Electrochimica Acta 188 (2016) 602–610

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Hydrogen bonding complexes in the quinone-hydroquinone system and the transition to a reversible two-electron transfer mechanism

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ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form 7 December 2015
Accepted 7 December 2015
Available online 10 December 2015

Keywords:
1,4-benzoquinone
hydroquinone
hydrogen bonding
dianionic quinhydrone
strong hydrogen bonds

ABSTRACT

The electrochemical reduction of 1,4-benzoquinone in acetonitrile in the presence of hydroquinone as a hydrogen bonding proton donor was studied. Different association modes and mechanistic regimes were found depending on the hydroquinone concentration. At stoichiometric concentrations, the formation of a dianionic quinhydrone linked by two-equivalent strong hydrogen bonds, was found. At higher concentrations of hydroquinone, the structure of this complex changes to another in which the monoprotonated quinone dianion is stabilized by interaction with hydroquinone and the supporting electrolyte cation. This complex is adsorbed on the glassy carbon electrode during its formation and the amount deposited is influenced by the concentration and size of the electrolyte cations. However, by further increasing of the hydroquinone concentration, the complex adsorption is totally inhibited and the cyclic voltammetry behaviour becomes reversible with the transfer of two-electrons.

1. Introduction

The quinone-hydroquinone systems are relevant due to their capability to participate as electron and proton carriers in complex biochemical mechanisms, such as photosynthesis and cellular respiration [1–5]. The electrochemical properties of quinones also play a key role in cellular defense since they show antibacterial [6,7], antifungal [8,9] and antiparasitic properties [10–12]. More remarkable is the fact that the quinone structure is essential to develop alternative biochemical functions such as cytotoxicity and, paradoxically, anticancer activity [13–17]. Direct electrochemical information from the complex biological media is not easy to obtain, which has promoted many electrochemical studies of a wide variety of quinones in aqueous medium [18,19] and organic solvents [20–22]. In the last case, it is well known that the full reduction of quinones, non substituted with acidic groups, proceeds via two electron transfer steps, where the first one produces the radical anion $Q^{\bullet-}$ (semiquinone) whereas the second one corresponds to the reduction of semiquinone to quinone dianion (Q^{2-}) (Eqs. (1) and (2)) [20–22].

$$Q + e^- \overset{E_1^0}{\rightleftharpoons} Q^{\bullet-} \quad (1)$$

$$Q^{\bullet-} + e^- \overset{E_2^0}{\rightleftharpoons} Q^{2-} \quad (2)$$

When the reduction of quinones such as 1,4-benzoquinone is carried out in the presence of an excess of strong to moderate proton donors (DH) such as carboxylic acids, the corresponding hydroquinone species (QH_2) is yielded following a global chemically irreversible two-electron and two-proton transfer mechanism [21]. The nature of the voltammetric behaviour observed under these conditions implies the formation of an association complex between QH_2 and the conjugated base of the proton donor (D^-), which revealed the high capability of QH_2 to form complexes with anionic species (Eq. (3)) [23–25].

$$Q + 2e^- + 2DH = QH_2 \cdots (D^-)_2 \quad (3)$$

However, when the quinone reduction is performed in the presence of stoichiometric amounts of this particular kind of proton donors, a broad reversible peak between the first and second reversible reduction waves has been observed in cyclic

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http://dx.doi.org/10.1016/j.electacta.2015.12.060
0013-4686/

voltammetry experiments. Due to the fact that the classical square mechanism of quinone reduction does not fully explain this behaviour, an explanation of the quinone electrochemistry in such conditions was reported [23]. In that work, the reduction of 1,4-benzoquinone performed in acetonitrile and DMSO in the presence of substoichiometric and stoichiometric concentrations of acetic acid revealed that this broad signal can be understood as the dimerization of the mono-protonated anion QH^- (Eq. (4)), which yields a new species consisting of a low-barrier proton transfer complex $[Q\cdots H,H\cdots Q]^{2-}$, which is a face-to-face structure that results from the easy interconversion between the species $Q^{2-}(QH_2)$ and $[QH^-, QH^-]$ (Scheme 1) [26]. It is worth mentioning that the same broad wave was also observed by Smith et al. [27] in a recent study about the reduction of quinones at very low concentrations on glassy carbon surfaces functionalized with acidic groups. The behaviour observed in this study is in agreement with our previous results in the sense that the small amount of acidic groups on the carbon surface protonates the first reduced quinone species (at very low concentration), permitting the appearance of the broad signal attributed to the dianionic quinhydrone complex $[Q\cdots H,H\cdots Q]^{2-}$ [26].

