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Electrochemistry in buffered organic solvents. Effect of the acidity level on the extension of total pathways of the organic molecules tranformation

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ABSTRACT

Anion radicals and dianions produced from the electrochemical reduction of organic molecules are basic species. Several types of bases and different modes of reactions with the acids present in the reaction medium may occur. In the case where the parent compound is a stronger acid than the acids present in the reaction medium, it may react with the basic species resulting from its reduction giving rise to a self-protonation process. Involving homogeneous proton transfers and heterogeneous electronic ones as well.

The present study using linear sweep voltammetry and single and double step chronoamperometry has been carried out on the examples of three molecules bearing acidic protons: perezone, horminone and *o*-nitrophenol and two molecules with no acidic protons: 2-phenylamino-1,4-naphthalendione (ANQ) and 2-methyl-1,4-naphthalendione (menadione). The electrolytic media in acetonitrile in the presence of phenol and benzoic acid, as well as in four buffers solutions of pH= 20, 17.2, 11.8 and 8.1 were used.

A wide spectra of mechanisms is observed which depends on the neutral or acidic properties of the parent compound, the pH of the studied solutions and the stability and basic properties of the electrogenerated intermediaries in the electrolytic media. Imposing the level of acidity of the electrolytic solution in order to control the extension of the protonation reactions coupled to the charged-transfer steps allows to choose the pathway of the electroreduction processes. These results are significant to electrosynthetic processes.

INTRODUCTION

The electrochemical reduction of organic

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molecules, such as quinones, aromatic nitro compounds, is compatible with several multi-electron and multi proton exchange reactions (1,2). These mechanisms involve anion radicals which behave as strong proton acceptors. The protons are taken from the solvent, acid compounds previously added (3) or the electroactive compounds themselves (self protonation reactions) (4).

In protic media due to proton donation of the solvent, it is not possible to follow the several intermediates of reaction, mainly the anion radicals, produced when changing the acidity level. For this reason, in these media, reduction pathways are carried out generally in a global form. In the case of quinones (3), these mechanisms involve two electron and two proton transfer reactions while in the case of aromatic nitro compounds (2), six electrons and proton reactions are involved.

In solvents of low proton availability (dimethyl sulphoxide DMSO, acetonitrile AN, dimethylformamide DMF), the electron addition can be observed with little or no complication by protonation: it is then possible to elucidate the changes in behaviour brought about when the rate of protonation is increased by addition of acidic compounds (3).

Generally in organic electrochemistry, modifications in the oxidation or reduction mechanisms are represented by means of square diagrams where electron and proton transfers are shown. Simple square mechanisms exist like the bielectronic reduction of quinones where an arrangement of nine species are involved (1,5,6), or much more complex ones, such as the hexaelectronic reduction of the nitro aromatic compounds that compromises more than 17 species (2).

Modifications of the reduction mechanisms by proton addition in aprotic solvents generally are performed adding an excess of organic proton donor (*i.e.* benzoic acid or phenol) with respect to the electroactive specie. However, in these conditions, global mechanistic information can be only obtained (3,7). In spite of the fact that the reduction mechanism depends on the stability of the anion radicals formed and on the acidity level of the reaction medium (8), few attention has been paid in the literature to the establishment of the correlation between the acidity level imposed by organic acid added and the mechanism governing the reduction process of organic molecules.

In our group we have been interested in searching the proper buffering systems to impose the acidity level of the electrolytic solution in order to control the extension of the protonation reactions coupled to the electron transfer steps. This buffering allows to choose the pathway of the electroreduction processes.

In this work different alternatives to modify the reduction mechanism through changes in the acidity levels of the reaction media, are presented in a systematic and progressive way. These changes in the acidity level are performed by several procedures: changing the quantity of organic acid added, modifying the type of acid or by the addition of organic buffering systems that allow to buffer the acidity level in the interphase. Stability of the intermediates is also considered when electrochemical studies are presented with the same functional group (quinones) but with different molecular structure.

With the purpose to clarify the concepts here presented, initially the modification of

reduction mechanism of several substituted quinones involving relatively few intermediates is presented. Figure 1 presents the structures of the compounds studied in this work. From the discussion of the electrochemical behaviour of the 2-phenylamino-1,4-naphtalendione (ANQ) **1**, 2-methyl-1,4-naphtalendione (menadione) **2**, perezone **3**, and the horminone **4**, different alternatives to modify the reduction mechanism are presented. As well as a methodology to measure and control the acidity level in a gradual way is presented, so it is possible to perform little modifications of the acidity level and monitoring modifications in the reduction mechanism. The importance of this method is focused in the fact that it allows control the reduction mechanism in more complicated systems such as the hexaelectronic transformation of an aromatic nitro compound (nitrophenol) **5**, to the hydroxyphenylamine derivative.

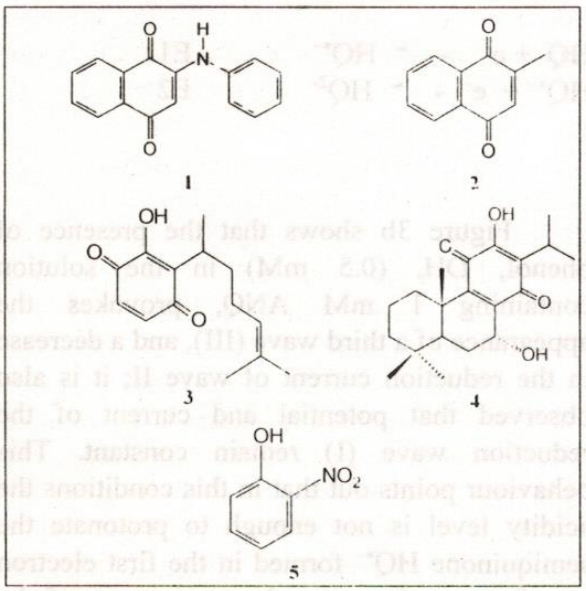

Figure 1. Chemical structures of **1**) 2-phenylamino-1,4-naphthalendione (ANQ), **2**) 2-methyl-1,4-naphthalendione (menadione), **3**) perezone, **4**) horminone, **5**) *o*-nitrophenol.

