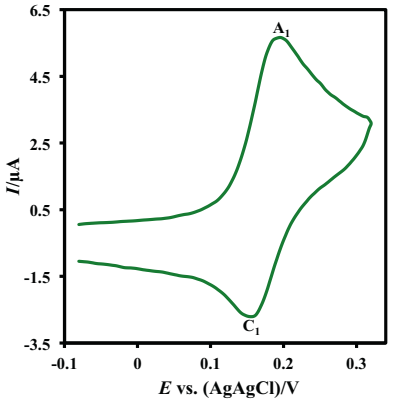


Fig. 1. CVs of 2,5-diethoxy-4-morpholinoaniline (**1**) (0.5 mM) at glassy carbon electrode, in phosphate buffer solution (*c* = 0.2 M, pH 6.5); scan rate: 200 mV s^{-1}. Starting potential = −0.08 V and switching potential = 0.32 V, *t* = 25 ± 1 °C.

The CVs of **1** in various pH values are shown in Fig. 2, part I. It was found that the peak potential for peak A_1 (E_{pA_1}) shifted to the negative potentials by increasing pH. This is expected because

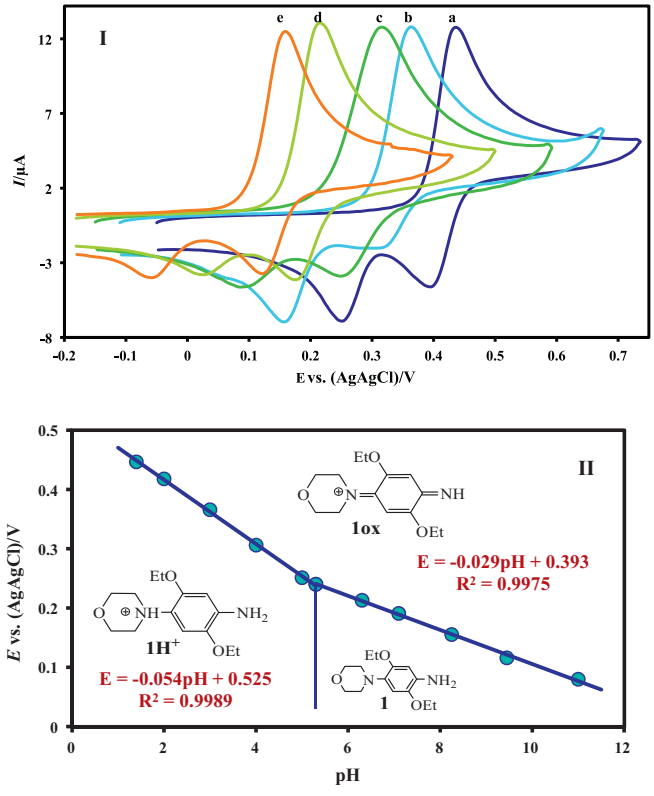
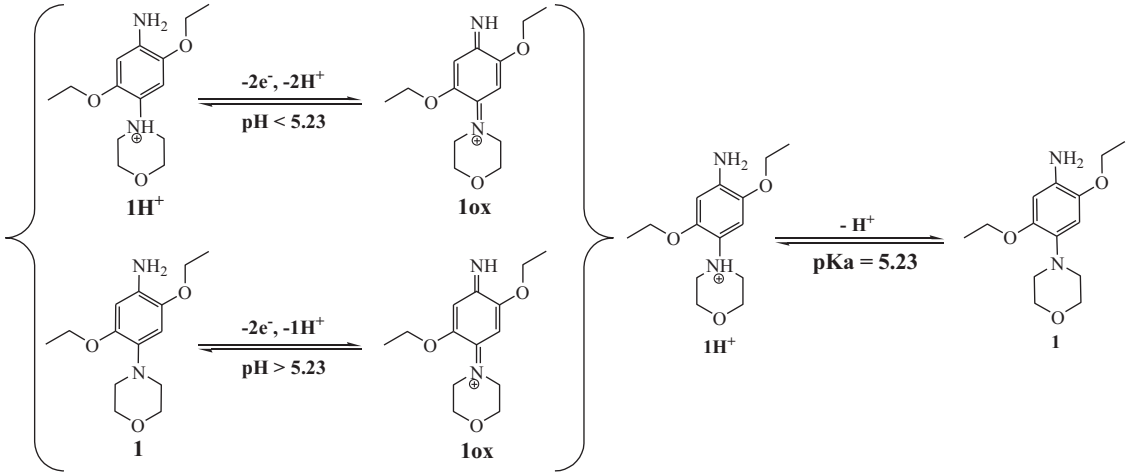


Fig. 2. (I) CVs of 2,5-diethoxy-4-morpholinoaniline (**1**) (1.0 mM) in buffer solution with various pH values at a glassy carbon electrode. pHs from (a) to (e) are 1.4, 3.2, 4.3, 6.2 and 8.3. Scan rate 100 mV s^{-1}. *t* = 25 ± 1 °C. (II) Potential-pH diagram of **1**.



