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REDOX CHEMISTRY OF 3,4-DIHYDROXY-2-BENZOIC ACID, ITS OXIDATION PRODUCTS AND THEIR INTERACTION WITH MANGANESE(II) AND MANGANESE(III)

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Abstract—The redox chemistry of the ligand 3,4-dihydroxybenzoic acid (3,4-DHBA) has been studied in dimethylsulphoxide and the conditions for the formation of the corresponding semiquinone and quinone have been determined. The manganese(II) and manganese(III) complexes with the different forms of this ligand have been characterized by cyclic voltammetry, UV–vis spectroscopy and magnetic susceptibility measurements. Neither the neutral nor the monoanionic form of the ligand show the formation of complexes with the metal ions. The dianion can be oxidized electrochemically to the corresponding semiquinone, at a more positive potential due to the presence of a deactivating group, forming a "peroxo-type" dimer. The subsequent oxidation of this species generates the corresponding quinone. The dianion and the semiquinone forms of the ligand produce manganese(II) and manganese(III) complexes with 1:2 stoichiometry, which is favoured by the *ortho* position of the hydroxide groups. These results may be relevant for the development of models for biological systems.

In recent years the study of manganese complexes in different oxidation states with catechols and naturally occurring quinones has been undertaken because they present a series of reversible one-electron transfer processes in which these species are involved.[1–6] Our group has studied the manganese complexes with lawsone,[7] lapacol,[8] juglone[9] and quinizarine,[10] along with the mixed-ligand complex formed by quinizarine and the cysteine analogue 2-mercaptobenzoic acid.[11,12]

The redox potential presented by these systems is not positive enough to allow the oxidation of molecules like water. Therefore, we have undertaken the study of different systems in order to find one, although not natural, which presents an adequate potential. Our first effort was to study the complexes with the ligand 2,5-dihydroxybenzoic acid,[13] which showed that in the presence of a deactivating group in the aromatic ring such as carboxylate the oxidation of the hydroquinonic system to generate the corresponding semiquinone takes place at potentials more positive than in the case of analogous compounds without that deactivating group. However, the coordinating power of this species was not very good because in this case the hydroxide groups are in a "*para*" position. Consequently, we have now considered the study of the complexes with the analogous ligand 3,4-dihydroxybenzoic acid, in which the hydroxide groups are in "*ortho*" positions and its coordinating ability or that of its oxidation products should be better. We will confirm that in this case the oxidations to the semiquinone and the quinone occur at more positive potentials and that the manganese complex species formed are stabilized.

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EXPERIMENTAL

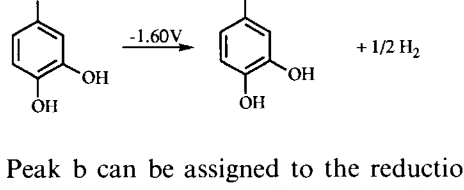
The equipment used in this study corresponds to that used in normal electrochemical and spectroscopic studies and it has been described previously in articles by our group.[8–13] The magnetic susceptibility measurements were made using the Evans method,[14] with a Bruker Model AC-200 P NMR spectrometer. Diamagnetic corrections were made.[15]

The ligand 3,4-dihydroxybenzoic acid (3,4-DHBA), the base tetrabutylammonium hydroxide (TBAOH), the salt tetramethylammonium chloride and dimethyl sulphoxide (DMSO; Gold Label) were obtained from Aldrich. The salt $Mn^{II}(ClO_4)_2 \cdot 6H_2O$ and the supporting electrolyte (tetraethylammonium perchlorate, TEAP) were obtained from G. Frederick Smith.

As the source of manganese(II) and manganese(III) the compounds $[Mn^{II}(DMU)_6](ClO_4)_2$ and $[Mn^{III}(urea)_6]\ (ClO_4)_3$ were synthesized following reported procedures.[16,17]

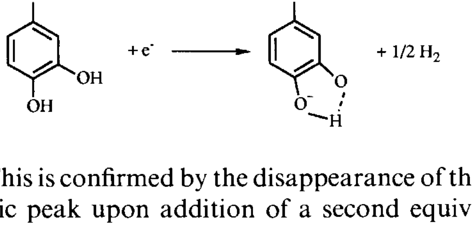
RESULTS AND DISCUSSION

The redox chemistry of the ligand 3,4-dihydroxybenzoic acid (3,4-DHBA) and its semiquinone form produced by oxidation has been studied. Fig. 1 illustrates that the original protonated ligand shows a reduction peak at −1.60 V vs SCE (peak a) corresponding to the reduction of the carboxylic proton to adsorbed hydrogen. This proton is the first to be reduced because it is the most acidic one in this ligand. Controlled-potential electrolysis at −1.65 V vs SCE indicates that one equivalent of charge has been transfered in the reduction process.