From this series of results it is possible to establish the importance of control and measuring the acidity level in the organic solvents during the electroreduction of organic molecules.

CONTROL OF THE REDUCTION MECHANISM OF SUBSTITUTED QUINONES

It has been described in the literature that when electrons are added to quinone structure HQ, the electron density on the oxygen atoms and the basicity of the molecule increases dramatically provoking that each one of the species $HQ^{\bullet -}$ and HQ^{2-} is capable of accepting one or two protons respectively (1). The possible oxidation and protonation states of the quinone, semiquinone and hydroquinone can be schematized by a nine species arrangement (figure 2) (5,6). In this work the quinoid compounds will be represented as HQ in order to generalize to all those quinone-type structures with acidic hydrogen in their molecules.

The series of reactions shown in figure 2 involves homogeneous proton transfers and heterogeneous electronic ones as well: E1, ..., E6 refer to electron transfer steps and E_1,...., E_6 to the formal potential associated to the corresponding redox pairs; meanwhile proton transfer reactions are represented by C1, ..., C6, with their corresponding protonation constants K_1, K_2, K_3, K_4, K_5 and K_6.

Considering that for the quinones system shown in figure 2, it is easier to reduce positive species than neutral or negatives ones (due to coulombic repulsion), then it is true that $E_1 > E_2$;

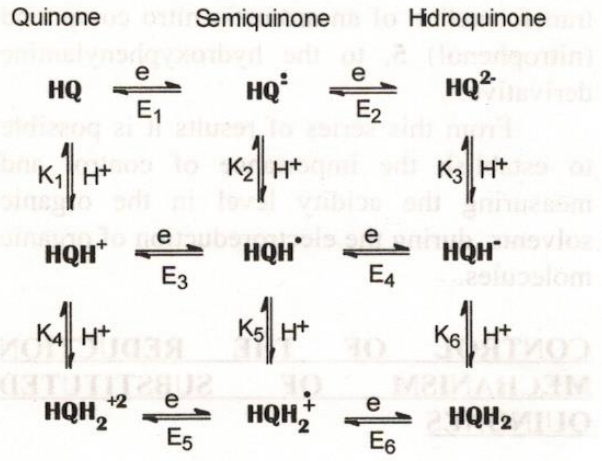

Figure 2. Electron and proton transfer reactions involved in the reduction of quinone, containing an acidic proton in the structure,HQ.

$E_3>E_4$ and $E_5>E_6$. It can be also considered that it is easier protonate negative species than neutral or positive ones, thus it can be established the following relations: $K_3>K_2>K_1$ and $K_6>K_5>K_4$.

Taking in account these considerations, it is possible to establish that the electrochemical reduction mechanism of quinoide compounds depends on the potential imposed to the electrode, on the concentration and strength of the proton donor, and on the strength of the generated base produced during the reduction process.

In the same way, this scheme (figure 2) can be modified by the presence of the acidic protons in the molecular structure of the quinone. This complicates the mechanism since a part of the electroactive compound takes the role of proton donor (self-protonation) and only a part of the compound is reduced. In this case the self-protonation reactions provoke a decrease in the stoichiometry relation quinone/electrons-exchanged. Now the reduction process of different quinoide systems are presented.

Successive protonation of the intermediates. Reduction of ANQ

Figure 3 shows a typical cyclic voltammogram of ANQ obtained in acetonitrile. The figure 3a shows that the electrochemical reduction proceeds in two successive one-electron transfer steps , waves I and II (9).

Wave I corresponds to the redox equilibrium between the quinone HQ and its corresponding anion radical semiquinone $HQ^{\bullet-}$ (E1), meanwhile wave II corresponds to the redox equilibrium between the anion radical semiquinone $HQ^{\bullet-}$ and the dianion HQ^{2-} (E2):

$HQ + e^- \rightleftharpoons HQ^{\bullet-}$ E1

$HQ^{\bullet-} + e^- \rightleftharpoons HQ^{2-}$ E2

Figure 3b shows that the presence of phenol, DH, (0.5 mM) in the solution containing 1 mM ANQ, provokes the appearance of a third wave (III), and a decrease in the reduction current of wave II; it is also observed that potential and current of the reduction wave (I) remain constant. This behaviour points out that in this conditions the acidity level is not enough to protonate the semiquinone $HQ^{\bullet-}$ formed in the first electron transfer step, however the appearance of the third reduction wave indicates that the specie HQ^{2-}, due to its higher basicity respect to $HQ^{\bullet-}$, it is being protonated (pathway E1→E2→C3), provoking that potential E_2 changes to a new potential E_2' (peak III) where $E_2'>E_2$.

