

## ELECTROCHEMICAL BEHAVIOUR OF 2,5-DIHYDROXYANISOLE ON A MERCURY ELECTRODE IN AQUEOUS MEDIA

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Electrochemical investigation of 2,5-dihydroxyanisole (2,5-DHA) has been carried out in aqueous solutions in pH range 2–11 on hanging mercury drop electrode (HMDE). The oxidation process in pH range 2–6 is a quasi-reversible electrode reaction which involves the transfer of two electrons and two protons. By use of semi-integration a dependence of the heterogeneous rate constant on the potential has been appreciated. Thus, the variation of peak current with pH changes can be explained. In more basic solutions the electrooxidation is complicated by subsequent chemical reactions as indicated from the calculated voltammetric and chronoamperometric parameters.

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The electrochemical oxidation of aromatic hydroxy-compounds has been studied by several authors, mainly in aqueous solutions<sup>1–4</sup>. Especially a wide series of 2-substituted hydroquinones was investigated by cyclic voltammetry on Carbon–Nujol paste electrodes<sup>3,4</sup>. Oxidation of monosubstituted hydroquinones on carbon electrodes first yields the corresponding *p*-quinones which frequently undergo nucleophilic attack.

Recently, the electrochemical behaviour of 2,5-dihydroxybenzoic acid (2,5-DHBA) was investigated by us in the pH range 5.5–12.7 in phosphate buffer, at a hanging mercury drop electrode (HMDE)<sup>5</sup>. However, under these voltammetric conditions no evidence for anodic hydroxylation appeared. In the present paper we deal with the oxidation of another 2-substituted hydroquinone, the 2-methoxy-hydroquinone which is known as 2,5-dihydroxy-anisole (2,5-DHA). This dihydroxy-compound shows a different voltammetric behaviour than the 2,5-DHBA in the same pH range. Its cyclic voltammograms show both anodic and cathodic processes which involve a two-electron and two-proton exchange. The rates of these two exchanges differ and are pH dependent. Therefore, we undertook voltammetric investigation of the 2,5-DHA in the whole pH range (2–12) and we paid special attention to different voltammetric parameters in order to obtain information about the overall electrochemical mechanism of this system.

## EXPERIMENTAL

The electrochemical procedures were conventional and need not be described in details. Cyclic voltammetric measurements were carried out on a HMDE (PAR 9323) with drop of surface area  $3.5 \cdot 10^{-2} \text{ cm}^2$ . A Pt sheet and a calomel electrode saturated with KCl were used as a counter and reference electrodes, respectively. The compartments of these electrodes were separated from the working electrode compartment by glass diaphragms. The experimental set-up included a Bank Electronic PCA-72M potentiostat, a Bank Electronic VSG-72L function generator and a Hewlett-Packard 7045A X-Y-recorder.

Electrolysis was carried out using a mercury pool working electrode. 2,5-dihydroxy-anisole (2,5-DHA) was purchased from Fluka A. G. and was purified by recrystallization from water and dried under vacuum. Phosphate buffers of different pH were used as supporting electrolytes.  $\text{Na}_2\text{HPO}_4$ -citric acid for pH 1.87–5.68,  $\text{NaH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$  for pH 6.23–8.12,  $\text{NaH}_2\text{PO}_4$ -borax for pH 9.77 and  $\text{NaOH}$ - $\text{Na}_2\text{HPO}_4$  for pH > 10.77. Concentrations of these buffers were slightly modified from those reported in tables given by Britton. Ionic strength was adjusted at  $0.3 \text{ mol l}^{-1}$  by addition of  $\text{NaNO}_3$  if this was needed.

The pH values were measured with a Radiometer Copenhagen pH-meter. All the reagents used for buffer solutions were Fluka A.G. "puriss p.a.". In order to avoid oxidation of 2,5-DHA by atmospheric oxygen, weighed amounts of 2,5-DHA were added after the deaeration of the supporting electrolyte. High purity nitrogen was used for oxygen removal and all measurements were carried out in a nitrogen atmosphere and a temperature of  $25 \pm 0.1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

*Voltammetric Behaviour of 2,5-DHA*

In Fig. 1 cyclic voltammograms of 2,5-DHA ( $2.5 \cdot 10^{-3} \text{ mol l}^{-1}$ ) in aqueous media at different pH buffers are shown. The influence of pH on the redox couples of this substituted hydroquinone is clear. This process is characterized by an overall two-electron and two-proton transfer. The number of electrons involved in this reaction

