Electrochemical oxidation of o-phenylenediamine and 1,3 Dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane]. A comprehensive study and introducing a novel case of CE mechanism

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 PII:
 S0013-4686(20)31093-8

 DOI:
 https://doi.org/10.1016/j.electacta.2020.136700

 Reference:
 EA 136700



Received date:10 April 2020Revised date:26 June 2020Accepted date:28 June 2020

Please cite this article as: Faezeh Zivari Moshfegh, Davood Nematollahi, Mahmood Masoudi Khoram, Abdollah Rahimi, Electrochemical oxidation of o-phenylenediamine Dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane]. 1.3 comprehensive and А studv and introducing a novel case of CE mechanism, *Electrochimica Acta* (2020), doi: https://doi.org/10.1016/j.electacta.2020.136700

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Highlights

- Introducing a rarely studied *CE*-mechanism.
- Comprehensive electrochemical studies of *o*-phenylenediamine and 1,3dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane].
- Potential-pH studies of *o*-phenylenediamine and 1,3-dihydrospiro[benzo[d]imidazole-2,1'cyclohexane].
- Kinetic studies of hydrolysis of 1,3-dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane.
- Hydrolysis study of 1,3-dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane].

 Mechanistic studies of the oxidation of *o*-phenylenediamine and 1,3dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane. **Research Paper**

Electrochemical oxidation of *o*-phenylenediamine and 1,3

Dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane]. A comprehensive study and

introducing a novel case of CE mechanism

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ABSTRACT

Electrochemical behavior of o-phenylenediamine (PDA) and 1,3dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane] (DBI) was extensively studied in water and water/ethanol mixture using different voltammetric techniques. Our data showed that the oxidation of PDA is highly dependent on pH, follows a complex pattern and participate in following chemical reactions such as polymerization. Unlike acidic and neutral solutions, in highly alkaline solutions (pH \geq 11), however, PDA shows a simple reversible redox system. Contrary to PDA, the presence of the cyclohexyl group in the structure of DBI makes its oxidation pattern less complex than that of PDA and causes the molecule less susceptible to participate in the following chemical reactions. Our results showed that DBI in aqueous solutions is unstable and undergoes acid catalyzed hydrolysis to give PDA. The instability of DBI in acidic solutions is so high that it turns completely into PDA in the time scale of the voltammetric experiments. Different from acidic media, in alkaline solutions (pH \ge 9.0), the hydrolysis rate is slow, so that DBI shows a reversible redox couple. The kinetic of DBI hydrolysis using differential pulse voltammetry method was studied and the apparent hydrolysis rate constants ($k_{\rm h}^{\rm obs}$) were found by assuming the pseudo-first order rate kinetics. In addition, in this work, adsorption activity, diffusion coefficient and pK_a values of **DBI** and **PDA** species were determined and the Pourbaix diagrams for these compounds were constructed. The most important part of this paper is devoted to introducing a rare type of mechanism in

electrochemical reactions. In this way, the rarely studied mechanism has been introduced in relation to the reaction of **PDA** with cyclohexanone and the formation of **DBI**.

Keywords: CE mechanism; *o*-phenylenediamine; 1,3-dihydrospiro[benzo[d]imidazole-2,1'cyclohexane]; Cyclic voltammetry; Differential pulse voltammetry; Pourbaix diagram.

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1. Introduction

Electrochemistry provides powerful techniques for the study and synthesis of organic compounds [1]. These techniques can be used to obtain some useful data on homogeneous reactions coupled with electron transfer reactions [2]. In this connection, to illustrate the mechanisms, E and C are used for the electron transfer and chemical reactions, respectively. Accordingly, many mechanisms such as EC [3], EE [4], ED (D: dimerization) [5], EC' (C': catalytic) [6], ECE [7], ECEC [8], ECECE [9], ECECEC [10], ECE-ECE [11], ECEC-ECEC [11], have been introduced and described. Despite the abundance of these mechanisms, however, CE compared to mechanisms such as EC, EC' and ECE is an infrequently observed mechanism [12]. In a typical CE mechanism, before the electron transfer step, the primary molecule, which is not electroactive, is converted to an electroactive compound (EAC). This compound (EAC), is formed by a reversible chemical reaction. A rare type of CE mechanism (compared to mechanisms such as EC, EC' and ECE), is a CE mechanism in which the primary molecule is electroactive. In this condition, the primary molecule, in addition to participating in the electrode process through the CE mechanism, can also directly participate in the electrode process. Of course, in such a situation, the oxidation of the primary molecule is more difficult than EAC. A rarer type of this mechanism consists of conditions in which the redox reaction of Y is reversible. In this paper, we are going to introduce one example of such mechanism.

o-Phenylenediamine (benzene-1,2-diamine) (**PDA**) is a molecule that has been used many times for electropolymerization [13-15]. However, in those papers, attention has been paid to the electrochemical properties of the polymer and less attention has been paid to *o*-

phenylenediamine itself. In addition, a literature search indicated that no electrochemical data were available concerning the voltammetric behavior of *o*-phenylenediamine derivatives. So, in this study, we decided that reporting the electrochemical behavior of *o*-phenylenediamine and 1,3-dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane] (**DBI**), a spiro derivative of *o*-phenylenediamine at different pH values, for the first time. In this connection, a novel *CE* mechanism has been proposed and characteristics, such as hydrolysis process, adsorption activity, diffusion coefficient and pK_a value and Pourbaix diagram was reported for **DBI**.