Scheme 1. Mechanism of the electrochemical oxidation of protonated and non protonated of 2,5-diethoxy-4-morpholinoaniline (**1**).

of the participation of proton(s) in the oxidation reaction of **1** to *p*-quinonediimine **1ox**.

$$\mathbf{1} \rightleftharpoons \mathbf{1ox} + m\mathrm{H}^+ + 2\mathrm{e}^-$$

where m is the number of protons involved in the reaction. The anodic peak potential (E_{pA_1}), is given by [12]:

$$E'_{pA} = E_{pA} - \left(\frac{2.303\,mRT}{2F}\right)\,\mathrm{pH}$$

where E_{pA} is the anodic peak potential at pH 0.0, R, T, and F have their usual meanings. A potential-pH diagram is plotted for **1** by plotting the E_{pA_1} values as a function of pH (Fig. 2, part II). The E_{pA_1} – pH diagrams comprise two linear segments with different equations and slopes around of pH 5.23.

In pHs < 5.23

$$E_{pA} = 0.52 - 0.054\,\mathrm{pH} \quad \text{or} \quad \text{slope} = -\frac{54\,\mathrm{mV}}{\mathrm{pH}} \tag{1}$$

In pHs > 5.23

$$E_{pA} = 0.34 - 0.029\,\mathrm{pH} \quad \text{or} \quad \text{slope} = -\frac{29\,\mathrm{mV}}{\mathrm{pH}} \tag{2}$$

On the basis of the above mentioned slope, it can be concluded that the reaction occurring at the pH below 5.23 is a two-electron, two-proton process involving the oxidation of "protonated" **1** (**1H**$^+$) to the *p*-quinonediimine **1ox** in the forward scan and reduction of **1ox** to **1H**$^+$ in the reverse scan (Scheme 1). Whereas, the electrode surface reaction at pH > 5.23, corresponds to the two-electron, one-proton process (Scheme 1). Also, the pK_a obtained in this work for acid/base equilibrium shown in Scheme 1 is 5.23.

3.2. Electrochemical study in pHs 1–3

As shown in Fig. 2a, the CV of 2,5-diethoxy-4-morpholinoaniline (**1**) exhibits one anodic peak A_1 at 0.44 V and two cathodic peaks C_1 and C_2 at 0.39 and 0.25 V vs. Ag/AgCl, respectively. The anodic and cathodic peaks A_1 and C_1 are counterpart and correspond to the transformation of **1H**$^+$ to the *p*-quinonediimine **1ox** and vice versa within a quasi-reversible two-electron process. The new cathodic peak C_2 can be related to the electrochemical reduction of the product of side reactions such as hydrolysis, hydroxylation, and dimerization reaction [12,35–40]. The current of the cathodic peak C_1 strongly depends on the potential scan rate. In lower scan rates, the peak current ratio (I_{pC_1}/I_{pA_1}) is less than one and increases with increasing scan rate. This result indicates that **1ox** in the time scale of our experiments is unstable and participates in a chemical following reaction.

Fig. 3 represents the first and second cycles of CV of **1H**$^+$ in lower scan rate. The voltammogram exhibits one anodic peak (A_1) and three cathodic peaks (C_1, C_2, and C_3). In the second cycle, the voltammogram shows that, parallel to the decrease in current of A_1, two new anodic peaks (A_2 and A_3) appear at less positive potentials. It is also seen that proportional to the increasing of the potential sweep rate, parallel to the increase in height of the C_1 the height of C_2 and C_3 decreases. The presence of two redox couples A_2/C_2 and A_3/C_3 peaks confirms two successive following chemical reactions.

To get better and more consistent data on the type of these following chemical reactions, electrochemical oxidation of **1** was performed in different concentration of **1**. The normalized CV of **1H**$^+$ in aqueous phosphate buffer solution (pH 2.0) at various concentration is shown in Fig. 4. Normalized cyclic voltammograms are obtained by dividing the current by the concentration (I/C). The results demonstrate that the peak current ratio (I_{pC_1}/I_{pA_1}) is nearly constant and independent on the concentration of **1**. Dimerization reactions can be recognized from the first-order one by the dependence of the peak current ratio (I_{pC_1}/I_{pA_1}) on concentration [8(page 498)]. Using this data it could be concluded that in this condition, the chemical following reaction is not the dimerization of **1** [4].