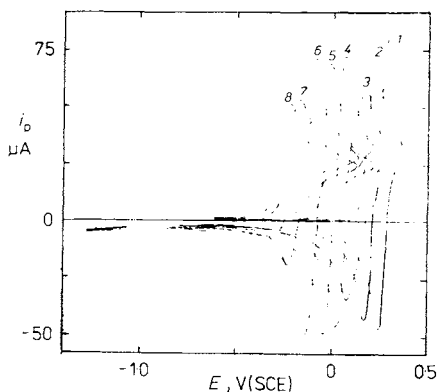


FIG. 1

Cyclic voltammograms of 2,5-DHA ( $2.5 \cdot 10^{-3} \text{ mol l}^{-1}$ ) at scan rate  $0.2 \text{ V s}^{-1}$  in different buffer solutions; pH: 1 1.87; 2 3.39; 3 4.92; 4 5.68; 5 6.23; 6 8.12; 7 9.77; 8 10.77

was determined by coulometric measurements. The same number of electrons and protons is also reported in the literature for other substituted or unsubstituted pyro-catechols or catechols<sup>1-13</sup>. The obtained oxidation product is always the corres-

TABLE I

Cyclic voltammetric parameters of 2,5-DHA ( $2.5 \cdot 10^{-3} \text{ mol l}^{-1}$ ) oxidation on HMDE in aqueous solutions

pH	$\nu$ $\text{mV s}^{-1}$	$E_p$ $\text{mV}$	$E_p - E_{p/2}$ $\text{mV}$	$E_{pa} - E_{pc}$ $\text{mV}$	$\frac{i_p / A \nu^{1/2}}{V^{-1/2} \text{ s}^{1/2}}$ $\text{A cm}^{-2} \text{ mol}^{-1} \text{ l}$	$i_{pa}/i_{pc}$
1.87	25	0.29	0.035	0.04	2.22	1.16
	64	0.298	0.033	0.053	1.95	1.15
	100	0.298	0.033	0.053	1.68	1.04
	196	0.300	0.030	0.058	1.67	1.13
	324	0.305	0.035	0.065	1.62	1.11
3.39	25	0.223	0.048	0.061	1.98	0.88
	64	0.228	0.048	0.073	1.91	0.85
	100	0.230	0.050	0.080	1.86	0.80
	196	0.240	0.055	0.090	1.79	0.95
	324	0.245	0.055	0.100	1.76	1.07
4.92	25	0.165	0.085	0.105	1.62	1.10
	64	0.170	0.090	0.115	1.48	1.00
	100	0.172	0.092	0.117	1.43	1.03
	196	0.175	0.093	0.125	1.42	1.19
	324	0.182	0.092	0.132	1.47	1.33
6.23	25	0.030	0.035	0.045	1.98	1.08
	64	0.035	0.040	0.055	1.77	1.14
	100	0.035	0.040	0.055	1.85	1.15
	196	0.040	0.050	0.060	1.81	1.13
	324	0.040	0.050	0.075	1.82	1.17
9.77	25	-0.180	0.060	0.045	1.5	2.37
	64	-0.178	0.067	0.052	1.4	1.29
	100	-0.175	0.070	0.057	1.41	2.22
	196	-0.170	0.065	0.065	1.37	2.00
	324	-0.168	0.067	0.072	1.33	1.85
10.77	25	-0.250	0.040	0.075	1.65	10.25
	64	-0.240	0.043	0.080	1.42	3.75
	100	-0.235	0.050	0.090	1.5	4.20
	196	-0.230	0.055	0.095	1.31	4.42
	324	-0.225	0.055	0.095	1.20	3.87

ponding substituted *para*- or *ortho*-quinone. This process is generally a reversible reaction and substantial amount of information could be obtained from the pH dependence of the peak voltammetric parameters.

