J. Braz. Chem. Soc., Vol. 16, No. 3A, 299-307, 2005.
Printed in Brazil - ©2005 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

The Role of Intramolecular Hydrogen Bonding in the Electrochemical Behavior of Hydroxy-Quinones and in Semiquinone Stability

Carlos Frontana and Ignacio González*

Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Apartado postal 55-534, 09340 México D.F., México

O estudo de um grupo selecionado de α e β-hidroxiquinonas ([α] 2-hidroxi-1,4-naftoquinona 2HNQ, [β] 5-hidroxi-1,4-naftoquinona 5HNQ and [β, β]5,8-dihidroxi-1,4-naftoquinona DHNQ) mostrou que ambos os tipos de funcionalidades diferem consideravelmente em termos de reatividade eletroquímica e química, e que essas diferenças também se manifestam na comparação de compostos do mesmo grupo. Os resultados provaram que a energia necessária para reduzir eletroquimicamente as hidroxoquinonas estudadas está relacionada com a estabilidade intramolecular das ligações de hidrogênio (IHBs) e com as reações de acoplamento que ocorrem durante a redução eletroquímica, tal como a seqüência de auto-protonação em 2HNQ. A análise da cinética de transferência de elétron associada com a redução monoeletronica que ocorre para 5HNQ e DHNQ mostraram que os efeitos IHB não afetam a cinética do primeiro processo de redução, mas induzem a grandes mudanças na cinética de segunda transferência eletrônica. Isso sugere que as semiquinonas são quimicamente diferentes dos compostos estudados, o que foi comprovado pela análise da estrutura eletrônica das semiquinonas por espectroscopia ESR. Essa análise parece relacionada com a perda de simetria no radical gerado eletronicamente e induz a valores *ks* de menor velocidade para a segunda redução de transferência de 5HNQ, comparada com DHNQ.

The study of a selected group of α and β-hydroxyquinones ([α] 2-hydroxy-1,4-naphthoquinone 2HNQ, [β] 5-hydroxy-1,4-naphthoquinone 5HNQ and [β, β]5,8-dihydroxy-1,4-naphthoquinone DHNQ) showed that both type of functionalities differ considerably in terms of electrochemical and chemical reactivity, and these differences are also manifest even upon comparison between compounds of the same group. The results proved that the energy needed to electrochemically reduce the studied hydroxyquinones is related both to the stability of intramolecular hydrogen bonds (IHBs) and coupled chemical reactions occurring during their electrochemical reduction such as self-protonation sequences in 2HNQ. The analysis of the electron transfer kinetics associated with the monoelectronic reductions occurring for 5HNQ and DHNQ showed that IHB effects do not affect the kinetics of the first reduction process, but induce great changes in the second electron transfer kinetics. This suggests that semiquinone species are chemically different for the studied compounds, as was corroborated by the analysis of the electronic structure of semiquinone species by ESR spectroscopy. This analysis seems to be related to the loss of symmetry in the electrogenerated radical and induces a lower rate *ks* value for the second reduction transfer of 5HNQ, compared with DHNQ.

Keywords: quinones, semiquinone, intramolecular hydrogen bond, self protonation, cyclic voltammetry, ESR

Introduction

The hydrogen bond is a commonly found interaction in the study of several biological systems of importance.[1] This electrostatic bond has been described as capable of sustaining the stabilization of supramolecular structures, such as DNA or the primary structure of proteins. It also can be of importance in molecular recognition between agonist or antagonist compounds and its proper cellular membrane receptors.[2]

Although most systems present this interaction as an intermolecular bond, there are also many cases in which the hydrogen bond occurs between different parts of the same molecule. The case of hydroxyquinones is one of great importance, since many of these compounds occur in large amounts in many vegetal species of well known biological activity.[3,4] Two main varieties can occur in the

* e-mail: igm@xanum.uam.mx

nature, both involving different types of hydrogen bond interactions (Figure 1): the α-hydroxy systems, in which the hydrogen bond forms a five-membered ring *via* the interaction between the oxygen atom of one of the carbonyl-quinonoid groups and another hydroxyl function supported by the α-carbon atom to the mentioned carbonyl function.[4] β-hydroxyquinones can present hydrogen bonding *via* the β-carbon to the carbonyl function leading to a six- membered ring structure (Figure 1); the hydroxyl group involved in these structures is usually part of a phenolic function.[5,6]

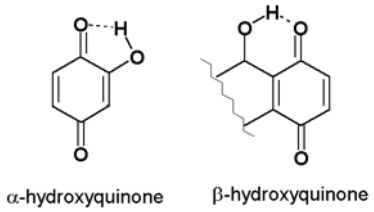

Figure 1. Main structures in α and β-hydroxyquinones. Intramolecular hydrogen bond interactions are depicted by the dashed line.