2. Experimental

2.1. Reagents and apparatus

Cyclic voltammetry, differential pulse voltammetry and chronoamprommetry were performed using an Autolab model PGSTAT 20 potentiostat/ galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 mm diameter) and a platinum wire was used as the counter electrode. The working electrode potentials were measured vs. SCE The glassy carbon electrode was polished using alumina slurry followed by washing with water and acetone. *o*-Phenylenediamine (**PDA**), cyclohexanone and ethanol were obtained from commercial sources and used without further purification. Prior to recording voltammograms, the solutions were purged with high-purity nitrogen gas. For kinetic studies, reactions were initiated by placing **DBI** (1.0 mM) in a mixture of water (phosphate buffer, pH, 8.0 or 7.0, *c* = 0.2 M)/ethanol (90/10 v/v) (10 mL) at room temperature. Then, at specific times, the corresponding differential pulse voltamgrams were recorded.

2.2. Synthesis of dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane] (DBI).

The synthesis of **DBI** was performed according to a modified procedure [16,17]. In a typical procedure, 4 mmol **PDA** and 0.5 ml cyclohexanone were added to 40 ml boiling water and the solution was stirred about 10 minutes. After completion of the reaction, the solution was placed at room temperature to obtain the yellow crystal of **DBI**. The resulting solid was filtered and washed several times with water (yield, 55%). The melting point of the crystal is 138-139°C (lit. [16] 139-140°C and lit. [17] 138-139°C). ¹H NMR (300 MHz, DMSO-*d*₆) δ 1.36 (m, 2H, CH₂), 1.57 (m, 8H, CH₂), 5.67 (s, 2H, NH), 6.25 (m, 2H, aromatic), 6.34 (m, 2H, aromatic). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 27.6, 30.1, 44.7, 85.1, 111.7, 122.7, 145.5.



3. Results and discussion

3.1. Mechanistic study of PDA

Herein, the voltammetric behavior of **PDA** in different pH values is investigated to obtain detailed information on the pH-dependent features of **PDA** and to gain insight into the pH-dependent processes that control chemical processes after electron transfer. Firstly, the voltammetric behavior of **PDA** was investigated at pH = 11, at the scan rate of 100 mV s⁻¹ when using glassy carbon electrode, (Fig. 1). In these conditions, cyclic voltammogram shows a two-electron reversible couple with $E_{1/2}$ = 0.029 V vs. SCE. The anodic and cathodic peaks A₁ and C₁ are assigned to the oxidation of **PDA** to its oxidized form cyclohexa-*o*-benzoquinonediimine (**BQD**) and vice versa, respectively (Scheme 1) [18,19]. The reversible feature of the

voltammogram, confirms the stability of the electrogenerated **BQD** at the time scale of the voltammetric experiment.



Scheme 1. Oxidation mechanism of PDA in more basic solutions.

The cyclic voltammograms of **PDA** at pH, 11 at different scan rates are compared in Fig. 1, part II. As can be seen, the peak current ratio (I_{pC1}/I_{pA1}) is scan rate dependent and decreases at lower scan rates. In addition, a new small cathodic peak C₂ concomitantly appears, with decreasing scan rate (Fig. 1, part II).

Figure 1

The decreasing peak current ratio (I_{pC1}/I_{pA1}) with decreasing scan rate, confirms the participation of **BQD** in the following chemical reactions such as dimerization and polymerization [7]. The peak current ratio (I_{pC1}/I_{pA1}) is also strongly related to the pH of the solution (Fig. 2). By reducing one unit of pH, the peak current ratio (I_{pC1}/I_{pA1}) is drastically decreased and by decreasing the pH value to 9, the peak C₁ is completely eliminated. By further decreasing the pH, a new anodic peak (A₀) appears at more positive potentials than the main peak and its current showed an increasing trend with decreasing pH up to pH 4. In addition, with the disappearing of peak C₁, two small cathodic peaks C₂ and C₃ appear at more negative potentials which their anodic counterparts (A₂ and A₃) are observed during the second cycle of the potential sweep. At more acidic conditions, for example pH 2, voltammograms become simpler and only A₁, C₃ and A₃ peaks are observed.