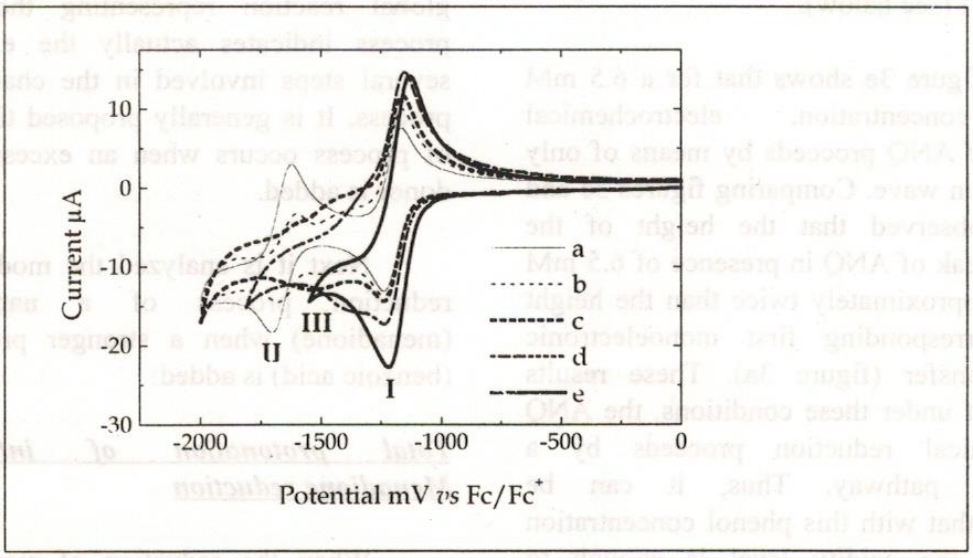

Figure 3. Cyclic voltammetry of 1 mM ANQ on a platinum electrode in 0.1M Et_4NBF_4 /acetonitrile, scan rate 0.1 Vs^{-1}; a) In the absence of phenol, b) 0.5 mM phenol, c) 1.0 mM phenol, d) 3.0 mM phenol, e) 6.5 mM phenol.

$HQ + e^- \rightleftharpoons HQ^{\bullet -}$ E1
$HQ^{\bullet -} + e^- \rightleftharpoons HQ^{2-}$ E2
$HQ^{2-} + DH \rightleftharpoons HQH^- + D^-$ C3

The fact that the second reduction wave still appears, indicates that the added acid is not enough in quantity to protonate all the HQ^{2-} produced from the reduction of $HQ^{\bullet -}$.

In figure 3c it is observed that an increment in phenol concentration (1.0 mM) promotes the increase of the reduction wave III and the complete disappearance of the reduction wave II, while wave I remains constant. These results indicate that the proton concentration in now high enough to protonate all HQ^{2-} produced. Therefore, it can be considered that under these conditions electrochemical reduction of ANQ follows the pathway E1→E2→C3 (figure 2). The overall mechanism has been changed to:

$HQ + e^- \rightleftharpoons HQ^{\bullet -}$ E1
$HQ^{\bullet -} + DH + e^- \rightleftharpoons HQH^- + D$ E_2'(E2C3)

In the figure 3d it is observed that for phenol concentrations higher than 3.0 mM, reduction wave I starts to move toward less cathodic potentials, and the magnitude of the corresponding current increases; so it can be considered that in these conditions a low enough acidity level is reached to perform the partial protonation of $HQ^{\bullet -}$ formed in E1, such protonation also displaces the potential from E_1 to E_1'. The fact that reduction from $HQ^{\bullet -}$ to HQH^- (wave III, pathway E2') still appears in the voltammogram indicates that acidity level is not enough low to protonate all $HQ^{\bullet -}$ formed in E1. According to literature and to our demonstration below, reduction of $HQH^{\bullet}$ occurs to a potential equal or higher to E_1', provoking a disproportionation stage that explains the increment of the reduction current

of the wave I (see below).

The figure 3e shows that for a 6.5 mM phenol concentration, electrochemical reduction of ANQ proceeds by means of only one reduction wave. Comparing figures 3e and 3a it is observed that the height of the reduction peak of ANQ in presence of 6.5 mM phenol is approximately twice than the height of the corresponding first monoelectronic electron transfer (figure 3a). These results indicate that under these conditions, the ANQ electrochemical reduction proceeds by a bielectronic pathway. Thus, it can be considered that with this phenol concentration (6.5 mM), the acidity level is enough to protonate completely all the $HQ^{\bullet -}$. Therefore, the reduction peak of ANQ may be interpreted as the result of one of the following reaction sequence, whose global contribution is two electrons for each ANQ molecule, (QH):

$HQ + e^- \rightleftharpoons HQ^{\bullet -}$ E1

$HQ^{\bullet -} + DH \rightleftharpoons HQH^{\bullet} + D^-$ C2

$HQH^{\bullet} + e^- \rightleftharpoons HQH^-$ E4

or

$HQH^{\bullet} + HQ^{\bullet -} \rightleftharpoons HQH^- + HQ$ DISP

$HQ + 2e^- + DH \rightleftharpoons HQH^- + D^-$ Global

Sequences:

Reactions E1, C2, E4 (ECE mechanism), slow step is C2

Reactions E1,C2,DISP (DISP1 mechanism), slow step is C2

Reactions E1,C2,DISP (DISP2 mechanism), slow step is DISP

It is important to point out that the cyclic voltammogram in figure 3e with an anodic wave coupled to the cathodic one with a ΔE_p = 85 mV and a relationship $(i_{pa}/i_{pc}) \cong 1$, suggests a quasi-reversible behavior: however, the global reaction representing the reduction process indicates actually the existence of several steps involved in the charge transfer process. It is generally proposed that this sort of process occurs when an excess of proton donor is added.

Next it is analyzed the modification of reduction process of a naphtoquinone (menadione) when a stronger proton donor (benzoic acid) is added:

Total protonation of intermediates. Menadione reduction

When the reduction of menadione, in anhydrous DMSO, is performed in the presence of a great excess of benzoic acid (figure 4) (10), the first signal of reversible monoelectronic reduction observed in aprotic media (r) is transformed to a bielectronic signal chemically irreversible (s), this behaviour is different to that observed for the reduction of ANQ in the presence of an excess of phenol, where a bielectronic quasi-reversible-like peak appears (figure 3e).