When electron transfer reactions occur, the acidity level of both hydroxy functionalities must be taken in account in front of the stability of the formed semiquinone / dianion intermediaries. These last species are related to the reactivity that hydroxyquinone compounds, as it has been reported in many biological essays, particularly in oxygen-quinone interaction studies.[6] A comparative study of both type of hydroxy substituted quinones is necessary, since some interpretations encountered in the literature tend to use indistinctly both type of compounds to account for equivalent behaviors.[6,7]

The present study is developed in an effort to emphasize the differences in reactivity between α and β-hydroxyquinone moieties, on the basis of the analysis of the energies of transformation and charge transfer kinetics, determined from cyclic voltammetry experiments of representative compounds in aprotic conditions. The employment of ESR measurement simultaneous to the electrochemical reduction allowed also to obtain structural data from the intermediate semiquinone estructures, and was correlated with the electrochemical data. This strategy has proven to be very useful in the characterization of hydrogen bonding effects in semiquinone species.[8]

Experimental

Chemicals

1,4-naphthoquinone (NQ, Figure 2) (Aldrich 98%, A. R. grade), was resublimed previous to its use. 2-hydroxy-1,4-naphthoquinone 2HNQ (Aldrich 98% A. R. grade), 5-hydroxy-1,4-naphthoquinone 5HNQ (Aldrich 98% A. R. grade), 5,8-dihydroxy-1,4-naphthoquinone DHNQ (Aldrich 90%, tech. grade), were used without further purification.

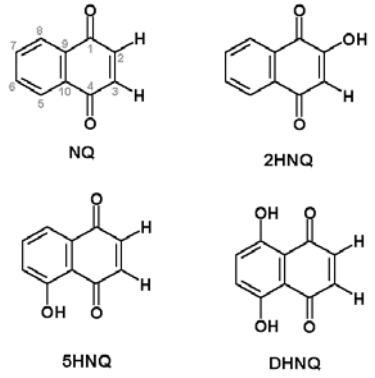

Figure 2. Structures for studied quinonoid compounds: NQ: 1,4-naphthoquinone; 2HNQ: 2-hydroxy-1,4-naphthoquinone; 5HNQ: 5-hydroxy-1,4-naphthoquinone, DHNQ, 5, 8-dihydroxy-1,4-naphthoquinone.

Solvent and supporting electrolyte

Anhydrous Acetonitrile (CH_3CN, Aldrich 98%) was dried overnight with P_2O_5, and distilled prior to use. The distillate was received over oven-activated 3 Å molecular sieve (Merck) and kept in a desiccator. The method is useful to obtain dry acetonitrile, characterized by the absence of OH bands in IR spectra. Tetraethylammonium tetrafluoroborate (Fluka Chemika, Electrochemical grade, Et_4NBF_4) was used as a supporting electrolyte. The salt was dried the night before use at 90 °C and 0.1 mol L^{-1} solutions were prepared and used as the supporting electrolyte.

Electrodes, apparatus and instrumentation

Cyclic voltammetry was performed with an AUTOLAB PGSTAT 30 potentiostat/galvanostat. IR Drop correction was applied during all the experiments, using Ru values (82 Ohms) obtained with the positive feedback technique. A conventional three electrode cell was used to carry out these experiments, employing as the working electrode a platinum microelectrode (BAS, Surface: 0.025 cm^2), polished using 0.05 μm alumina (Büehler), sonicated in distilled water for 10 minutes and acetone rinsed prior to its use. A platinum mesh was used as counterelectrode (Surface: 0.6 cm^2). The potential values were obtained against the reference (BAS) of Ag/0.01 mol L^{-1} $AgNO_3$ + 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP) in acetonitrile, separated from the medium by a Vycor

membrane. Ep values are reported *versus* the ferricinium/ferrocene couple (Fc^+/Fc), according to the IUPAC recommendation.[9] The potential of the Fc^+/Fc couple against this reference electrode was 0.25 V. Solutions of quinones were prepared by dissolving the desired compound with 0.1 mol L^{-1} Et_4NBF_4 (NQ: 5.1 X 10^{-3} mol L^{-1}; 2HNQ: 2.8 X 10^{-3} mol L^{-1}; 5HNQ: 6.3 x 10^{-3} mol L^{-1}; DHNQ: 5.7 x 10^{-3} mol L^{-1}). The solution was deoxygenated for 30 minutes and the cell was kept under a nitrogen atmosphere (grade 5, Praxair) throughout the experiment.

The *ks* values were obtained by the Nicholson method, referred by Rosanske and Evans, employing digital simulations to reproduce the experimental ΔEp differences for different values of *ks* as referred by Rosanske and Evans,[10] until the mean errors are lower than 3%. The employed diffusion coefficient was 1.9 x 10^{-5} cm^2 s^{-1} for 1, 4-naphthoquinone, obtained by chronoamperometric plots.

EC-ESR spectroscopy experiments

ESR spectra were recorded in the X band (9.85 GHz) using a Jeol FA-300 instrument with a cylindrical cavity. A commercially available spectroelectrochemical cell (Wilmad) was used, employing as the working electrode a 0.02 mm platinum wire (3.1 cm^2), introduced in the flat path of the cell. Another platinum wire was used as counter electrode (2.5 cm^2). The reference of Ag/0.01 mol L^{-1} $AgNO_3$ + 0.1 mol L^{-1} TBAP in acetonitrile (BAS) was employed as the reference electrode. Potential sweep control was performed with a 100 B/W Voltammetric Analyzer of Bioanalytical Systems (BAS) interfaced with a personal computer.

It is important to note that under the experimental conditions, the thin layer EC-ESR cell can have some problems on potential control in the desired region.[11] To minimize this problem, low scan rates were used, leading to good measurements. The technique proved to be fairly suitable, as the stable benzoquinone radical anion structure is obtained, and its appearance corresponds exactly to that reported in the literature.[12] Positive feedback is also performed during these experiments, Ru values are 350 Ohms, higher than in typical voltammetric experiments (82 Ohms). This occurs since the electrode arrangement is different in the EC-ESR from that used in the electroanalysis cell.