Controlled-potential coulometry was performed in aqueous solution containing 0.05 mmol of **1H**$^+$ in a divided cell at 0.40 V

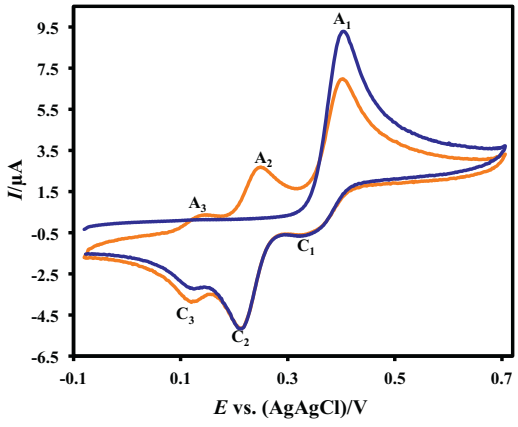


Fig. 3. The first and the second cycle of CVs of 2,5-diethoxy-4-morpholinoaniline (**1**) (1.0 mM) at a glassy carbon electrode, in phosphate buffer solution (c = 0.2 M, pH 2.0); scan rate: 50 mV s^{-1}. Starting potential = −0.07 V and switching potential = 0.70 V, t = 25 ± 1 °C.

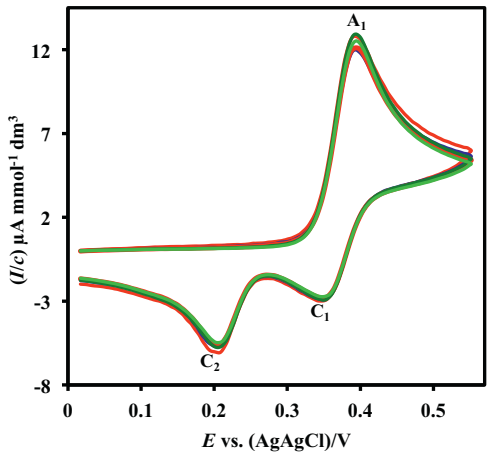


Fig. 4. Normalized CVs of 2,5-diethoxy-4-morpholinoaniline (**1**) at glassy carbon electrode, in phosphate buffer solution (c = 0.2 M, pH 2.0) at various concentrations of **1** (0.6, 1.0, 1.25, 1.6 and 2.0 mM). Scan rate = 100 mV s^{-1}. Starting potential = 0.02 V and switching potential = 0.55 V, t = 25 ± 1 °C.

vs. Ag/AgCl. Monitoring of the progress of the electrolysis was carried out by CV (Fig. 5). As shown, during coulometry, in parallel with the decrease in height of the anodic peak A_1 and its cathodic counterpart (C_1), new anodic peaks (A_2 and A_3), and cathodic counterpart of A_3 (C_3) appear and the height of them increases. At the end of the coulometry all anodic and cathodic peaks disappear and only anodic and cathodic peaks A_3 and C_3 remain. The anodic peak A_1 disappears when the charge consumption becomes about 2e^- per molecule of **1H$^+$**. These observations allow us to propose the pathway in Scheme 1 for the electrochemical oxidation of **1H$^+$** at pH 2.0. In addition, the results show that the current of starting potential for curve (a) is zero, but curves (b)–(d) show that proportional to the advancement of coulometry, a cathodic current appears at starting potential (Fig. 5, curve e). This current increases with progress of coulometry and shows the progressive formation of a reducible compound during coulometry. According to our results, it seems that the hydrolysis reaction of *p*-quinonediimine **1ox** leads to *p*-quinoneimine **2a** or **2b**. The hydrolysis of compound **2** in the next step, converts it into the final product *p*-benzoquinone **3ox**.