This latter behaviour indicates that the acidity of the media as well as the basicity of the intermediates involved in the menadione reduction, are such, that it is possible the protonation of the base $HQ^{\bullet -}$ formed in E1 (reaction C2), and they also permit protonate the other base HQH^- (reaction C6) present in the reduction process. The global mechanism representing the menadione reduction process in the presence of benzoic acid is:

$HQ + 2e^- + DH \rightleftharpoons HQH^- + D^-$

$HQH^- + DH \rightleftharpoons HQH_2 + D^-$ C6

$HQ + 2e^- + 2\,DH \rightleftharpoons HQH_2$ Global

In the case of the electrochemical

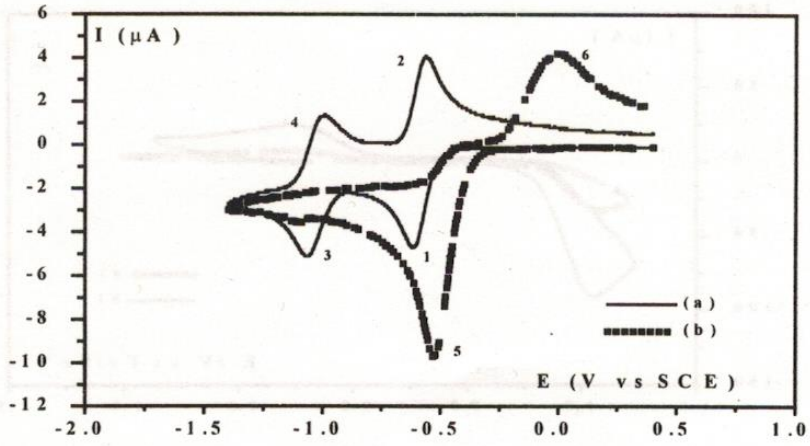

Figure 4. Cyclic voltammetry of menadione (2 mM) on a glassy carbon electrode in DMSO +0.2 M n-Bu_4NPF_6 at 0.1 Vs^{-1}. a) In the absence of benzoic acid. b) In the presence of benzoic acid 20 mM.

reduction of menadione in the presence of benzoic acid, the mechanism was characterized as ECE or DISP1 (10). For this compound it has been shown that depending on the acidity of the reaction medium, the reduction process of the quinone might look like a bielectronic step reversible or irreversible.

Next, the effect of the presence of acidic protons in the electroactive molecule itself is presented.

Self protonation effect. Perezone reduction

Hydroxysubstituted quinones are a special kind of compounds that show self-protonation reactions during their electrochemical reduction. Perezone is a natural type hydroxysubstituted quinone whose electrochemical behaviour has been characterized previously (11). Figure 5a shows the voltammetric behaviour of this compound in the absence of any added proton donor.

The observed peak pattern is basically different to those observed for a non-hydroxisubstituted quinone under similar conditions (figures 3a and 4a). However, the shape of the former voltammogram (figure 5a) is similar to that obtained in the case of the reduction of menadione in the presence of benzoic acid (figure 4b). The analysis of the voltammetric and chronoamperometric behaviour of perezone in acetonitrile allowed to show that the reductive process takes place following a DISP1 self-protonation mechanism.

The first reduction step (E1) of perezone HQ, yields to the formation of its anion radical semiquinone $HQ^{\bullet -}$. However, contrary to the reduction of menadione in aprotic solvent, this anion radical semiquinone $HQ^{\bullet -}$ can not be stabilized since the self-protonation reaction (C2′) yields to a protonated neutral radical $HQH^{\bullet}$. The reactivity of this latter species promotes its disproportionation DISP, yielding the initial HQ and the specie HQH^{-}. A second self-protonation reaction C6′ provokes that this species to be transformed finally into

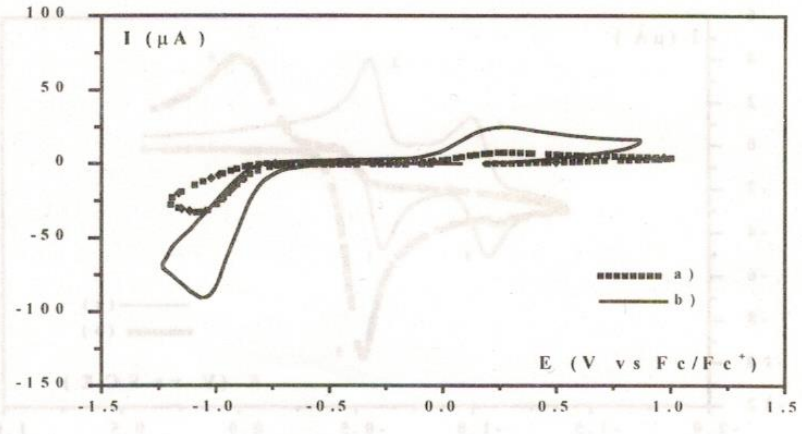

Figure 5. Cyclic voltammetry of perezone 2 mM on a platinum electrode in acetonitrile + 0.1M Et4NClO4, at 0.1 Vs^{-1}. a) In the absence of benzoic acid. b) In the presence of benzoic acid 10 mM (11).

hydroquinone HQH_2. The presence of this reactions sequence provokes the uncontrolled transformation of the perezone HQ into the leucoperezone HQH_2 with a low yield and an 2/3 electronic stoichiometry:

$HQ + e^- \rightleftharpoons HQ^{\bullet -}$ E1

$HQ^{\bullet -} + HQ \rightleftharpoons HQH^{\bullet} + Q^-$ C2'

$HQH^{\bullet} + HQ^{\bullet -} \rightleftharpoons HQH^- + HQ$ DISP

$HQH^- + HQ \rightleftharpoons HQH_2 + Q^-$ C6'

$HQ + 2/3\ e^- \rightleftharpoons 1/3HQH_2 + 2/3Q^-$ Global

When the reduction of perezone is performed in the presence of an excess of benzoic acid DH, the voltammetric pattern is similar to that observed in the absence of this acid (figure 5b). However, in the first case is observed that the reduction signal in much more intense. The voltammetric current function analysis, $i_p/v^{1/2}$, reveals that the observed current in presence of benzoic acid is three times greater than that observed in the absence of such acid.