Solutions of quinones were prepared by dissolving the desired compound with 0.1 mol L^{-1} Et_4NBF_4 (NQ: 5 x 10^{-4} mol L^{-1}; 2HNQ: 1 x 10^{-3} mol L^{-1}; 5HNQ: 1.1 X 10^{-3} mol L^{-1}; DHNQ: 1.2 x 10^{-3} mol L^{-1}). The solutions were deoxygenated for 30 minutes and the cell was kept under a nitrogen atmosphere (grade 5, Praxair) throughout the experiment.

ESR simulations

PEST WinSim free software Version 0.96 (National Institute of Environmental Health Sciences) was used to perform simulation of the ESR experimental spectra, from the measured hyperfine coupling constant values (*a*). This program was also useful to evaluate *a* values when a direct measurement would be difficult in the conditions where the spectra acquisition was performed.

Cyclic voltammetry simulations

Bioanalytical Systems (BAS) Digisim 3.03 was employed to perform simulations of electrochemical mechanisms.

Results and Discussion

Acidity level of the OH functionality and the electrochemical behavior

Typical cyclic voltammograms for compounds 2HNQ, 5HNQ and DHNQ are depicted in Figure 3 compared to the typical NQ voltammetric response.

Two reversible pairs of peaks are present in the voltammograms of 5HNQ and DHNQ, such as those appearing in NQ (Figures 3A and 3B). This behavior occurs typically for the reduction of quinones in aprotic conditions and is related to the transformation of the quinone into a stable semiquinone (peak Ic). The latter species is reduced at peak IIc into a dianion, being both electron transfer processes reversible under the time scale of the experiments (equations 1 and 2). The electrochemical behavior of 5HNQ and DHNQ indicates that the β-hydroxy group is not acidic enough to protonate the semiquinone or dianion species.

$$Q + e^- \lozenge \; Q^{\bullet -} \quad (1)$$

$$Q^{\bullet -} + e^- \lozenge \; Q^{=} \quad (2)$$

It is noticeable the change in the electrochemical behavior of peak Ic´ for 2HNQ, an α-hydroxyquinone, (Figure 3C) from the first reduction signal of NQ. As it has been previously described for α-hydroxyquinones (Q-OH), the first reduction occurs as a 2/3 electron per mole of quinone transfer process,[13-15] where self-protonation reactions[16] consume the semiquinone formed during the first electron transfer process via ECE/DISP reactions (equations 3-7). This is due to the higher acidity of the

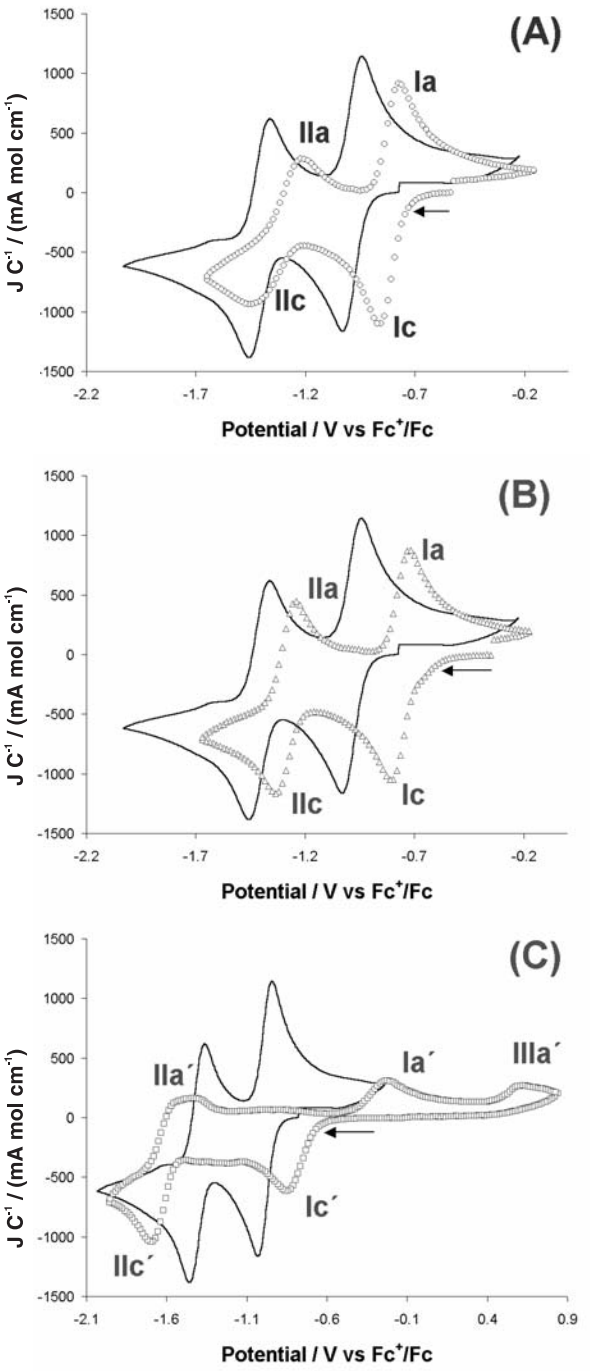

Figure 3. Typical cyclic voltammograms of (**A,** ○) 6.3 x 10^{-3} mol L^{-1} 5-hydroxy-1,4-naphthoquinone 5HNQ; (**B,** △) 5.7 x 10^{-3} mol L^{-1}, 5,8-dihydroxy-1,4-naphthoquinone DHNQ and (**C,** □) 3.9 x 10^{-3} mol L^{-1} 2-hydroxy-1,4-naphthoquinone 2HNQ in 0.1 mol L^{-1} Et_4NBF_4/CH_3CN. Platinum surface: 0.025 cm^2 *v*: 1000 mVs^{-1}. 5.1 x 10^{-3} mol L^{-1}; 1,4-naphthoquinone, is used as comparison with each compound as a solid line inner voltammogram. Both cathodic and anodic peaks are indicated.