Figure 2

Based on these electrochemical data and also with the help of valuable information provided by Losito et al. [20,21], we propose the following mechanism for electrochemical oxidation of **PDA** (Scheme 2). After generation of **BQD** at the electrode surface, as a Michael type acceptor it is attacked by **PDA** and after aromatization to yield **PDA** dimer (**DPDA**). The oxidation of **DPDA** due to its structure being easier than the oxidation of **PDA** and therefore becomes oxidized to the corresponding *p*-quinonediimine (**PQDI**) which is in equilibrium with *o*quinonediimine form (**OQDI**) during the anodic scanning. The formation of **PQDI** dimer was proved by electrospray ionization ion trap sequential mass spectrometry (ESI-ITMSn), during the oxidation of **PDA** by Losito et al [20,21]. In the next step, the intramolecular addition of amine group causes the formation of the corresponding dihydrophenazine (**DHP**). The successive inter and intramolecular Michael additions of a bis-nucleophile would provide a useful method for the synthesis of the cyclic compounds. On the other hand, the hydrolysis of **PQDI** and the formation of the corresponding *p*-quinoneimine (**PQI**) is possible [22]. The formation of **PQI** dimer was also proved by Losito et al [20].



Scheme 2. Oxidation mechanism of PDA.

According to the proposed mechanism, the anodic and cathodic peaks A_2/C_2 are assigned to the redox couple phenazine (**DHP**_{ox})/dihydrophenazine (**DHP**). In this way, the anodic and cathodic peaks A_3/C_3 are assigned to the redox couple *p*-quinoneimine (**PQI**)/*p*-hydroxyaniline (**PHA**). Since, the rate of hydrolysis increases with decreasing pH, in more acidic solutions (pH, 2), A_3/C_3 peaks become more intense while the A_2/C_2 peaks disappear. On the other hand, it is

suggested that peak A_0 is associated with over oxidation of DHP_{ox} or BDQ. This peak is dependent on the A_2/C_2 peaks. It appears with the appearance of A_2/C_2 peaks and disappears with the disappearance of them. Oxidized aromatic compounds can usually be further oxidized at higher potentials. These over oxidations often result in irreversible ring cleavage reactions [23].

3.2. Pourbaix diagram of PDA

Electrochemical oxidation of organic compounds is often associated with proton elimination. Fig. 3 part I, shows the linear sweep voltammograms of **PDA** in various pHs in the range of 1–11.6. As can be seen the anodic peak (E_{pA1}) shifts to negative potentials with increasing pH. A Pourbaix diagram was constructed based on the data of part I and is shown in Fig. 3 part II.

Figure 3

The diagram consists of four zones and identifies four species. Two of these species are in the oxidation states and the other two are in the reduction forms. At pH values less than 5.2, the slope of the line is 58 mV/pH, which is close to 59 mV/pH for a redox process with an equal number of protons and electrons. The equation describing this process is outlined in Scheme 3 (Eq. 1).



Scheme 3. Redox and acid/base behaviors of PDA and BQD at different pH values.

At pH values more than 5.2 and less than 8.0, the slope of the line is 24 mV/pH, which is close to 29 mV/pH for a two-electron/one-proton process. The equation describing this process is shown in Scheme 3 (Eq. 2). And finally at pH values more than 8.0, the slope of the line is 68 mV/pH, which is in consistence with a two-electron/two-proton process (Eq. 3). The pKa values for protonated **PDA** and **BQD** are determined using the equation of the lines. According to the calculations, the pK_a values for **PDA** and **BQD** are 5.2 (Ref. [24], 4.6) and 8.0, respectively (Eqs. 4 and 5).

3.3. Mechanistic studies of DBI

The cyclic voltammograms of **DBI** (1.0 mM) in water (pH=10.0, carbonate buffer, c = 0.2 M)/EtOH mixture (90/10, v/v) is shown in Fig. 4. They exhibit one anodic peak (As₁) which is assigned to the two electron oxidation of **DBI** to its oxidized forms, spiro[benzo[d]imidazole-2,1'-cyclohexane], (**DBI**_{ox}) and corresponding cathodic peak (Cs₁) which is related to the reduction of **DBI**_{ox} to **DBI**.

Figure 4

Contrary to PDA, the peak current ratio (I_{pAS1}/I_{pCS1}) is independent of scan rate and equal to unity which can be considered as a criterion for the stability of DBI_{ox} under the experimental conditions at the time scale of the voltammetric experiments. In other words, any side reactions, such as hydroxylation, hydrolysis, dimerization, oxidative ring cleavage on electrochemically generated DBI_{ox} are too slow to be observed at these time scales. The stability of DBI_{ox} over BQD at pH 10, can be due to the electron donating effect of the cyclohexyl group, as well as its steric hindrance.

The cyclic voltamograms of **DBI** and **PDA** at various pH values are compared in Figure 5. At pH 10, both **DBI** and **PDA** show typical cyclic voltammograms with $\Delta E_{1/2} = E_{1/2}^{PDA} - E_{1/2}^{DBI} = 0.44 v$. The easier oxidation of **DBI** than **PDA** can be related to the electron-donating character of the aliphatic cyclohexane attached to nitrogen atoms. The voltammogram also confirm the stability of **DBI** under the conditions of these experiments at pH 10. These conditions are also present at pH 9. Contrary to the results obtained at pH values 10 and 9, the cyclic voltammogram of **DBI** at pH 8 shows a new redox couple (A₁ and C₁) which their peak potentials are close to that of **PDA**. The results obtained at lower pH values (7 to 5) show a decrease in peak currents associated with the **DBI/DBI**_{ox} couple (As₁ and Cs₁ peak) parallel with an increase in *I*_{pA1}. Finally, the cyclic