On the other hand, it is also worth mentioning that this dianionic complex can also be chemically formed from the product of half-deprotonation of QH_2, which supports the proposal about dimerization of the monoprotonated anion QH^- (Eq. (4)).

$$2QH^- \rightarrow [Q\cdots H, H\cdots Q]^{2-} \tag{4}$$

This proposal was confirmed by ^1H NMR experiments from the total disappearance of the hydroxyl proton signal, still at very high chemical shift, which is a classical behaviour of a low barrier proton transfer complex [26,28]. In accordance with this last result, electronic structure calculations show that the energy separating the structures depicted in Scheme 1 [26,29] is small, although slightly favoured towards the dimer $[QH^-, QH^-]$. low values For the purpose of the subsequent discussion, the complex $[Q\cdots H, H\cdots Q]^{2-}$ will be considered as the dimer $[QH^-, QH^-]$.

Supporting these ideas, the broad signal in voltammetry was also observed when benzoquinone is reduced in the presence of substoichiometric and stoichiometric amounts of hydroquinone [26] indicating the presence of the same complex. Following up this study of the quinone reduction and its interaction with hydroquinone as a proton donor, we report here the formation of an alternative complex that is formed as an adsorbate on the electrode surface when the quinone reduction is performed in acetonitrile solutions beyond stoichiometric hydroquinone concentrations. The structure of this new complex was analyzed by single crystal X-ray diffraction, which shows even more the relevant role of the supporting electrolyte cations on the adsorption process. A further increase in the hydroquinone concentration inhibits the complex adsorption and the transition towards a reversible two electron transfer behaviour was observed. Cyclic voltammetry, chronoamperometry and X-ray diffraction were used to explain these results.

2. Experimental

2.1. Chemicals and procedures

1,4-Benzoquinone 99% and hydroquinone 99% were Aldrich chemicals. 1,4-benzoquinone was previously purified by sublimation under reduced pressure. Anhydrous acetonitrile (Aldrich, 99.8%) was the solvent used for the electrochemical experiments and it was used as received. Tetrahexylammonium hexafluorophosphate 98% (Fluka), and tetrabutylammonium hexafluorophosphate 98% (Aldrich) recrystallized from absolute ethanol and vacuum-dried overnight in a Schlenck tube at ~80 °C, were used as the supporting electrolyte. The chemical and electrochemical experiments were performed at room temperature (~25 °C). All the working solutions were deoxygenated with dry argon bubbling directly to the bulk solution before every voltammetric scan, and the cell was kept under inert atmosphere during each experiment.

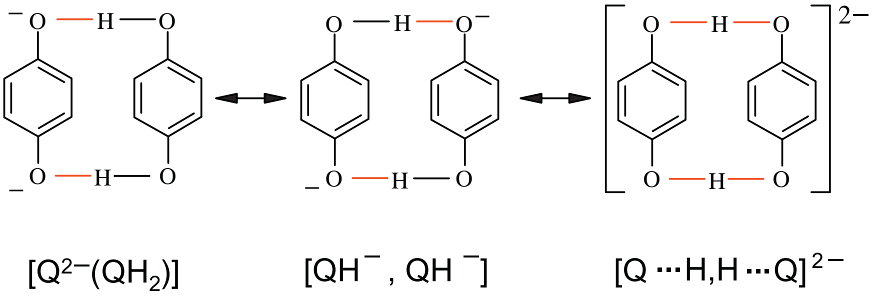
2.2. Instrumentation, cell and electrodes

An Autolab 302N potentiostat was used for all the electrochemical experiments applying positive feedback resistance compensation. Voltammetric experiments were performed in a conventional three-electrode cell. A 3 mm diameter glassy carbon disk (Sigradur G, from HTW Germany) was used as working electrode, which was polished with 1 μm alumina powder (Buehler) and ultrasonically rinsed with anhydrous ethanol before each run. The auxiliary electrode was a platinum mesh and the reference electrode an aqueous saturated calomel electrode (SCE). A salt bridge, containing a solution of 0.1 M or 0.2 M n-Bu_4NPF_6 in acetonitrile, was used to connect the cell with the reference electrode.

2.3. X-ray analysis

Crystals were grown from a solution of 56 mM QH_2 + 16 mM n-Bu_4NOH + 0.2 M n-Bu_4NPF_6 in acetonitrile under argon atmosphere. Once the mixture was prepared, the precipitation of a white solid was observed. This solution was allowed to rest for at least 24 h to complete the crystallization process. The crystals formed were washed with acetonitrile containing the electrolyte and then with pure acetonitrile. Finally, the acetonitrile from the last step was filtered and the crystals dried under an argon flux.

Diffraction data were collected using a Brucker-Nonius Kappa-CCD diffractometer using standard MoKα radiation. Data were processed using the Denzo software. Structure solution and



Scheme 1. Resonant structures of the quinhydrone-type dianionic complex.