enolic α-hydroxy function compared to the β-hydroxy group. Oxidation signals Ia' and IIIa' appearing at more positive potentials in α-hydroxyquinones are therefore related to the oxidation of the intermediates formed during the self-protonation pathway. This fact does not mean that a stable semiquinone cannot be formed. Since one of the products of the self-protonation pathway (equation 7) is the deprotonated original quinone ($Q\text{-}O^-$) , the second reduction signal IIc´ for compound 2HNQ corresponds to the monoelectronic reduction of this intermediate, forming a detectable semiquinone-type radical species,[17] at more negative potentials (equation 8).

$$Q\text{-}OH + e^- \Diamond \quad (Q\text{-}OH)^{\bullet -} \tag{3}$$

$$(Q\text{-}OH)^{\bullet -} + Q\text{-}OH \Downarrow \quad (HQ\text{-}OH)^{\bullet} + Q\text{-}O^- \tag{4}$$

$$(HQ\text{-}OH)^{\bullet} + e^- \Diamond \quad (HQ\text{-}OH)^- \tag{5}$$

$$(HQ\text{-}OH)^- + Q\text{-}OH \Downarrow \quad H_2Q\text{-}OH + Q\text{-}O^- \tag{6}$$

$$3Q\text{-}OH + 2\,e^- \Downarrow \quad H_2Q\text{-}OH + 2\,Q\text{-}O^- \tag{7}$$

$$Q\text{-}O^- + e^- \Diamond \quad Q\text{-}O^{\bullet =} \tag{8}$$

The presented behavior shows that the reactivity of both types of quinones differs in terms of the acidity level of the hydroxyl groups present. It is important to insist in this fact, since some authors tend to use the same set of general reactions to study compounds where both type of hydroxy functionalities occur.[6,7] This should be considered when more accurate descriptions of the mechanisms involved in the interaction of hydroxyquinones with added bases are proposed.

Intramolecular hydrogen bonding (IHB) effects in the electrochemical behavior

Other important feature of the obtained voltammograms (Figure 3) is the shift in peak potentials for signals Ic, Ic' and IIc presented for each compound to less negative potentials compared with the NQ standard, except for signal IIc' in 2HNQ. These shifts cannot be explained by the electronic inductive effect of the hydroxy functionality, since it should act as an electrodonating substituent. Contrary, the shift direction indicate that the electron density in the quinone function decreases and this effect is associated to the presence of intramolecular hydrogen bonds (IHB) present in each compound.[18,19] IHB effects also occur for systems where stable semiquinone species can be formed at the interface (peak IIc, Figures 3A and 3B). The shape of the second wave IIc-IIa in 5HNQ suggests that additional kinetic considerations takes place and will be discussed below.

By using the strengths of the IHBs reported in the literature[20] (5.34 and 5.38 kcal mol^{-1} per single hydrogen bond in 5HNQ and DHNQ respectively), a graphic trend was constructed with the magnitude of the potential shift

associated to the first electron transfer compared with NQ (Table 1). The shift for 2HNQ is not considered in the figure since it is not only related to the formation of the hydrogen bond, but also to the presence of the self-protonation pathway. The trend of Figure 4 increases in an exponential fashion and from this curve it is possible to estimate the shift in potential expected in 2HNQ by interpolation of its corresponding IHB strength, without the presence of self-protonation reactions, determining an IHB shift of nearly 0.1 V.

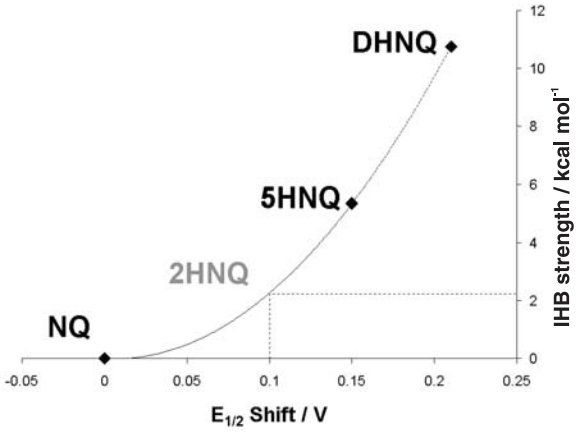

Figure 4. Shift in the half-wave potential *vs*. IHB strength relationship for 1,4-naphthoquinone NQ, 5-hydroxy-1,4-naphthoquinone 5HNQ and 5, 8-dihydroxy-1,4-naphthoquinone DHNQ (for which sum of IHB strength is plotted in the graph). The estimated shift value for 2-hydroxy-1,4-naphthoquinone is obtained by interpolation in this curve.