This result is explained by means of the change in the electronic stoichiometry of the reduction process, from a global exchange of 2/3 electron per reduced molecule to a global mechanism exchanging 2 electrons per reduced molecule. This change is due to the fact that benzoic acid is a stronger acid than the perezone itself allowing the elimination of the self protonation reaction and the reduction of the perezone until its corresponding leucoperezone by means of a classic bielectronic mechanism of the ECE-DISP1-DISP2 type.

In this case, the global reaction is the same than the corresponding to the menadione reduction in the presence of an excess of benzoic acid. Voltammetric and chronoamperometric analysis of the perezone reduction in the presence of benzoic acid allowed also to show that the reduction mechanism is of the DISP1 type (11).

From the above discussion it is shown

that depending on the type and quantity of the added acid to the reaction medium, as well as to the particular molecule to be reduced, it is possible modify the reaction mechanism. However, it is necessary to be able to perform such modifications in a more systematic and predictive way. To achieve the latter purpose, we have proposed a quantitative measurement of the acidity level, as well as a method for its control, making use of buffering systems in aprotic solvents. Now this latter is briefly described.

Buffer preparation and pH determination in pure acetonitrile

As it was shown above, mechanism and stoichiometry of reduction pathway of quinones depends on the type and extension of proton donors. Therefore, in order to control in a precise way these mechanisms, it is necessary to perform the electrochemical experiments in the presence of the proper buffering systems to impose the level acidity of the electrolytic solution. The acidity level can be determined potentiometrically if suitable calibration plots of the glass electrode are made as proposed by Kolthoff&Chantooni (12).

The calibration is performed according to the spectrophotometric method using o-nitroaniline as indicator and measuring the absorption of the yellow at 410 nm. Absorption of o-aniline alone A_o, and mixed with several aliquots of 0.5 M anhydrous perchloric acid A_i, is measured to determine the pH values of the calibration curve and buffer solutions, both in 0.1 M TBAP in AN according to:

$$pH = 4.85 + \log\frac{A_i}{A_o - A_i}$$

For the glass electrode, used in this study the calibration plot pH vs the e.m.f. in milivolts, yields a straight line, with a slope of 56.3 mV, in a good agreement with those reported in the literature (12). An equation for our glass electrode, obtained by means of a linear regression analysis of the calibration plot data is used to determine the pH of buffers solutions employed.

$E = 0.605 \pm 0.005V - 0.056.3 \pm 0.002V(pH)$

Buffer solution preparation was performed by mixing equal quantities (0.5 mmol) of base and acid pairs, previously dried overnight, with 25 ml of 0.1 M TBAP in AN. The following acid-base pairs were employed:

a) benzoic acid/sodium benzoate ↓ (HBZ/NaBz); BBS

b) salicylic acid/sodium bisalicylate↓ (H_2Sal/NaHSal); SBS

c) oxalic acid/sodium oxalate↓ (HOx/Na_2Ox),

d) methanesulfonic acid/sodium methanesulfonate ↓ (HMet/NaMet).

Heterogeneous (↓) buffer solutions are obtained. The pH values obtained with these buffer systems are in the range 20 <pH<8.0.

Tetrabutyl-ammonium perchlorate has no acid-base properties in acetonitrile. The buffer solutions prepared do not show electrochemical properties when solid electrodes or Hg^0 were used.

Control of the mechanism of reduction by pH buffering. Reduction of horminone in buffered acetonitrile solutions.

In this section, we present the significant results of a previous study of the reduction mechanism of another natural product: horminone (13). It was performed in acetonitrile, as aprotic medium, in the presence

of two different buffer solutions in this solvent, in order to show that acidity level determines the type of mechanism of the reduction of horminone

From figure 6a, it is observed that horminone, in the absence of buffer solutions, presents a reduction peak at a high negative value and an oxidation peak at more positive potentials with respect to its corresponding cathodic peak. The latter behaviour suggests the existence of chemical reactions coupled to the charge-transfer step. Since in this experiment no donor proton is present, then the acidic hydrogen of the *o*-phenol present in the molecule of horminone acts as inner proton donor in a typical self-protonation reaction (4).

In order to control the self-protonation reaction and to show the influence of acidity level on the mechanism of the reduction of horminone the BBS (pH=17.2) and the SBS (pH=15.5) buffers solutions were used. The voltammogram profiles in these media are different (figure 6b and 6c). At both pH values it is observed an increment of the cathodic current peak. It can be demostrated that in the absence of a proton donor, the global reduction reaction of horminone requires 2/3 e^- for each reduced molecule, according to the self-protonation mechanism mentioned above (4). For the reduction peaks of horminone in BBS and SBS, it is observed that the current function values, $i_p/v^{1/2}$, are three times bigger than that obtained in the unbuffered solution