voltammogram of **DBI** at pH 5, is quite similar to the cyclic voltammogram of **PDA** (Figs. 2 and 5). These results show that **DBI** is only stable in alkaline media (pHs > 8), but, its stability due to hydrolysis to **PDA**, is strongly affected by decreasing pH. The hydrolysis of **DBI** to **PDA**, is shown in Scheme 4. According to this Scheme, protonation of **DBI** is an important and rate limiting step in the hydrolysis of **DBI**. So, despite its rapid hydrolysis in acidic solution, **DBI** has relative stability in the alkaline solutions.



Scheme 4. Hydrolysis of DBI to PDA.

3.4. Pourbaix diagram of PDA

The effect of pH on the differential pulse voltammograms of **DBI** was studied in the range of 4.0-11.2 (Fig. 6 part I). At the pH values lower than 4.0, **DBI** completely hydrolyzed to **PDA** and do not have any peak in differential pulse voltammetry. The results indicate that at all studied pHs, the differential pulse voltammograms show one anodic peak (As₁) which is assigned to the oxidation of **DBI** to its oxidized form, spiro[benzo[d]imidazole-2,1'-cyclohexane], (**DBI**_{ox}). Increasing in pH values caused the peaks shifted to negative potentials. The Pourbaix diagram

of **DBI** is shown in Fig. 6 part II. It consists of two lines with slopes 56 and 30 mV/pH. As can be seen, at pH values less than 8.8, the slope of E_{pAs1} -pH line is 56 mV/pH, which is consistent with the theoretical value for the same numbers of electrons and protons in the redox processes (59.2 mV/pH). The electrode reaction for this line is given in Scheme 5 Eq. 1. At pH values more than 8.8, the slope of E_{pAs1} -pH line is 30 mV/pH which is consistent with the theoretical value for a two-electron/one-proton process (29.6 mV/pH). The electrode reaction for this line is shown in Scheme 5 Eq. 2. The pK_a of **DBIH**⁺ is found to be 8.8 by equating the equations of the two lines. It is close to that of 8.3 predicted for *N*,*N*-dimethyl-1,2-phenylenediamine [25]. The acid/base equilibrium of **DBI** is shown in Scheme 5 Eq. 3.

Figure 6



Scheme 5. Redox and acid/base behaviors of DBI at different pH values.

3.5. Diffusion/adsorption studies

The diffusion/adsorption properties of **DBI** and **PDA** was studied in water (pH = 10.0, carbonate buffer, c = 0.2 M)/EtOH mixture (90/10 v/v) to comparison of diffusion coefficient

and adsorption activity of the compounds in the same conditions at glassy carbon electrode (see Supplementary data). In this way, $\log I_{pAs1}$ and I_{pA1} vs. $\log v$ for **DBI** and **PDA** were plotted, respectively. The slope of the line is a measure of the diffusion/adsorption activity of the compound at the electrode surface. The slopes of the pure diffusion and adsorption processes are 0.5 and 1, respectively [2]. The slopes of the lines for **DBI** and **PDA** is 0.53 and 0.51, respectively, which means that the electrochemical oxidation of both compounds are diffusion-controlled processes and also shows that the presence of the cyclohexyl group has little effect on increasing the adsorption capacity of the **DBI**.

The diffusion coefficient of the **DBI** was determined by chronoamperometric method (Fig. 7). To achieve this goal the Shoup and Szabo equations were used (Eqs. 1-3) [26]. In this way, a potential of -0.27 V applied for 12 s and the resulting current was measured over time.

$$I = -4nFrDcf(\tau) Eq. 1$$

$$f(\tau) = 0.7584 + 0.8863\tau \cdot 1/2 + 0.2146 \exp(-0.7823\tau \cdot 1/2)$$
 Eq. 2

where *D* is the diffusion coefficient, *n* is the number of electrons, *r* is the radius of the disk electrode (r = 0.09 cm) which was calculated as described previously [27], *c* is the initial concentration, *F* is the Faraday constant, and τ is the dimensionless time parameter, given by:

$$\tau = 4Dt/r^2$$
 Eq. 3

The calculated diffusion coefficients of **DBI** and **PDA** in water (pH=10)/ethanol mixture (90/10, v/v) at room temperature, are 1.55 (\pm 0.24) × 10⁻⁵ cm²/s and 2.96 (\pm 0.76) × 10⁻⁵ cm²/s, respectively.