The remaining experimental shift in peak potential between 2HNQ and NQ is expected to be related to the self-protonation pathway. During the continuous potential sweep, 2HNQ is being consumed both by reduction and during the self-protonation steps (see equations 4 and 6) and the maximum concentration gradient is attained at less negative potentials that those expected for a monoelectronic reduction step, giving rise to the shift of the peak potential. This can be simply demonstrated by using cyclic voltammetry simulations considering reactions 4 and 6 fast enough so they consume quickly the formed semiquinone and the dianion (Figure 5).

During the simulation process it was possible to obtain a shift in potential between NQ and 2HNQ of nearly 0.07 V using a self-protonation set of reactions. It should be stated that the overall procedure would give more accurate values if more scan rates are used to simulate the resulting voltammograms. For the purpose of this work, the above strategy shows that the experimental peak potential shift in 2HNQ with respect to NQ (0.17 V) is both caused by self-protonation (approximately 0.07 V) and IHB effects (0.1 V).

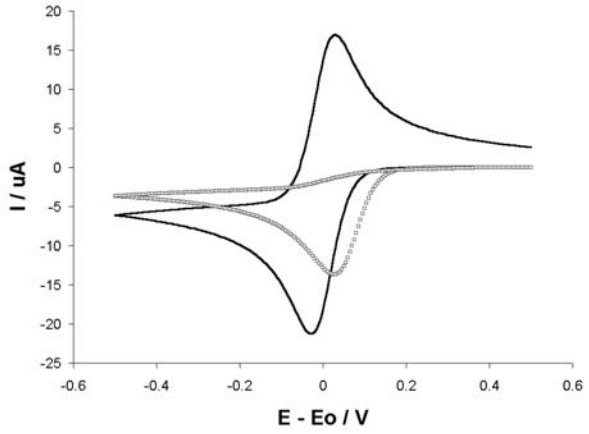

Figure 5. Simulated cyclic voltammograms for single electron transfer process (solid line), and ECEC self-protonation process (dotted line). Simulation conditions are: C_o: 1 x 10^{-3} mol L^{-1}, working electrode area: 0.025 cm^2, Do: 1.9 x 10^{-5} cm^2 s^{-1}; *v*:1000 mV s^{-1}. All standard rate of electron transfer constants were set to 0.05 cm s^{-1}. Self-protonation reactions (equations 4 and 6) were simulated using K_{eq} = 10000 and kf = 1000000.

Electrochemical experiments are therefore proven to be useful in the characterizations of the energetics of the reduction processes in quinones both considering IHB effects and self-protonation reactions.

Intramolecular hydrogen bonding (IHB) effects in the stability of the semiquinone in β-hydroxyquinones

For the following discussions, only 5HNQ and DHNQ are considered, since stable semiquinone structures can be formed in the interface after the first electron transfer. Since semiquinone species can interact between them by disproportionation reactions (equation 9), it is possible to determine the disproportionation constants (K_{disp}) from half-wave potential separations, as is referred in the literature.[21] The sequence of disproportionation equilibrium constant values is DHNQ> 5DHNQ> NQ (Table 1).

$$2Q^{\bullet -} \Diamond \quad Q + Q^{=} \qquad (9)$$

This indicates that hydrogen bonding also diminishes the "chemical resistance" to the formed semiquinone, since the amount of disproportionation of the radicals of NQ is lower than those for 5HNQ and DHNQ. Furthermore, it is remarkable to note that this stability decreases slightly as the number of hydrogen bonds present in the structure increases.

It can therefore be proposed that disproportionation constants determined by electrochemical experiments provide a first insight of the stability of the radical species. However, kinetic data is also needed to indicate trends in

Table 1. Obtained values for peak potential electrochemical data and analysis for: 1,4-naphthoquinone NQ; 5-hydroxy-1,4-naphthoquinone 5HNQ, 5,8-dihydroxy-1,4-naphthoquinone DHNQ and 2-hydroxy-1,4-naphthoquinone 2HNQ.

Compound	Ep (Ic) (V)[a]	Ep (IIc) (V)[a]	ΔEp (NQ-Q) (V)	ln Kdisp = $E_{1/2}^{1} - E_{1/2}^{2}$ $(RT/F)^{-1}$
NQ	-1.04	-1.47	0	0.000171
5HNQ	-0.88	-1.46	0.15	0.000206
DHNQ	-0.82	-1.35	0.21	0.000211
2HNQ	-0.87	-1.71	0.17 [b]	n.d.

[a] Obtained for 1000 mVs^{-1} *vs*. Fc^{+}/Fc; [b] Determined by interpolation (see description in the text); n.d.: ΔEp values are not available since no signal is detected for the reduction of the corresponding semiquinone.

the lability of the semiquinones and are discussed in the next sections.

It is interesting to note that even when an stable semiquinone signal can be obtained upon reduction of 2HNQ at potentials more negative than peak IIc´, no further signals are detected, since reduction of the electrochemical medium employed occurs first. Therefore, with this radical is not possible to perform a similar analysis as with the previous quinones and its behavior will not be discussed furthermore in this study.