In this section, we tried to identify the more probable pathway for the synthesis of **3ox**. Our previous work explains that

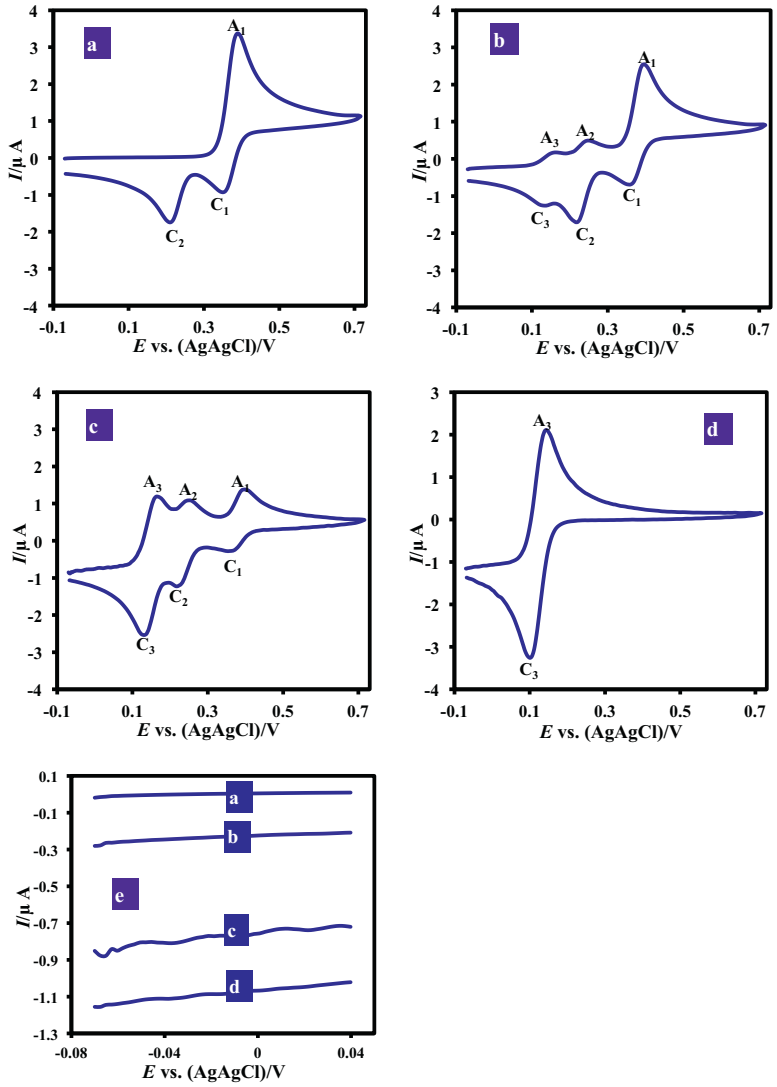
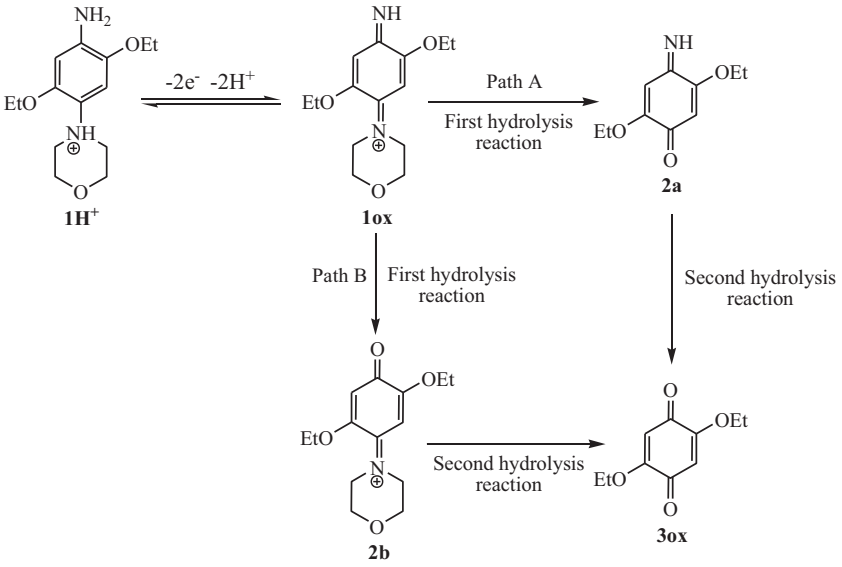


Fig. 5. CVs of 2,5-diethoxy-4-morpholinoaniline **(1)** (0.05 mmol) during controlled potential coulometry at 0.40 V vs. Ag/AgCl in aqueous solution containing phosphate buffer (pH 2.0, c = 0.2 M), after the consumption of: (a) 0 C, (b) 3 C, (c) 7 C and (d) 10 C. Scan rate: 100 mV s^{-1}. Starting potential = −0.05 V and switching potential = 0.70 V, t = 25 ± 1 °C.