Figure 7

3.6. Kinetic studies

As shown in Scheme 5, **DBI** is hydrolyzed and converted to **PDA**. So we decided to study the kinetic of **DBI** hydrolysis using differential pulse voltammetry method. Fig. 8 part I, shows the DPVs of **DBI** (1.0 mM) at pH, 8.0 (phosphate buffer, c = 0.2 M) at different times. The DPVs show two-anodic peaks at -0.20 and 0.18 V vs. SCE, which correspond to the oxidation of **DBI** and **PDA**, respectively. During the first scan, I_P^{DBI} and I_P^{PDA} were 10.2 μ A and 0.9 μ A ($I_P^{\text{DBI}}/I_P^{\text{PDA}}$ = 11.3), respectively. Upon further scans at different times, I_P^{DBI} decreases and I_P^{PDA} increases, indicating continuous hydrolysis of **DBI**. At the last scan recorded at 65 min, I_P^{DBI} and I_P^{PDA} were 4.4 μ A and 4.8 μ A ($I_P^{\text{DBI}}/I_P^{\text{PDA}}$ = 0.9), respectively. Based on Scheme 4 and assuming the pseudo first-order reaction kinetics, the apparent hydrolysis rate constants (k_h^{obs}), was determined from the slope of ln I_P/I_{p0} versus electrolysis time, as shown in the inset of Fig. 8, in accordance with the kinetic equation (Eqs. 4 and 5):

$$\ln c/c_0 = -k_h^{obs}t \qquad \text{Eq. 4}$$
$$\ln l_p/l_{p0} = -k_h^{obs}t \qquad \text{Eq. 5}$$

where, c_0 and I_{p0} are concentration and peak current of **DBI** at the beginning of hydrolysis. Since the peak current of **DBI** (I_p) is proportional to its concentration, the hydrolysis rate constant was obtained by measuring the ln I_p/I_{p0} as a function of time. Based on the slope of the line in Fig. 8 inset, k_h^{obs} is obtained 1.3×10^{-2} min⁻¹ at pH, 8.0. Fig. 8 inset, shows also the plot of I_p vs. time for **DBI**. The influence of pH on the hydrolysis of **DBI** has also been examined. Fig. 8 part II shows the effect of initial pH on the peak current ratio (I_p/I_{p0}) during the hydrolysis time. Our results show that in more acidic solutions, **DBI** was hydrolyzed faster than at higher pHs, which confirms acid catalyzed nature of the reaction (Scheme 4 and Fig. 5). In the same conditions, the apparent hydrolysis rate constants (k_h^{obs}) for **DBI** was obtained 7.1×10⁻² min⁻¹ at pH 7.0.

Figure 8

3.7. CE mechanism

This section deals with the influence of hydrolysis on the electrochemical responses of **DBI**. As mentioned in the preceding sections, **DBI** is hydrolyzed to **PDA** and cyclohexanone. To elucidation of the reaction mechanism, cyclic voltammograms of **DBI** were recorded at different times and also at different scan rates (after 120 min of preparing the solution) (Fig. 9). Fig. 9 part I shows the cyclic voltammograms of **DBI** at different times (5, 30 and 120 min) at high scan rate (40 V/s). At *t* = 5 min (curve a), the **DBI** peak currents, As₁ and Cs₁ are high, while **PDA** peak currents, A₁ and C₁ are much lower than those of **DBI**. With increasing time to 30 min (curve b), the currents of **DBI** peaks decreased, while, the currents of A₁ and C₁ peaks increased. With further increasing time, after reaching equilibrium (120 min, curve c), the current of As₁ decreased markedly and its shape changes from *peak-shape* to *S-shape* which is a sign of a *CE* mechanism in kinetic region [2]. Under these conditions, the **PDA** peaks (A₁ and C₁) reached to their maximum amounts while *I*_{pCs1} is minimized. The equilibrium between **PDA** and **DBI** is shown below (Eq. 6).





The effect of potential scan rate on the voltammetric responses of **DBI** after reaching equilibrium (120 min at pH 8.0), is shown in Fig. 9 part II. This Figure clearly shows the three

distinct regions, diffusion pure, kinetic intermediate and kinetic pure that generally characterize *CE* mechanism (preceding reaction) in electrochemical oxidation of **DBI** [2]. At the scan rate of 20 V/s, the system is in the diffusion pure region, and a diffusion-controlled voltammogram (an unperturbed reversible reaction) including two redox couples (As₁/Cs₁ and A₁/C₁) is observed. As the scan rate increases (for example, 35 V/s), it enters the kinetic intermediate region. In this region, As₁ is partially governed by the rate at which **DBI** is supplied by the forward reaction (Eq. 6). At the scan rate of 45 V/s, it enters the pure kinetic region. In this region, (As₁) is totally controlled by the rate at which **DBI** is produced by the forward reaction (Eq. 6). Since the rate of **DBI** formation is constant, the current attains a steady-state value and voltammogram takes on an S-shape. The *CE* mechanism (preceding reaction) for **DBI** oxidation at equilibrium condition is shown in Scheme 7.