Some of these results are summarized in Table I. At low pH values we have a relatively large current function and a narrow peak width,  $E_p - E_{p/2}$ . As the pH increases the current function decreases and the wave becomes broader. This behaviour is well shown in Fig. 1. At pH < 5 the form of the wave changes again and the voltammetric parameters are similar to those for very acidic solutions. It must be noted that the pH value at which this change takes place is not close to the  $pK_1$  of this compound ( $pK_1 = 9.5$ ). Thus, this change cannot be attributed to the dissociation of the 2,5-DHA. The ratio  $i_p/Asc^{1/2}$  is changed with the scan rate along the pH region 1.87–12.00. In additions the ratio  $i_{pc}/i_{pa}$  increases with increasing scan rate above pH 6.23 as a result of the relative increase of the cathodic current which was lowered for lower polarization rates due to inactivation of the product of anodic oxidation by a subsequent chemical reaction.

Appearance of one more cathodic wave during the reverse negative scan (Fig. 1) confirms the existence of a following chemical reaction and formation of an electroactive product in basic media. However, in acidic solutions this wave does not emerge but the decrease of peak current with increasing pH (pH < 6.23) implies a pH dependent mechanism for this redox process. At pH greater than 7, the oxidation wave becomes progressively broader and the current function decreases remarkably.

#### Dependence of Peak Potential, $E_p$ , on pH

The dependence of peak potential ( $E_p$ ) on pH is shown in Fig. 2. In acidic range the  $E_p$  is negatively shifted by  $55 \pm 5$  mV per pH unit whereas the slope at pH's of 9.5–12 is equal to  $28 \pm 5$  mV per pH unit. The two lines with slopes  $-0.055$  and  $-0.028$  V/pH in pH ranges 1.87–9.5 and 9.5–12 respectively, intersect at a point

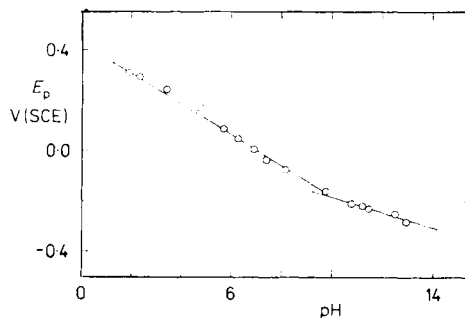


FIG. 2

Dependence of peak potential on pH for the oxidation of 2,5-DHA ( $2.5 \cdot 10^{-3}$  mol l $^{-1}$ ); scan rate:  $0.2$  V s $^{-1}$

corresponding to a pH value which is identical with the  $pK_1$  of 2,5-DHA. Dissociation constants for 2,5-DHA are not available in literature. Our attempts for potentiometric determination of the two dissociation constants resulted in values around  $8 \cdot 10^{-10}$  ( $pK_1 = 9.1$ ) and  $1.25 \cdot 10^{-12}$  ( $pK_2 = 11.9$ ).

Taking into account the estimated  $pK_1 = 9.5$  from electrochemical results ( $E_p$ -pH), we can see that this value sufficiently agrees with potentiometric results. From the slope  $(\partial E_p/\partial \text{pH})_c = (-0.059/n) p$  the number of protons,  $p$ , involved in the overall process can be calculated. The estimated slope values  $-0.055$  and  $-0.028 \text{ V}/\text{pH}$  indicate that the redox process involves two protons in pH range 1.87–9.5 and one in pH range 9.5–12.

#### *Dependence of Peak Current, $i_p$ , in Acidic Solutions (pH 1.87–6.23)*

As Fig. 1 shows, the peak current for the 2,5-DHA oxidation varies with pH. Our observations and results show that during the investigation of 2,5-DHA on mercury electrode there are no significant adsorption phenomena and disproportionation or dimerization mechanisms do not occur in acidic range (pH < 6.23). It is also important to note that although adsorption phenomena of phenolic compounds at platinum electrode have been reported to take place<sup>14</sup>, we have no evidence for adsorption on mercury electrode under the conditions used in this study. In acidic range (pH < 6.23) there is no evidence for subsequent chemical reactions. In contrast such chemical reactions clearly take place in basic solutions of 2,5-DHA.