Scheme 2. Oxidation pathway of 2,5-diethoxy-4-morpholinoaniline in acidic pHs.

the *N*—*C* bond order (WBIs) and charge on the reaction sites (C_1, C_4) play significant roles on the rate of hydrolysis reaction [39]. WBIs (Wiberg bond indexes), is an indication of bond order and it was concluded that increasing in WBIs or bond order leads to increasing in the strength of bonds, The more positive charge on the C_4 or C_1 atom creates a more suitable site for the nucleophilic addition of water to **1ox**. Therefore, the rate of hydrolysis reaction increases by increasing the positive charge. In addition, the hydrolysis rate is inversely proportional to the strength of N_1—C_1 and N_2—C_4 bonds, so that increase in the WBIs led to the decrease in the hydrolysis rate [39]. Using NBO analysis charge on the reaction sites and WBIs of N_1—C_1 and N_2—C_4 bonds were calculated which are shown in Fig. 6. As can be seen not only positive charge on C_4 is higher than C_1, but also WBIs of C_4—N_2 is lesser than N_1—C_1. So, it can be concluded that hydrolysis rate on C_4 atom is higher than C_1. In other word, since the formation rate of **2a** is higher than **2b**, we can conclude that, path A is more probable than B (Scheme 2). Accordingly, the anodic peak A_1 pertains to the oxidation of protonated 2,5-diethoxy-4-morpholinoaniline (**1H**$^+$) to the *p*-quinonediimine **1ox**. Obviously, the cathodic peak C_1 corresponds to the reduction of **1ox** to **1H**$^+$. The cathodic peaks C_2 and C_3 can be related to electrochemical reduction of **2a** and **3ox** to the hydroquinones **2r** and **3r**, respectively (Scheme 3). Clearly, the anodic peaks A_2 and A_3 correspond to the oxidation of the hydroquinones **2ar** and **3r** to **2a** and **3ox**, respectively.

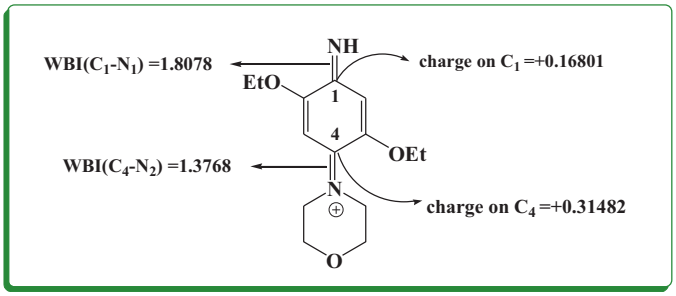
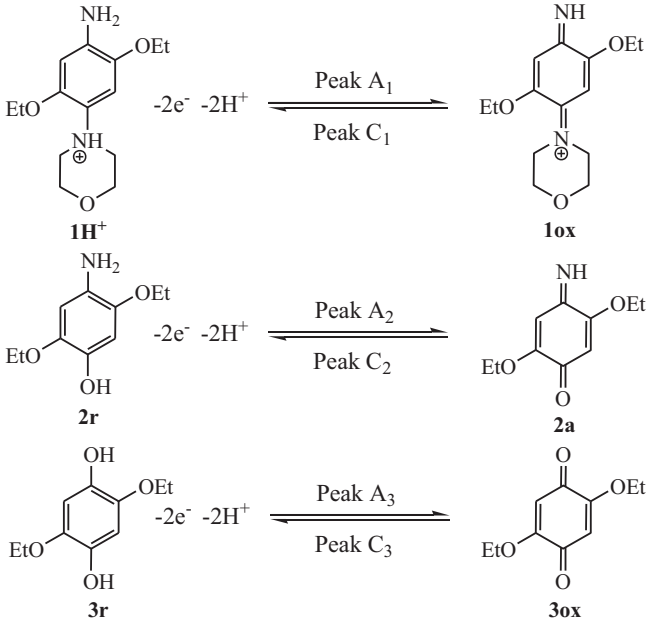


Fig. 6. Calculated charge on the reaction sites (C_4 and C_1) and WBIs of C_4—N_2 and N_1—C_1 bonds, using B3LYP level of theory and 6-311G+ (p,d) basis set.

3.3. Electrochemical study in pHs 4–9

The normalized CVs of 1.0 mM solution of **1** in aqueous phosphate buffer solution (c = 0.2 M, pH 6.5) at various potential sweep rate are shown in Fig. 7. Normalized CVs are obtained by dividing the current by the square root of the scan rate ($I/\nu^{1/2}$). The voltammograms show one anodic (A_1) and two cathodic peaks (C_1 and C_t). According to Scheme 3, the anodic peak A_1 pertains to the oxidation of **1** to the *p*-quinonediimine **1ox** and cathodic peak C_1 is its counterpart. These voltammograms show that, **1ox** at pH 6.5 is also unstable and participates in a chemical following reaction. The results also show that proportional to the increasing of the potential sweep rate, the cathodic peak C_1 appears and in parallel with the decrease in current of C_t, the height of it increases.