The formation constant of **DBI** (Eq. 6) can be roughly calculated by the following equations (Eqs. 7-11) and using the peak currents of **DBI** (I_{pAs1}) and **PDA** (I_{pA1}) in equilibrium condition (Fig. 8, DPV at 65 min), as well as by considering the **DBI** and **PDA** diffusion coefficients (*D*) (1.55 × 10^{-5} cm²/s and 2.96 × 10^{-5} cm²/s, respectively).

$$K = \frac{k_f}{k_b} = \frac{\text{[DBI]}}{\text{[PDA] [Cyclohexanone]}}$$
Eq. 7

$$I_{pAs1} = \text{Constant} \times (D_{DBI})^{1/2} \times [DBI]$$
 Eq. 10

$$I_{\text{pA1}} = \text{Constant} \times (D_{\text{PDA}})^{1/2} \times [\text{PDA}]$$
 Eq. 11



Scheme 7. *CE* mechanism for oxidation of **PAD** in the presence of cyclohexanone at equilibrium condition.

Based on calculations, the values of 6.0×10^{-4} M, 4.0×10^{-4} M and 3.75×10^{3} M⁻¹, were calculated for [DBI], [PDA] and *K*, respectively. In addition, the values of $k_{\rm f}$ and $k_{\rm b}$ can be roughly calculated by the following equations (Eqs. 12 and 13) [2]:

$$\frac{I_k}{I_d} = \frac{1}{1.02 + 0.471/K\sqrt{\lambda}}$$
Eq. 12
$$\lambda = \frac{(k_f + k_b)}{v} \left(\frac{RT}{nF}\right)$$
Eq. 13

where, I_k is the kinetic peak current, I_d is the diffusion-controlled current and v is scan rate. In fact, I_k is I_{pAs1} in kinetic region (Fig. 9 part II, v = 45 V/s). On the other hand, I_d is I_{pAs1} in diffusion region (Fig. 9 part II, v = 20 V/s). But to calculate I_k/I_d , the diffusion current (I_d) must first be calculated at v = 45 V/s using Randles-Sevcik equation. According to these equations, the values of 2.8×10^{-3} M⁻¹ s⁻¹ and 7.5×10^{-6} s⁻¹ were roughly calculated for k_f and k_b , respectively.

4. Conclusion

In this paper, the electrochemical oxidation of **PDA** and **DBI** was extensively studied. The data, contributes to the increasing scientific knowledge about the oxidation mechanism of these compounds and understanding the role of the cyclohexyl group attached to amine groups in oxidation pathway of **DBI**.

Our data showed that the oxidation of **PDA** is highly dependent on pH and follows a complex pattern that is shown in Scheme 2. However, the presence of the cyclohexyl group in **DBI** makes its oxidation pattern less complex than **PDA** and also makes the molecule less susceptible to participate in the following reactions such as polymerization.

One of our objectives in this paper is the evaluation of the stability of **DBI** in aqueous solutions. Our results showed that **DBI** in aqueous solutions is unstable and undergoes acid catalyzed hydrolysis to give **PDA**. This converting reaction is highly pH-dependent so that it is completely performed in acidic solutions, in the time scale of our voltammetric experiments. In this regards, in this paper we are introducing a rarely studied *CE* mechanism for oxidation of **PAD** in the presence of cyclohexanone at equilibrium condition.

Additionally we provided the specific electrochemical information of these compounds such as pourbaix diagram, diffusion coefficient and adsorption studies by CV, DPV and chronoamperomettry methods and also showed that DPV is very useful technique in kinetic studies and calculating apparent reaction rate constant at different pH values.

Acknowledgements

The authors wish to acknowledge Iran National Science Foundation (INSF) for financial support of this work. We also acknowledge the Bu-Ali Sina University Research Council and

Center of Excellence in Development of Environmentally Friendly Methods for Chemical Synthesis (CEDEFMCS) for their support of this work.

Credit Author Statement

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data including cyclic voltammograms of DBI and PDA at different scan rates,

¹H NMR and ¹³C NMR of **DBI** associated with this article can be found, in the online version, at

http://dx.doi.org

References

[1] O. Hammerich, B. Speiser (Eds.) Organic Electrochemistry, 5th ed., CRC Press, Boca Raton

(2016).

[2] A.J. Bard, L.R. Faulker, Electrochemical Methods, second ed., Wiley, New York, 2001.

- [3] A. Daneshyar, D. Nematollahi, F. Varmaghani, H. Goljani, H. Alizadeh, Electrochemical synthesis of a new phosphonium betaine. Kinetic evaluation and antibacterial susceptibility, Electrochim. Acta 324 (2019) 134893.
- [4] M. Masoudi-Khoram, D. Nematollahi, Sh. Momeni, M. Zarei, M.A. Zolfigol, Electrochemical study of dibenzo-xanthene and dihydrobenzochromono pyrazole derivatives, Electrochim. Acta 326 (2019) 134990.
- [5] D. Nematollahi, M. Joudaki, S. Khazalpour, F. Pouladi, Electrochemical oxidation of sulfinic acids: efficient oxidative synthesis of diaryl disulfones, J. Electrochem. Soc. 164 (2017) G65-G70.
- [6] H. Salehzadeh, B. Mokhtari, D. Nematollahi, Selective electrochemical determination of homocysteine in the presence of cysteine and glutathione, Electrochim. Acta 123 (2014) 353-361.
- [7] M. Jamshidi, D. Nematollahi, Green electrochemical synthesis of *N*-Phenylquinoneimine derivatives: dual action of 4-Morpholinoaniline and *N*-(4aminophenyl) acetamide, ACS Sustain. Chem. Eng. 5 (2017) 9423-9430.
- [8] X. Zhang, E.L. Clennan, T. Petek, Computational and cyclic voltammetry studies of high effective-molarity assisted reversible reductions of [4]-and [5] heli-viologens: Potential building blocks for new materials, Tetrahedron 75 (2019) 2965-2970.
- [9] N. Pakravan, D. Habibi, F. Varmaghani, M. Rahmati, The electrochemical synthesis of new benzofuran derivatives, J. Electroanal. Chem. 801 (2017) 206-214.