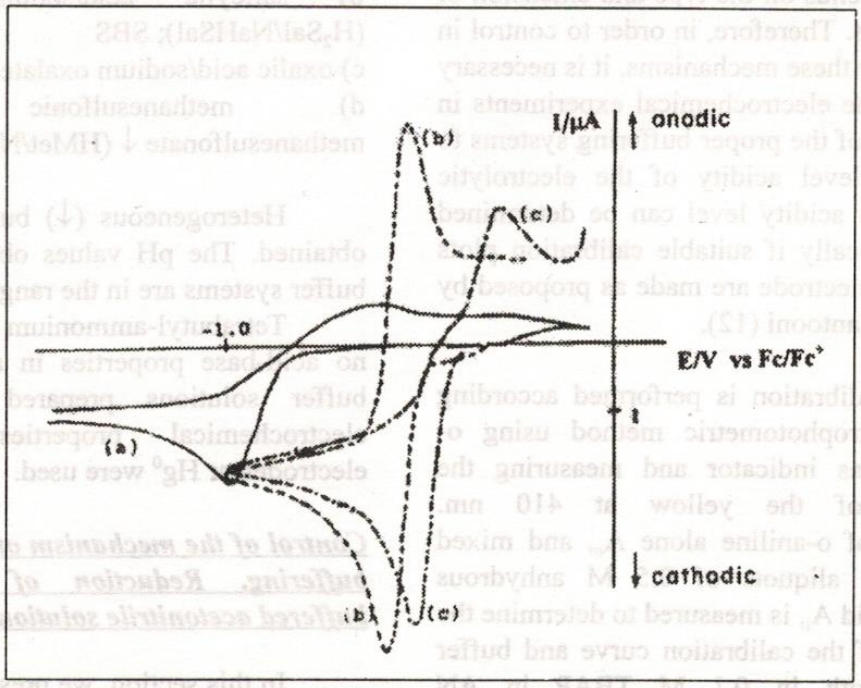

Figure 6. Voltammetric behavior (v= 160 mV s^{-1}) of horminone (0.4 mM) on HMDE in 0.1 M TBAP in AN in different buffer solutions: (a) unbuffered; (b) HBz = NaBz buffer solution (BBS) pH= 17.2; (c) H_2Sal + NaHSal buffer solution (SBS) pH= 15.5.

where self-protonation takes place. This increment is an indication that the electron-transfer number is two, then the global reduction reaction of horminone requires two electrons for each reduced molecule.

From the voltammetric study (the non-dimensional cathodic current function and the cathodic peak variations as a function either of the sweep rate potential or the horminone concentration) it is suggested that the mechanism of the horminone reduction could be ECE-DISP1 at pH=15.5, and DISP2 at pH=17.2 (13).

According to the behaviour reported for the horminone, it has been possible to show the possibility to change gradually the acidity level in such a manner that it was possible to avoid the protonation of HQH^- formed in the bielectronic reduction process of the quinone (pH=17.2), showing voltammetric peaks similar to a quasireversible system (see the ANQ case in the presence of an excess of phenol). When the acidity level was slightly modified, it was possible to protonate the specie HQH^- and to obtain an irreversible behavior (see the case of menadione reduction in the presence of an excess of benzoic acid).

Once it was shown the advantage of a continuos control of the pH, the application of this methodology to the control of a more complicated reduction mechanism, the reduction of *o*-nitrophenol is presented.

CONTROL OF THE MECHANISM REDUCTION BY PH BUFFERING. REDUCTION OF *o* -NITROPHENOL IN BUFFERED ACETONITRILE SOLUTIONS

In this section, a study of the reduction mechanism of *o*-nitrophenol was performed in acetonitrile (14), as the aprotic medium. From Figure 7, it is observed that *o*-nitrophenol, in acetonitrile, presents a wide reduction wave followed by small oxidation peak at more positive potentials. The later behaviour suggests the existence of a typical self-

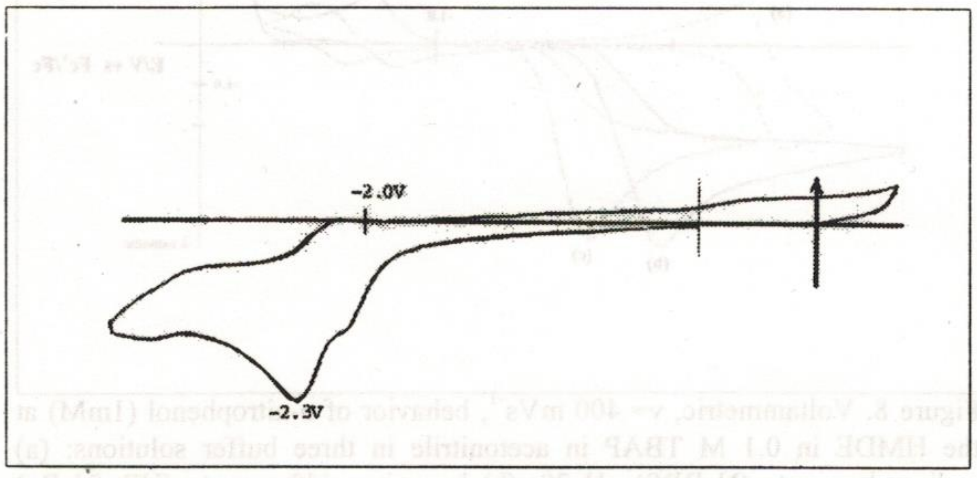

Figure 7. Voltammetric behavior of *o-nitrophenol* (1mM) at HMDE in 0.1 M TBAP in dried acetonitrile in unbuffered solution.

protonation reaction from the acidic hydrogen of *o*-phenol provoking a very complicate reduction pathway for the transformation of *o*-nitrophenol to the hydroxiphenylamino derivative, by a four electrons and protons transfer.

An electrochemical study, including, linear sweep voltammetry using hanging mercury drop electrode HMDE, DC polarography and some coulometric techniques was performed in order to show that acidity levels determine the type of mechanism of the reduction of *o*-nitrophenol. The acidity level of buffer solutions used in acetonitrile were: pH=20, 17.2, 11.8 and 8.1.