An understanding of the effect of pH on the kinetics of 2,5-DHA electrooxidation (-reduction) in acidic media on mercury is important for appreciation of the nature of this electrode process. It is well known that protons can play a decisive role in some heterogeneous electron transfer reactions<sup>15</sup>. According to the analysis by Laviron the order of electron and proton transfer in the quinone–hydroquinone couples in aqueous solutions is directly related with the  $E^0$  of the couples involved, the rates of electron transfer in the system, the solution pH and  $pK$  values of the reactants, intermediates and products<sup>10,16</sup>. The shape of the cyclic voltammogram in the acidic pH range (pH < 6.23) is indicative of the microscopic reactions which take place during electron transfer, since no dissociation effects occur in the electrochemical reaction in this pH region. On the basis of the above considerations we attempt to evaluate the kinetics of these reactions by means of semi-integral analysis in order to be able to explain the peak current variation with pH changes. The semi-integral method is a proper method for evaluation of the kinetics of these reactions, but in the present study it is only used as a tool for qualitative results. Semi-integration of cyclic voltammograms was performed according to the method of Oldham<sup>17</sup>.

Current–potential curves obtained in a potential range of 1.0 V were integrated with respect to the inverse square root of time. Analysis of the semi-integral is made according to the method of Imbeaux and Savéant<sup>18</sup>. The curves of  $I(t)$  vs  $E$  for the

forward and backward scans do not superimpose as expected for a reversible reaction even after correction for the uncompensated resistance,  $R_u$ . Thus, apart from the voltammetric parameters of Table I, the  $I(i)$ - $E$  curves show that the oxidation of 2,5-DHA on Hg must be considered as a quasi-reversible process instead of a reversible one. The rate of electron transfer  $k(E)$  for quasireversible systems on the positive scan can be expressed by the equation:

$$k(E) = D^{1/2} \frac{i}{I_{lim} - I_{(E)} \{1 + \exp [(nF/RT)(E^{0'} - E)]\}} \quad (1)$$

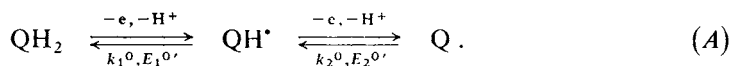
In Eq. (1)  $I$  and  $i$  are the semi-integral and the current, respectively, at different potential values ( $E$ ),  $D$  is the diffusion coefficient and  $E^{0'}$  is the formal potential of the two-electron process. If the  $(E^{0'} - E)$  is replaced by  $(E - E^{0'})$ , then the same expression is also valid for the reverse sweep. This equation can be used under assumption that this electrode reaction is uncomplicated in the investigated pH region.

The formal potential  $E^{0'}$  of the system 2,5-dihydroxyanisole/2-methoxybenzoquinone could be estimated using the following equation<sup>19</sup>:

$$E^{0'} = E_{i=0} - \frac{RT}{nF} \ln \frac{I_{lim} - I_{i=0}}{I_{i=0}}, \quad (2)$$

where  $E_{i=0}$  and  $I_{i=0}$  is the potential and the semi-integral, respectively, where the current,  $i$ , passes through zero on the reverse scan of the cyclic voltammogram.

For the two-electron process of hydroquinones the reaction sequence can be expressed by the equations



The following equations are valid for the potential dependent rate constants for each electron transfer step, in the case of quasi-reversible system<sup>20</sup>

$$\frac{1}{k(E)} = \frac{1}{k_1^0 \exp \{(-0.5F/RT)(E_1^{0'} - E)\}} + \frac{1}{k_2^* \exp \{(-1.5F/RT)(E^{0'} - E)\}} \quad (3)$$

$$k_2^* = k_2^0 \exp \{-0.5F/RT(E^{0'} - E_2^{0'})\}, \quad (4)$$

where  $k(E)$  is the apparent rate constant for the overall reaction at an applied potential  $E$ ;  $k_1^0$ ,  $E_1^{0'}$  and  $k_2^0$ ,  $E_2^{0'}$  are the apparent rate constants and the formal potential for the first and the second steps respectively and  $E^{0'}$  is the formal potential for the overall reaction.

As indicated from Eq. (3), if the first electron transfer is the rate determining step (r.d.s.),

$$k(E) = k_1^0 \exp \{ -0.5F/RT(E_1^{0'} - E) \} \quad (5)$$

and if the second electron transfer is rate determining.

$$k(E) = k_2^* \exp \{ -1.5F/RT(E^{0'} - E) \} . \quad (6)$$

By evaluating values of apparent transfer coefficients from the plot of  $\ln k(E)$  vs  $E$  at different pH values the r.d.s. for the 2,5-DHA oxidation can be determined and consequently, the effects of pH on the kinetics of this process can be appreciated.