- [10] A. Amani, S. Khazalpour, D. Nematollahi, Electrochemical oxidation of acetaminophen and
 4-(Piperazin-1-yl) phenols in the presence of 4-Hydroxy-1-methyl-2(1*H*)-quinolone, J.
 Electrochem. Soc. 160 (2013) H33-H40.
- [11] P.T. Sanecki, P.M. Skitał, The mathematical models of kinetics of the E, EC, ECE, ECEC, ECE– ECE and ECEC–ECEC processes with potential-dependent transfer coefficient as a rationale of isoalpha points, Electrochim. Acta 53 (2008) 7711-7719.
- [12] B. Bennett, J. Chang, A. J. Bard, Mechanism of the Br⁻/Br₂ redox reaction on platinum and glassy carbon electrodes in nitrobenzene by cyclic voltammetry, Electrochim. Acta 219 (2016) 1-9.
- [13] R.A.S. Couto, S.S. Costa, B. Mounssef Jr, J.G. Pacheco, E. Fernandes, F. Carvalho, C.M.P. Rodrigues, C. Delerue-Matos, A.A.C. Braga, L. Moreira Gonçalves, M. Beatriz Quinaz, Electrochemical sensing of ecstasy with electropolymerized molecularly imprinted poly(ophenylenediamine) polymer on the surface of disposable screen-printed carbon electrodes, Sensor Actuat. B-Chem. 290 (2019) 378-386.
- [14] D. Sačer, I. Spajić, M. Kraljić Roković, Z. Mandić, New insights into chemical and electrochemical functionalization of graphene oxide electrodes by *o*-phenylenediamine and their potential applications, J. Mater. Sci. 53 (2018) 15285–15297.
- [15] J. Jiang, G.M. Zhang, L. Li, H. Zhang, N. Li, Y.Y. Wang, J. He, F.J. Mao, K. Yu, On-line monitoring of transient radicals and oligomers: *o*-Phenylenediamine electrooxidation mechanism study by mass spectrometry, Microchem. J. 153 (2020) 104390.
- [16] J.T. Kuethe, J. Varon, K.G. Childers, Rearrangement of spiro-benzimidazolines: preparation of *N*-alkenyl- and *N*-alkyl-benzimidazol-2-ones, Tetrahedron 63 (2007) 11489-11502.

- [17] R. Garner, G.V. Garner, H. Suschitzky, Heterocyclic syntheses. Part XXIII. Synthesis and reactions of 2,3-dihydrobenzimidazoles, J. Chem. Soc. (1970) 825-829.
- [18] D. Feng, Z.Y. Gu, J.R. Li, H.L. Jiang, Z. Wei, H.C. Zhou, Zirconium-Metalloporphyrin PCN-222: Mesoporous metal–organic frameworks with ultrahigh stability as biomimetic catalysts, Angew. Chem. Int. Ed. 51 (2012) 10307-10310.
- [19] P.H. Cheng, H.Y. Cheng, C.C. Lin, S.M. Peng, Oxidations of N,N'-disubstituted ophenylenediamine in the presence of metal ions and the crystal structure of N,N'dimethylbenzimidazolium perchlorate, pyridine-bis (o-benzosemiquinonediimine) cobalt (iii) chloride and bis (pyridine)(N,N'-bistoluene-p-sulfonyl-o-phenylenediiminato)-copper (ii), Inorg. Chim. Acta. 169 (1990) 19-21.
- [20] I. Losito, N. Cioffi, M.P. Vitale, F. Palmisano, Characterization of soluble oligomers produced by electrochemical oxidation of *o*-phenylenediamine by electrospray ionization sequential mass spectrometry, Rapid Commun. Mass Spectrom. 17 (2003) 1169-1179.
- [21] I. Losito, F. Palmisano, P.G. Zambonin, *o*-Phenylenediamine electropolymerization by cyclic voltammetry combined with electrospray ionization-ion trap mass spectrometry, Anal. Chem. 75 (2003) 4938–4995.
- [22] M. Jamshidi, D. Nematollahi, F. Taheri, H. Alizadeh, Paired electrochemical method for synthesis of new phenylcarbonimidoyl dicyanide dyes. ACS Sustainable Chem. Eng. 7 (2019) 1956-1962.
- [23] A. Maleki, D. Nematollahi, F. Rasouli, A. Zeinodini-Meimand, Electrode instead of catalyst and enzyme. A greener protocol for the synthesis of new 2-Hydroxyacetamide derivatives containing γ-lactone ring, Green Chem. 18 (2016) 672-675.