From figure 8a, pH=20, it is observed that *o*-nitrophenol presents a reduction peak at a large negative potential and an oxidation peak in the reverse scan, with $(i_p^a/i_p^c) \cong 1$. The latter behaviour suggests a reversible reduction. Exhaustive microcoulometry with a Hg^o pool yields a value of n = 1.2 when 2 mL of 2 mM *o*-nitrophenol in 0.1M TBAP in AN and NaBSS pH = 20 were electrolyzed at E_{imp}= -2.1V.

Since at pH=20, a neutralizing base is present, then the acidic hydrogen of the *o*-phenol cannot act as inner proton donor in a self-protonation reaction (4) since it is already neutralized.

It is important to indicate that the effect of a strong basic medium, provokes a change in the chemical nature of the electroactive compound. Thus *o*-nitrophenolate presents under these conditions, a mono electronic reversible electrochemical behaviour, that

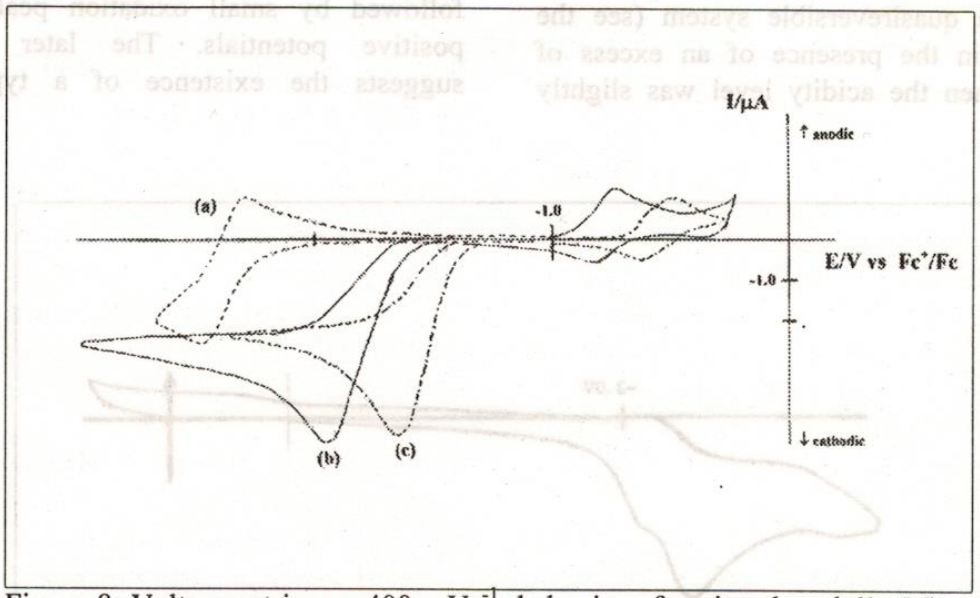

Figure 8. Voltammetric, v= 400 mVs^{-1}, behavior of o-nitrophenol (1mM) at the HMDE in 0.1 M TBAP in acetonitrile in three buffer solutions: (a) sodium benzoate (NaBBS) pH 20; (b) benzoic acid/benzoate (HBz/NaBz) buffer solution (BBS) pH 17.2; (c) salicylic acid/bisalicylate (H2Sal/NaHSal) buffer solution (SBS) pH 15.5.

implies the stabilization of a "stable" dianion radical according to the "time-window" of the electrochemical techniques employed.

From figure 8b and 8c it is observed that at pH=17.2 (BBS) and pH=15.5 (SBS), an increment of the cathodic peak is observed. The current function values, $i_p/v^{1/2}$, for the reduction peaks in the above reaction media, were constant with the scan rate potential. Thus, the electrochemical process is controlled by diffusion. In these conditions these values are approximately twice times as great at pH= 17.2 and 15.5 than at pH=20. This fact is an indication that the electron-transfer number in BBS and SBS is twice as great as that at pH=20 (NaBBS). The values at pH=17.2, n = 2.3 by exhaustive coulometry and n = 1.87 by the polarographic method, support the results obtained by voltammetry given above.

By exhaustive coulometry with a Hg^o pool, as described above, the following results were obtained: at pH= 16.2, n = 1.98; at pH= 11.8, n = 2.9 and at pH=8.1, n = 4.3.

The results obtained by cyclic voltammetry and coulometry show that it is possible to stop the overall reduction pathway by fixing the acidity level of the reaction medium (14). It is possible to get different reduction intermediates according to the acidity level of the media since the number of electrons that are needed for each reduction depends on the chosen acidity level of the reaction media.

The first two reduction steps of the nitro aromatic compounds ($HArNO_2$) can be stated according to a square scheme of electron and proton tranfer reactions, similar to the one used in the case of quinones (figure 2), where the final product, in the former case, is the nitrosocompound, HArNO.

The hydrolysis of the acidic proton of the molecule to be studied is not considered in the scheme of the figure 2. In the case of the nitro compounds, at pH=20, the involved species is precisely the deprotonated form of the electroactive molecule: *o*-nitrophenolate. In this case, the reactions that involve this species will be identified as E0 in order to establish an analogy with the systems studied throughout.

At pH=20 a single reversible one-electron reduction of the deprotonated *o*-nitrophenol is found:

$$ArNO_2^- + 1e^- \rightleftharpoons ArNO_2^{\bullet -} \qquad E0,$$
$$E_0 = -2.4V(Fc^+/Fc)$$

At pH = 17.8, a DISP2 mechanism (order two) was found (14). The disproportionation is the limiting step

$$HArNO_2 + 1e^- \rightleftharpoons HArNO_2^{\bullet -} \qquad E1$$
$$HArNO_2^{\bullet -} + H^+ \rightleftharpoons HArNO_2H^{\bullet} \qquad C2$$
$$pK_2' \cong 18$$
$$HArNO_2H^{\bullet} + HArNO_2^{\bullet -} \rightleftharpoons HArNO_2H^- +$$
$$+HArNO_2 \qquad DISP$$

The overall reaction at this pH value is represented by the following chemical equation:

$$HArNO_2 + 2e^- + HBz \rightleftharpoons HArNO_2H^- + Bz^-$$

It is important to note that the values of the thermodynamic constants associated to the proton transfer reactions have been evaluated for the *o*-nitrophenol reduction, in the presence of the six different buffered conditions. The strategy to evaluate these values was described elsewhere (14).