In a first-order reaction, the characteristic lifetime of a chemical reaction with k (rate constant) can be taken as $t_1 = 1/k$, while for a



Scheme 3. Redox behavior of couples **1H**$^+$/**1ox**, **2r**/**2a** and **3r**/**3ox**.

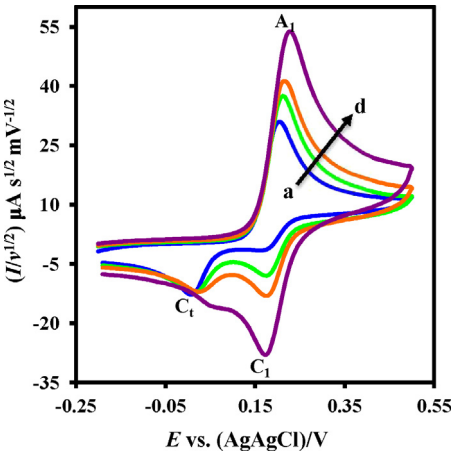


Fig. 7. Normalized CVs of 2,5-diethoxy-4-morpholinoaniline (**1**) (1.0 mM) at glassy carbon electrode in phosphate buffer solution (c = 0.2 M, pH 6.5), at various scan rates. Scan rates from a to d are 10, 50, 100 and 500 mV s^{-1}. Starting potential = −0.20 V and switching potential = 0.50 V, t = 25 ± 1 °C.

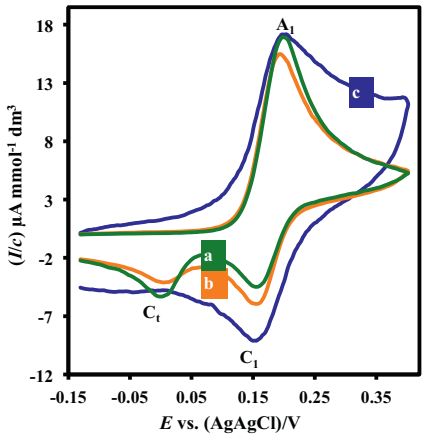


Fig. 8. Normalized CVs of 2,5-diethoxy-4-morpholinoaniline (**1**) at glassy carbon electrode, in phosphate buffer solution (c = 0.2 M, pH 6.5) at various concentrations. (a) 2.0 mM, (b) 1.0 mM and (c) 0.5 mM. Scan rate = 150 mV s^{-1}. Starting potential = −0.12 V and switching potential = 0.40 V, t = 25 ± 1 °C.

second-order reaction (such as dimerization), $t_2 = 1/kC_i$, where t_1 is the time required for the reactant concentration to drop to 37% of its initial value in a first-order process, C_i is the initial concentration of reactant, and t_2 is the time required for the concentration to drop to one-half of C_i in a second-order process. Therefore, dimerization or trimerization reactions can be recognized from the first-order one by the dependence of the electrochemical response on C_i [8(page 498)]. Fig. 8 exhibits the effect of concentration of **1** on the normalized CVs of **1** at pH 6.5. Normalized CVs are obtained by dividing the current by the concentration (I/C). As is shown in Fig. 8, the peak current ratio (I_{pC_1}/I_{pA_1}) is dependent to the concentration of **1** and proportional to the increasing it, the peak current ratio (I_{pC_1}/I_{pA_1}) decreases. The dependence of peak current ratio (I_{pC_1}/I_{pA_1}) on the concentration of **1** is indication of dimerization reaction after electron transfer process [8(page 498),40].

Electrolysis of 1 was performed in aqueous phosphate buffer solution (c = 0.2 M, pH 6.5) at 0.25 V vs. Ag/AgCl. Cyclic voltammetric analysis was carried out during the electrolysis (Fig. 9). It was observed that, proportional to the advancement of electrolysis, anodic peak A_1 decreases and peak A_2 increases. These observations allow us to propose the pathway in Scheme 4 for the electrooxidation of **1** at pH 6.5.