- [24] Dissociation Constants of Organic Acids and Bases. In CRC Handbook of Chemistry and Physics, 91th ed.; W. M. Haynes, Ed.; CRC Press: Boca Raton, 2010. Available online: <u>https://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/dissociation</u> %20constants%20of%20organic%20acids%20and%20bases.pdf
- [25] https://www.chemicalbook.com/ChemicalProductProperty_US_CB31531926.aspx.
- [26] L. Xiong, L. Aldous, M.C. Henstridge, R.G. Compton, Investigation of the optimal transient times for chronoamperometric analysis of diffusion coefficients and concentrations in non-aqueous solvents and ionic liquids, Anal. Methods 4 (2012) 371-376.
- [27] M.J.A. Shiddiky, A.A.J. Torriero, C. Zhao, I. Burgar, G. Kennedy, A.M. Bond, Nonadditivity of faradaic currents and modification of capacitance currents in the voltammetry of mixtures of ferrocene and the cobaltocenium cation in protic and aprotic ionic liquids, J. Am. Chem. Soc. 131 (2009) 7976-7989.

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Figures

Fig. 1. Cylic voltammograms of **PDA** (1.0 mM) at glassy carbon electrode in carbonate buffer solution (pH = 11, c = 0.2 M). Part I: Scan rate 100 mV s⁻¹. Part II: Scan rates are: a) 10 mV s⁻¹, b) 25 mV s⁻¹, c) 50 mV s⁻¹ and d) 100 mV s⁻¹. Temperature: 25 ± 1 °C.

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Fig. 2. First (---) and second (—) cyclic voltammograms of 1 mM **PDA** at glassy carbon electrode in aqueous solutions at different pH valus. Scan rate: 100 mV s⁻¹ Temperature: 25 ± 1 °C.



Fig. 3. Part I: linear sweep voltammograms of **PDA** (1.0 mM) in buffer solution with various pH values. pHs from a to I are: 1.2, 2.2, 3.3, 4.2, 5.2, 6.1, 7.0, 8.0, 9.1, 10.0, 10.7 and 11.6. At the glassy carbon electrode, temperature = $25 \pm 1^{\circ}$ C. Part II: Pourbaix diagram of **PDA**.



Fig. 4. Cylic voltammograms of 1.0 mM 1,3-dihydrospiro[benzo[*d*]imidazole-2,1'-cyclohexane] (**DBI**) at glassy carbon electrode in water (pH = 10.0, carbonate buffer (c = 0.2)/EtOH mixture (90/10, v/v). Scan rates from a to d are: 10, 25, 50 and 100 mV s⁻¹. Temperature: 25 ± 1 °C.

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Fig. 5. Cyclic voltammograms of (a) **DBI** (1.0 mM) and (b) **PDA** (1.0 mM) at glassy carbon electrode, in water/EtOH mixture (90/10 v/v/) at different pHs. Scan rate: 100 mV s⁻¹. Temperature: 25 ± 1 °C.



Fig. 6. Part I: Diffrential puls voltammograms of 1.0 mM **DBI** in buffer solution with various pH values/ethanol mixture (90/10, v/v). pHs from a to i are: 4.3, 5.2, 6.5, 7.1, 7.7, 9.0, 9.6, 10.1 and 11.2. At the glassy carbon electrode. Temperature = $25\pm1^{\circ}$ C. Part II: Pourbaix diagram for **DBI**.



Fig. 7. Choronoamperograms of **DBI** and **PDA** in different concentration at glassy carbon electrode, in water (pH 10.0, carbonate buffer, c = 0.2 M)/ethanol mixture (10/90, v/v). Concentrations from a to c are: 1.0, 2.0 and 3.0 mM. Temperature = 25 ± 1 °C.



Fig. 8. Part I: DPVs as a function of time during **DBI** (1.0 mM) hydrolysis at pH 8.0 (phosphate buffer, c = 0.2 M)/ethanol mixture (90/10 v/v) at glassy carbon electrode. Times from a to i are: 1, 4, 10, 20, 33, 40, 50, 55 and 65 min. Inset: Plots of I_p and $\ln I_p/I_{p0}$ of the remaining concentration of **DBI** versus time. Part II: Plots of peak current ratio (I_p/I_{p0}) versus time during the hydrolysis **DBI** at pH7.0 and pH=8.0. Temperature = 25 ± 1 °C.



Fig. 9. Part I: Cyclic voltammograms of **DBI** (1.0 mM) in water (pH 8.0, phosphate buffer, c = 0.2 M)/EtOH mixture (90/10 v/v/) at different times of preparing the solution. Times from a to c are: 5, 30 and 120 min. Scan rate = 40 V/s. Part II: Cyclic voltammograms of **DBI** after 120 min of preparing the solution at different scan rates. Scan rates from a to e are: 20, 30, 35, 40 and 45 V/s. Temperature = 25 ± 1 °C.

Graphical Abstract