Intramolecular hydrogen bonding (IHB) effects in the rate of the electron transfer in β-hydroxyquinones

Changes in shape for the voltammetric couples Ic-Ia and IIc-IIa (Figures 3A and 3B) are indicative of the presence of kinetic complications in 5HNQ and DHNQ. The shape of couples IIc-IIa shows more noticeable changes. The difference of the peak potential between peaks Ic and Ia (ΔEp_{Ic-Ia}) and IIc and IIa ($\Delta Ep_{IIc-IIa}$) increases with the scan rate (Figures 6 and 7, respectively), indicating limitations by the rate of the corresponding electron transfer process in the compounds studied.[23] Since the peak current of first electron transfer for 5HNQ and DHNQ is comparable with that of NQ (Figures 3A and 3B), it may be presumed that diffusion coefficient values of the three compounds are nearly of the same value. Therefore, the differences observed in Figures 6 and 7 are directly associated with different apparent rate constant of electron transfer *ks* and were evaluated by the method described in the literature (Table 2).[22, 23] In this context, *ks* values are in the sequence NQH≅5HNQ<DHNQ for peak couple Ic-Ia, while the *ks* value sequence for peak couple IIc-IIa differs (Figure 7), and is in the sequence 5HNQ<<NQ<DHNQ. These behaviors indicate that although the thermodynamics of the system is directly affected by hydrogen bonding effects, as was described earlier (Figure 4), the kinetics of electron transfer of both reduction processes does not show a simple trend with IHB magnitudes. These effects indicate that new chemical interactions via IHB occur in the semiquinone intermediates and are responsible for the changes of the rate transfer values.

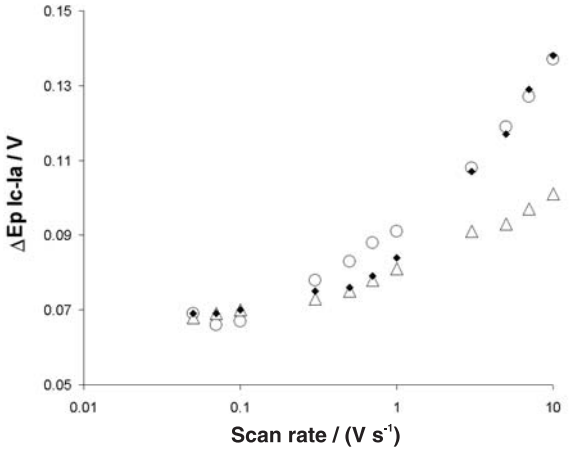

Figure 6. Peak potential difference Ic-Ia, for 1, 4-naphtoquinone (NQ, ◆); 5-hydroxy-1,4-naphthoquinone (5HNQ, ○) and 5, 8-dihydroxy-1,4-naphthoquinone (DHNQ, △), as a function of the scan rate. Hermano, dá pra usar (V s^{-1}) ?

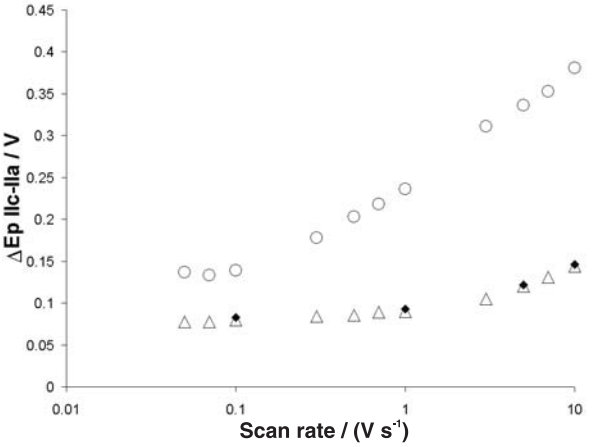

Figure 7. Peak potential difference IIc-IIa, for 1, 4-naphtoquinone (NQ, ◆); 5-hydroxy-1,4-naphthoquinone (5HNQ, ○) and 5, 8-dihydroxy-1,4-naphthoquinone (DHNQ, △), as a function of the scan rate.

Table 2. Obtained values for electrochemical kinetic and ESR simulation analysis for: 1,4-naphthoquinone NQ; 5-hydroxy-1,4-naphthoquinone 5HNQ, 5,8-dihydroxy-1,4-naphthoquinone DHNQ and 2-hydroxy-1,4-naphthoquinone 2HNQ

Compound	*ks* values Ic-Ia (cm s^{-1}) [a]	*ks* values IIc-IIa (cm s^{-1}) [a]	*g* value	*a* values (mT)
NQ	0.04	0.04	2.0052	$H_{2,3}$: 0.318 $H_{5,6,7,8}$: 0.0463
5HNQ	0.04	0.004 [b]	2.0047	$H_{2,3}$: 0.3592 $H_{6,7,8}$: 0.0534; H_{OH5}: ND
DHNQ	0.06	0.05	2.0048	$H_{2,3,6,8}$: 0.24 $H_{OH5, OH8}$: 0.05

[a]Obtained by the Nicholson[22] method, using D_o determined by chronoamperometric experiments: $D_{o1\text{-}3}$ – 1.9 x 10^{-5} cm^2 s^{-1}. All data were obtained employing α = 0.5 except for [b] where α employed is 0.35.

Electronic structure of the semiquinone by ESR spectroscopy

In order to provide some information on how does the properties of this intermediate change with the hydrogen bond structure, ESR-electrochemical experiments were performed in the region of potential between peak Ic and IIc.