For the evaluation of the one-electron pH-dependent rate constants  $k_1^0$  and  $k_2^0$ , the two formal potential values must be known<sup>12,13</sup>. Since the one-electron processes could be divided into several elementary steps according to Laviron "9-member box"<sup>21</sup>, calculation of the two formal potentials is dependent on the  $pK_a$ 's of all the electroactive species in solution. Some of these  $pK_a$ 's are known but others which must be accurately known are not easily measured. Therefore, we hesitate to give values of these elementary rate constants without sufficient accuracy.

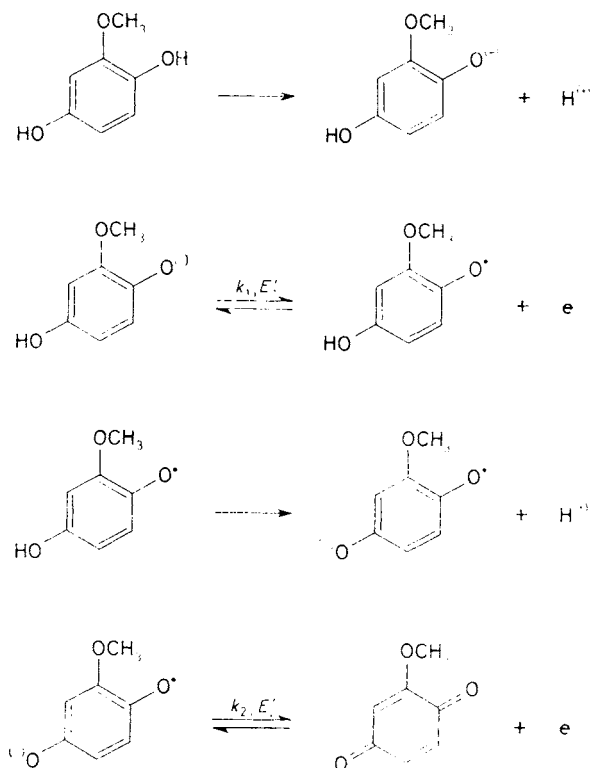
In Fig. 3 the dependence of  $k(E)$  on potential is illustrated for the anodic and cathodic processes of 2,5-DHA in acidic solutions (pH 1.87–6.23). Values of  $\ln . (k(E)/D^{1/2})$  are evaluated from the semi-integral data. The anodic and cathodic segments for each pH intersect at a potential which corresponds to the formal potential for the overall two-electron reaction. An almost linear dependence of the  $k(E)$  on potential is observed. This implies that the r.d.s. is approximately unchanged with the potential. Since it is not easy to know exactly the formal potential values of the individual oxidation steps, it is difficult to exactly determine the slopes  $F/\beta nRT$  and consequently the fractional current passing through each pathway of the general Laviron "9-member box"<sup>21</sup> scheme as a function of pH. These data could explain the peak current change with the pH variation in acidic media. Thus, the varied participation of the first and second step as rate-limiting is qualitatively evaluated by inspecting the slopes of the curves illustrated in Fig. 3.

pH	1.87	3.39	4.92	5.68	6.23
Slope	$\frac{1.34F}{RT}$	$\frac{1.21F}{RT}$	$\frac{1.12F}{RT}$	$\frac{1.21F}{RT}$	$\frac{1.18F}{RT}$

The above values of the apparent transfer coefficient show that the second electron transfer is mainly the rate determining step. Moreover the curves of the anodic branch in Fig. 3 display a vertical displacement equal to or larger than 2.0 log units at relatively high overpotentials and low pH values. This shift is close to values

consistent with first-order dependence on hydrogen ions. For the curves corresponding to the cathodic process a smaller change ( $\approx 0.5$  log units) in the vertical position is observed at the same potentials used in the case of the anodic branch. This is indicative for a dependence of close zero order in protons.

Although an exact mechanism could not be deduced, the above observations provide information about the reaction sequence. Thus in acidic solutions the first-electron oxidation of 2,5-DHA is first order in protons and the first-electron reduction on the reverse scan is zero order in protons. This qualitative evaluation is consistent with a pathway of sequence  $H^+e$   $H^+e$ , which can be expressed by the following scheme:



SCHEME 1

With increasing pH the vertical difference in Fig. 3 changes. This fact implies that for this step the order is not zero in protons in these solutions and the sequence  $H^+e$   $H^+e$  changes. In conclusion, it should be noted that to a great extent the analysis



of the results presented in this study provides a satisfactory explanation for the fact that changes of the solution pH affect both the peak current and the shape of the cyclic voltammograms, obtained during the oxidation of the 2,5-DHA.