At pH = 16.2 the acidity level is low enough to allow reaction C6 to be the limiting step in a DISP1 (14) which can be represented by the following sequence of reactions:

$$HArNO_2 + 1e^- \rightleftharpoons HArNO_2^{\bullet -} \quad E1$$

$$HArNO_2^{\bullet -} + H^+ \rightleftharpoons HArNO_2H^{\bullet} \quad C2$$

$$pK_2' \cong 18$$

$$HArNO_2H^{\bullet} + HArNO_2^{\bullet -} \rightleftharpoons HArNO_2H^- + HArNO_2$$

$$HArNO_2H^- + H^+ \rightleftharpoons HArNO_2H_2 \quad C6$$

$$pK_a' \cong 16$$

$$HArNO_2H_2 \rightarrow HArNO + H_2O$$

At this pH the nitroso derivative is stabilized. The whole process can be represented by the following chemical equation:

$$HArNO_2 + 2e^- + 2HSal^- \rightleftharpoons HArNO + H_2O + 2Sal^{2-}$$

It is important to emphasize that the possibility of stabilizing a nitroso compound, represents an important perspective from the synthetic point of view.

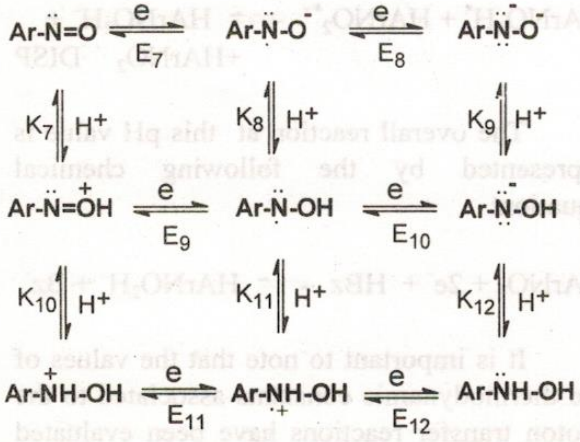

Figure 9. Electron and proton transfer involved in the reduction of nitrosoaromatic compound to hydroxylaminoaromatic compound.

In order to describe by means of a suitable scheme the transformation of the nitroso compound to the corresponding hydroxilamine, a square diagram is built (figure 9) in a similar way to that one shown in figure 2.

At pH = 11.8, the pH is low enough to protonate the nitroso derivative which can disproportionate in a DISP2 mechanism (order two) according to the following sequence of equations:

$$HArNO_2 + 2e^- + 2H^+ \rightleftharpoons HArNO + H_2O$$

$$HArNO + H^+ \rightleftharpoons HArNOH^+ \quad C7$$

$$pK_7' \cong 12$$

$$HArNOH^+ + HArNO_2^{\bullet -} \rightleftharpoons HArNOH^{\bullet} + HArNO_2 \quad DISP'$$

The whole reaction that occurs at pH= 11.8 can be represented by the following chemical equation:

$$HArNO_2 + 3e^- + 3HOx^- \rightleftharpoons HArNOH^{\bullet} + H_2O + 3Ox^{2-}$$

At pH = 8.2, the acidity of the media is low enough to protonate the $HArNOH^{\bullet}$ which once protonated disproportionates to yield the hydroxylamine intermediate according to the following sequence of reactions:

$$HArNO_2 + 2e^- + 2H^+ \rightleftharpoons HArNO + H_2O$$

$$HArNO + H^+ \rightleftharpoons HArNOH^+ \quad C7$$

$$pK_7' \cong 12$$

$$HArNOH^+ + HArNO_2^{\bullet -} \rightleftharpoons HArNOH^{\bullet} + HArNO_2 \quad DISP'$$

$$HArNOH^{\bullet} + H^+ \rightleftharpoons HArNHOH^{\bullet +}$$

$$pK_a' \cong 8$$

$$HArNHOH^{\bullet +} + HArNO_2^{\bullet -} \rightleftharpoons HArNHOH + HArNO_2$$

The whole reaction that occurs at pH = 8.2 can be represented by the following chemical equation:

$$HArNO_2 + 4e^- + 4HMet \rightarrow HArNHOH + H_2O + 4Met^-$$

CONCLUSIONS

A great variety of reductive processes follow several sequences of both electrochemical and coupled chemical reactions. In the scale of time of the electrochemical experiments, each one of these reactions can conduce to transient formation of stable product and neutral or charged intermediates. When the reactivity of these intermediates is determined only by the presence of external donor protons added to the work solution, the mechanism occurs globally in spite of kinetical reasons. So, many products of interest could be naturally consumed. In order to stop an overall mechanism of reaction at a specific stage of formation of products or stabilize certain intermediates, it is necessary to achieve experimentally a thermodynamic situation where the kinetical factors, favoring the overall mechanism, could be less important than that in the non controlled reactions. In reduction processes coupled with protonation steps such thermodynamical situation can be controlled by an appropriate choose of buffered work solutions. So, the extension and the type of partial mechanism of the reaction could be intentionally induced. The latter actually has an interesting impact in preparative electrosynthesis as well as in free radical chemistry and electrochemistry, since several intermediates can be stabilized by buffering the acidity level of the reaction media.

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