ESR spectra reveal a quite distinctive coupling structure for the studied compounds (Figure 8). For 5HNQ (Figure 8B), the ESR spectrum structure is similar to the one obtained for NQ (Figure 8A), as it is seen the appearance of a triplet main coupling, arising from interactions of the added electron with H-2 and H-3 atoms (Figure 2). However, hyperfine splitting constants differ for both quinones (NQ: a_{H2}=a_{H3} 0.318 mT; 5HNQ: a_{H2}–a_{H3}: 0.3592 mT, Table 2), indicating changes in spin densities for the same type of protons,[8, 24] and shows that electron density is higher in 5HNQ than in NQ. The presence of IHB interactions also induces a higher degree of delocalization of the added electron between the two rings (NQ: $a_{H5\text{-}8}$ 0.0463 mT, 5HNQ: $a_{H6\text{-}8}$ 0.0534 mT, Table 2). The *a* value for the hyperfine coupling constant with the proton at the OH moiety cannot be obtained from the analysis, but the influence that exerts in the electronic structure can be seen from comparison between NQ and 5HNQ spectra, as the triplet signal is not completely fulfilled in the latter compound and unavoids a proper fitting of the spectrum (Figure 8B).

The case of DHNQ is completely different, as the ESR spectrum obtained differs from the triplet signal of NQ (Figures 8A and 8C). The obtained spectrum consists of a doubleted quintet, indicating that in this system two hyperfine coupling constants occur: a_{H2} = a_{H3} = a_{H6} = a_{H7} = 0.24 mT; and $a_{H1,8}$ (hydrogen bonded between O-1 and O-8) = $a_{H4,5}$ (hydrogen bonded between O-4 and O-5) = 0.05 mT, Table 2. This pair of values is in perfect agreement with those previously reported for this compound in THF,[8] and indicates the high symmetry of the system in terms of electron delocalization, differing from the case of compound 5HNQ.

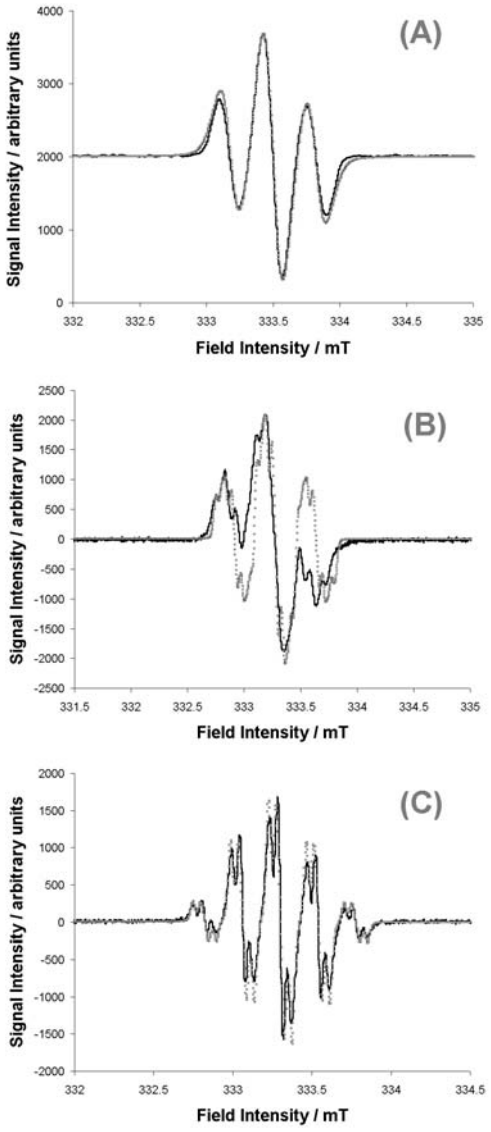

Figure 8. ESR spectra obtained for different quinoid compounds in the potential region for semiquinone formation. **A**: 5 x 10^{-4} mol L^{-1} 1,4-naphthoquinone NQ semiquinone (Applied potential: -1.24 V vs Fc^+/Fc); **B**: 1.1 x 10^{-3} mol L^{-1} 5-hydroxy-1,4-naphthoquinone 5HNQ semiquinone (Applied potential: -1.08 V vs Fc^+/Fc); **C**:1.1 x 10^{-3} mol L^{-1} 5, 8-dihydroxy-1,4-naphthoquinone DHNQ semiquinone (Applied potential: -1.02 V vs Fc^+/Fc). Solid line represents experimental spectrum. Dotted line depicts simulated one.

Relationships between ESR data and electrochemical response

ESR results can be related to the electrochemical response, since electron density differs in both compounds. Since for all the compounds studied, with and without hydrogen bonding effects, the first electron transfer (Ic-Ia) occurs at almost the same rate, it can be stated that the electron transfer kinetics of the mentioned process are little affected by IHB effects. The small variation occurring for DHNQ is associated to differences in electron delocalization compared with 5HNQ (see above text).

Since the presence of the hydrogen atom at the β-hydroxy moiety modifies the shape of the ESR spectrum, some changes are expected to be occurring in the chemical properties of the corresponding semiquinones. By the look of the shape of system IIc-IIa for 5HNQ (Figure 3A), it is possible to propose that a change in the transfer coefficient may be occurring related to the lost of symmetry in the β-monohydroxysemiquinone, determined to be nearly 0.35. Also, a lower value of *ks* compared to that obtained for the reduction of 1,4-naphthosemiquinone occurs (Table 2). ESR data for DHNQ indicates that the delocalization of charge occurs in a more effective way than in NQ radical, but also in a symmetrical pattern. This effect explains that both electron transfer rate constants for DHNQ are little higher than the corresponding for NQ.

Therefore, during the uptake of one electron in the hydroxyquinone structure, IHB induces changes in the delocalization patterns for the semiquinone structures and changes the rates of electron transfer kinetics. Since in these nuclear rearrangement processes, solvent or ion electrolyte interactions are of importance, they are being currently studied by quantum chemical calculations.