### Neutral and Basic Media

In neutral and basic media the character of the 2,5-DHA oxidation becomes more complicated. The fact that deprotonation processes are also at equilibrium for these neutral and basic media is clearly evident in Fig. 1. In solutions with pH around 9,

TABLE II  
Variation of the chronoamperometric parameter  $it^2$  with the change of the time for the oxidation of 2,5-DHA

$t$ s	pH 8-12		pH 9-77		pH 10-77	
	$i$ , $\mu\text{A}$	$it^2$ , $\mu\text{A s}^2$	$i$ , $\mu\text{A}$	$it^2$ , $\mu\text{A s}^2$	$i$ , $\mu\text{A}$	$it^2$ , $\mu\text{A s}^2$
0.50	40.00	28.28	35.00	24.75	33.00	23.33
0.75	33.25	28.79	29.00	25.55	28.00	24.25
1.00	29.25	29.25	26.25	26.25	25.00	25.00
1.25	26.37	29.48	24.00	26.83	23.00	25.71
1.50	24.37	29.85	22.25	27.25	21.50	26.33
1.75	22.75	30.09	20.75	27.45	20.25	26.79
2.00	21.50	30.40	20.00	28.28	19.50	27.58
2.25	20.50	30.75	19.00	28.50	18.62	29.93
2.50	19.62	31.03	18.25	28.86	19.75	31.22

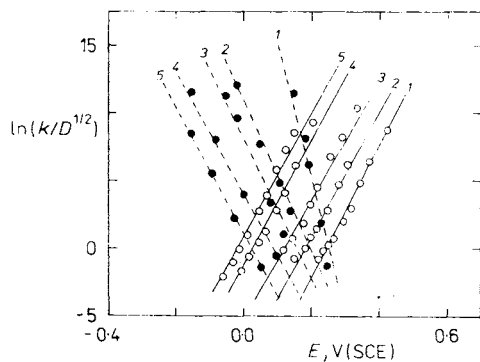


FIG. 3

Dependence of  $\ln(k/D^{1/2})$  on potential for the oxidation (-reduction) of 2,5-DHA ( $2.5 \cdot 10^{-3} \text{ mol l}^{-1}$ ) on pH: 1 1.87; 2 3.39; 3 4.92; 4 5.68; 5 6.23. (○) anodic reaction; (●) cathodic reaction

where the dissociation of 2,5-DHA takes place, the cyclic voltammetric curves for the oxidation of this substituted hydroquinone dramatically change. Additionally, at these basic solutions the ratio  $i_p/Asc^{1/2}$  significantly increases with decreasing sweep rate indicating follow-up reactions. The variation of  $i_p/Asc^{1/2}$  with change of scan rate is shown in Table I. In the same table values of the ratio  $i_{pa}/i_{pc}$  at different scan rates are included. This ratio becomes smaller with increasing scan rates as this is expected for the electrochemical reactions involving chemical steps. Also, chronoamperometric measurements show an increase of  $it^{1/2}$  with increasing time. Some of these results at different pH values (in basic media) are included in Table II. In conclusion, all the above described findings are consistent with a two-electron transfer electrode reaction which is followed by a chemical reaction.

At solutions of pH 10.77 during the cathodic scan one more cathodic wave appears at more negative potentials than that corresponding to the reduction of the 2,5-DHA oxidation product. The current of the second reduction increases as the electrode is kept for some time at 0 V. Several types of reactions could be assigned to the subsequent chemical step. It is known that in alkaline media quinones form semi-quinones by a one-electron reduction<sup>22</sup>. The anion radicals undergo dimerization or disproportionation forming different products<sup>23</sup>. Also a nucleophilic attack of the substituted quinone by hydroxide ion is likely to occur since the hydroxyl group is a strong electron donor. Hydroxylation reactions have been reported in acidic solutions for mono-substituted hydroquinones with strong electron withdrawing substituents<sup>3,4</sup>.

However, no evidence exist about the nature of the chemical reaction which appears in alkaline solutions after the reduction of 2,5-DHA. A detailed study of the chemical reaction following the electroreduction of different monosubstituted hydroquinones in basic media is the subject of a future work.

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