According to the obtained electrochemical and spectroscopic data, the electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (**1**) leads to the formation of *p*-quinonediimine **1ox**. In path A, the hydrolysis of *p*-quinonediimine **1ox** in the next step, converts it into the *p*-benzoquinone **3ox**. The Michael addition reaction of **1** to *p*-benzoquinone **3ox** and aromatization leads to hydroquinone **4h**. The oxidation of compound **4h** is easier than the oxidation of **1** by virtue of the presence of an electron-donating

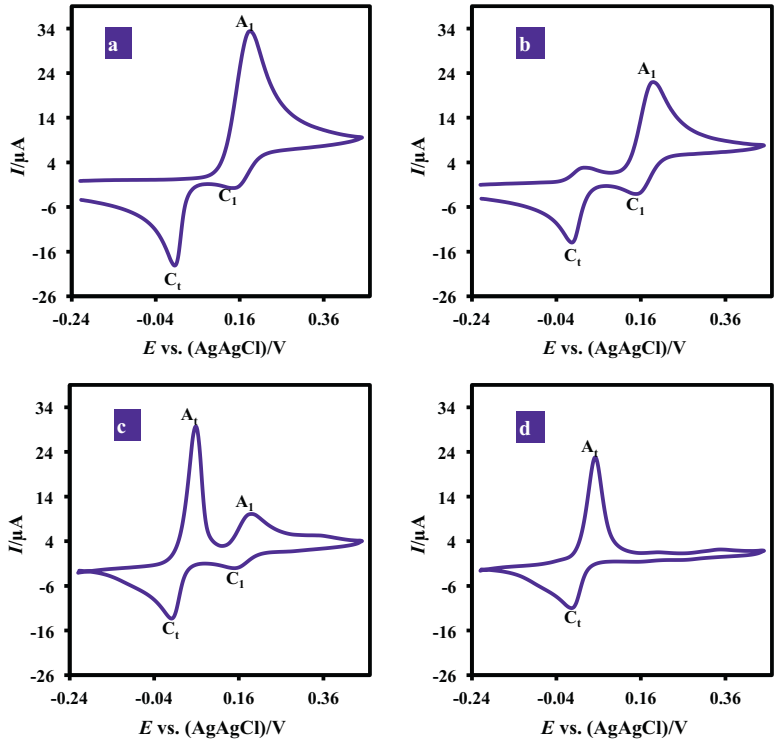
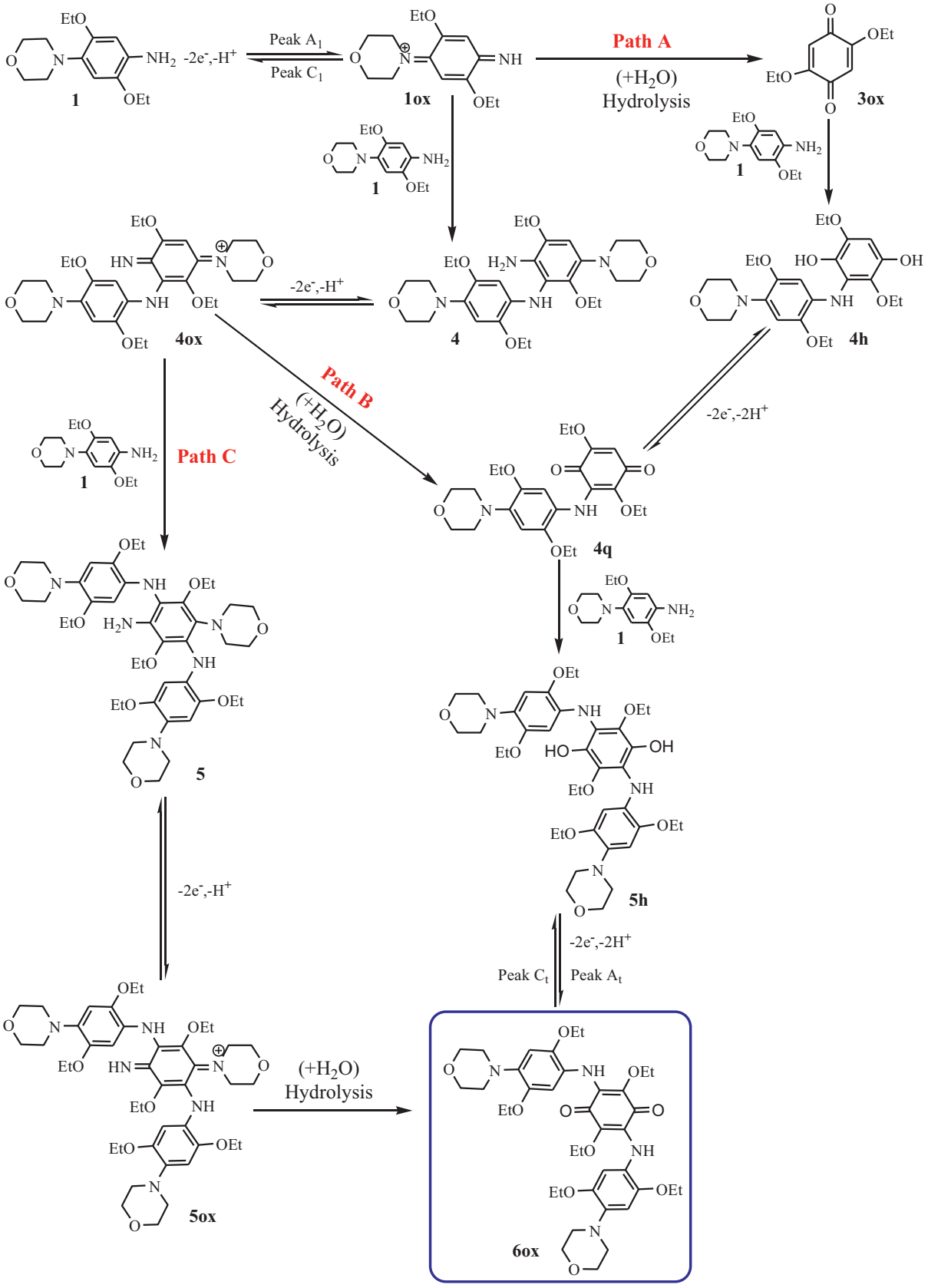