Conclusions

The study of a selected group of α and β-hydroxyquinones ([α] 2-hydroxy-1,4-naphthoquinone 2HNQ, [β] 5-hydroxy-1,4-naphthoquinone 5HNQ and [β,β]5,8-dihydroxy-1,4-naphthoquinone DHNQ) showed that both type of functionalities differ considerably in terms of electrochemical and chemical reactivity, and these differences are also manifest even upon comparison between compounds of the same group. The results proved that the energy needed to electrochemically reduce the studied hydroxyquinones, in terms of reduction peak potential, is related both to the formation and stability of intramolecular hydrogen bonds (IHBs), and coupled reactions occurring during their electrochemical reduction such as self-protonation sequences in 2HNQ. The analysis of the electron transfer kinetics associated with the monoelectronic reductions occurring for 5HNQ and DHNQ showed that IHB effects do not affect the kinetics of the first reduction process, but induce great changes in the second electron transfer kinetics. This suggests that semiquinone species are chemically different for the studied compounds, as was corroborated by the analysis of the electronic structure of semiquinone species by ESR spectroscopy. This analysis seems to be related to the loss of symmetry in the electrogenerated radical and induces a lower rate *ks* value for the second reduction transfer of 5HNQ, compared with DHNQ.

Acknowledgments

The authors kindly thank Dr. Bernardo A. Frontana-Uribe and Ms. Sc. Virginia Gómez (I.Q.-UNAM, México), for their technical assistance in the electrochemical and ESR experimental manipulations. C. Frontana thanks CONACyT-Mexico and SNI for the scholarship granted.

References

1. Jeffrey, G. A.; Sawnger, W.; *Hydrogen Bonding in Biological Structures*, Springer-Verlag: Berlín, 1991; Zafran, M.; *J. Mol. Struc. (THEOCHEM)* **1996**, *381*, 39; Akerön, C. B.; Seddon, K. R.; *Chem. Soc. Rev.* **1993**, 397.
2. Anthony, C.; *J. Bio-Chem.* **1996**, *320*, 697.
3. Cárdenas, J.; Rodríguez-Hahn, L.; *Phytochemistry* **1995**, *38*, 199.
4. Esquivel, B.; Calderón, J.; Sánchez, A.; Ramamoorthy, T.P.; *Rev. Latinoam. Quim.* **1996**, *24*, 44.
5. Piljac, I.; Murray, R.W.; *J. Electrochem. Soc.* **1971**, *118*, 1758.
6. Ossowski, T.; Pipka P.; Liwo, A.; Jeziorek, D.; *Electrochim. Acta* **2000**, *45*, 3581.
7. Goulart, M.O.F.; Lima, N.M.F.; Sant, A.E.G.; Ferraz, P.A.L.; Cavalcanti, J.C.M.; Falkowski, P.; Ossowski, T.; Liwo, A.; *J. Electroanal. Chem.* **2004**, *566*, 25.
8. Gendell, J.; Miller, W., R.; Fraenkel, G. K.; *J. Am. Chem. Soc.* **1969**, *91*, 4369.
9. Gritzner G.; Küta, J.; *Pure Appl. Chem.* **1984**, *4*, 462.
10. Rosanske, T. W.; Evans, D. H.; *J. Electroanal. Chem.* **1976**, *72*, 277.
11. Bard, A. J.; Goldberg, I. B.; Feldberg, S. W.*; J. Phys. Chem.* **1972**, *76*, 2550.
12. Yonezawa, T.; Kawamura, T.; Ushio, M.; Nakao, Y.; *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1022.
13. González, F.J.; Aceves, J.M.; Miranda R.; González I.; *J. Electroanal. Chem.* **1991**, *310*, 293.
14. Aguilar-Martínez, M.; Bautista, J.A.; Macías-Ruvalcaba, N.A.; Cuevas, G.; *J. Org. Chem.* **2001**, *66*, 8349.

15. Ferraz, P.A.L.; Abreu, F.C.; Pinto, A.V.; Glezer, V.; Tonholo, J.; Goulart, M.O.F.; *J. Electroanal. Chem.* **2001**, *507*, 275.
16. Amatore, C.; Capobianco, G.; Farnia, G.; Sandoná, G.; Saveant, J.M.; Severin, M.G.; Vianello, E.; *J. Am. Chem. Soc*. **1985**, *107*, 1815.
17. Frontana, C.; Frontana-Uribe, B. A.; González, I.; *J. Electroanal. Chem*. **2004**, *573*, 307.
18. Gómez, M.; González, F. J.; González, I.; *J. Electroanal. Chem.*, in press.
19. Gómez, M.; González, I.; González, F. J.; Vargas, R.; Garza, J.; *Electrochem. Comm.* **2003**, *5*, 12.
20. Khan, M. S.; Khan, Z. H.; *Spectrochim. Acta. Part A* **2005**, *61*, 777.
21. Bard, A. J.; Faulkner, L. R.; *Electrochemical Methods. Principles and Applications*, 2nd edition, John Wiley and Sons: USA, 2001, p.508.
22. Nicholson, R. S.; *Anal. Chem*. **1965**, *37*, 1351.
23. Rosanske, T.; Evans, D. H.; *J. Electroanal. Chem*. **1976**, *72*, 277.
24. McConnell, H. M. ; *J. Chem. Phys*. **1956**, *224*, 764 and references cited therein.

Received: October 29, 2004
Published on the web: April 12, 2005