Fig. 9. CVs of 2,5-diethoxy-4-morpholinoaniline **(1)** during electrolysis at 0.25 V vs. Ag/AgCl in aqueous solution containing phosphate buffer (pH 6.5, c = 0.2 M). (a) At beginning. (b)–(d) During electrolysis. Scan rate: 50 mV s^{-1}. Starting potential = −0.20 V and switching potential = 0.45 V, t = 25 ± 1 °C.



Scheme 4. Electrochemical oxidation pathways of 2,5-diethoxy-4-morpholinoaniline (**1**) at intermediate pH values.

group. In the next step, *p*-benzoquinone **4q**, via a Michael reaction and aromatization, is converted to hydroquinone **5h**. Further oxidation converts hydroquinone **5h** into the final product **6ox**. In paths B and C, it seems that 1,4-(Michael) addition reaction of **1** to **1ox** is faster than other secondary reactions such as hydrolysis, hydroxylation [38] and oxidative ring cleavage [41,42] leading to **4**. The oxidation of this compound (**4**) is easier than the oxidation of **1** by virtue of the presence of an electron-donating morpholinoaniline group. Therefore in the applied potential it is converted to **4ox**. In path B, **4ox** via hydrolysis reaction is changed to *p*-benzoquinone **4q**. Next Michael addition, aromatization and oxidation processes converts **4q** to the final product **6ox**. In path C, the generated *p*-quinonediimine **4ox** is subjected to another Michael addition reaction with **1**. In the next step, intermediate **5** after two-electron oxidation is converted to disubstituted *p*-quinonediimine **5ox**. And in the final step, this compound (**5ox**) after hydrolysis reaction is converted to the final product **6ox**. Under these conditions (pH 6.5), it seems that the rate of hydrolysis reaction is less than the rate of Michael addition reaction of **1** to *p*-benzoquinone **3ox**, thus, it can be conclude that in Scheme 4, path A is improbable. In addition, since, the Michael addition reaction takes place prior to the hydrolysis reaction; we think that path C is more probable than path B.

It should be noted that, in the mass spectra of aminoquinonic compounds such as **6ox**, the molecular ions [M+3H] were recorded. This mass is related to protonation of the quinonic moiety and amino groups [43–45].

4. Conclusions

Cyclic voltammetry, controlled potential coulometry and spectroscopic data indicate that the mechanism of the electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (**1**) in aqueous acidic media (ca pH 2) is hydrolysis. Under these conditions, in the first step **1** is oxidized to *p*-quinonediimine **1ox** in a two-electron process. In the second step, electrochemically generated **1ox** via two successive hydrolysis reactions is converted to 2,5-diethoxy-*p*-benzoquinone (**3ox**). In addition, in this work, the electrochemical oxidation of **1** has been investigated at intermediate pH values (ca pH 6.5). Under these conditions, the data show that **1ox** via trimerization and hydrolysis is converted to 2,5-bis(2.5-diethoxy-4-morpholinophenylamino)-3,6-diethoxy-*p*-benzoquinone (**6ox**). Our data show that at intermediate pH values, the Michael addition reaction takes place prior to the hydrolysis reaction.

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