(1)

Peak b can be assigned to the reduction of the second proton, corresponding to one of the hydroxy groups, according to the following process:



(2)

This is confirmed by the disappearance of the cathodic peak upon addition of a second equivalent of base (Fig. 1C). On the other hand, one equivalent of charge is transferred in a controlled-potential electrolysis at −2.00 V vs SCE.

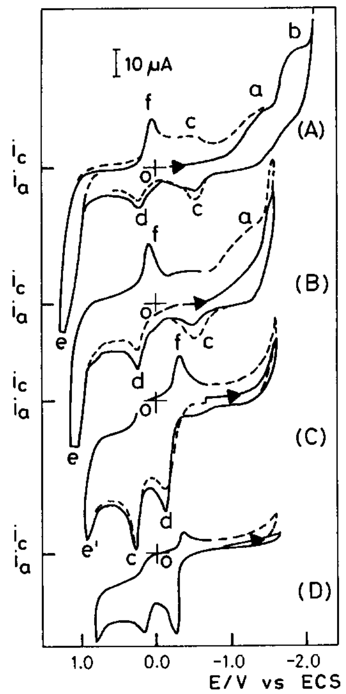


Fig. 1. Cyclic voltammograms of solutions that are: (A) 1.0 mM in the ligand 3,4-DHBA; (B) the same as A but in the presence of 1.0 mM TBAOH; (C) the same as A but in the presence of 2.0 mM TBAOH; (D) the same as A but in the presence of 3.0 mM TBAOH. The supporting electrolyte is 0.1 M TEAP and the scan rate is $0.1\ V\ s^{-1}$.

With respect to the anodic processes shown in Fig. 1, peak c corresponds to the oxidation of gaseous hydrogen produced in process (2) which remains in the vicinity of the electrode. In this case the peak current does not show a linear dependence with the square root of the scan rate.

This phenomenon has been observed in aprotic solvents and the explanation of its origin arises from the study of the activation of molecular hydrogen on platinum electrodes.[18] The formation of hydrogen ions on the surface of the electrode might reprotonate the dianion of the ligand, and peak d in Fig. 1(A) would correspond to the oxidation of the resulting monoanion of the ligand, yielding the corresponding semiquinone and releasing a proton.

In the presence of two equivalents of base the cyclic voltammogram of the solution is illustrated in Fig. 1(C). The oxidations observed at −0.14 V (peak d), +0.30 V (peak e) and +0.96 V vs SCE (peak e′) clearly correspond to the formation of the semiquinone, the formation of the quinone and the oxidation of the carboxylic group.

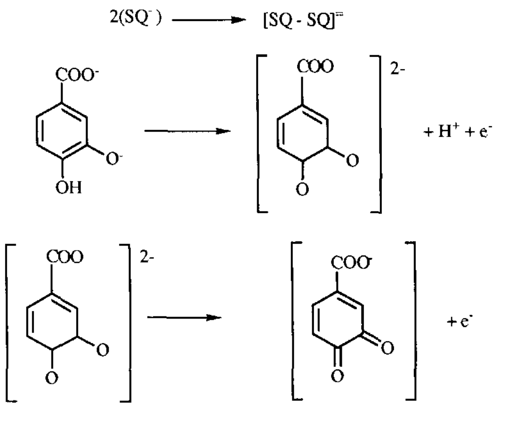


Fig. 2 shows the UV–vis spectra of the ligand in the presence of different amounts of base. The original ligand presents two bands at 295 ($\varepsilon = 700$ M^{-1} cm^{-1}) and 260 nm ($\varepsilon = 1150$ M^{-1} cm^{-1}) that correspond to the *B* and E_2 bands of benzene shifted by the presence of the substituents in the molecule.

In the presence of manganese(II), the cyclic voltammogram shown in Fig. 3 indicates that a complex between the dianion of the ligand and manganese(II) is formed with a 1 : 2 metal-to-ligand stoichiometry. If the amount of manganese(II) is higher than 0.5 times the amount of the dianion of the ligand, the electrochemical experiment is consistent with the presence of an excess free metal ion [reduction of free manganese(II) ion to manganese metal at −1.2 V vs SCE and oxidation of the manganese metal to manganese(II) at −0.3 V vs SCE].

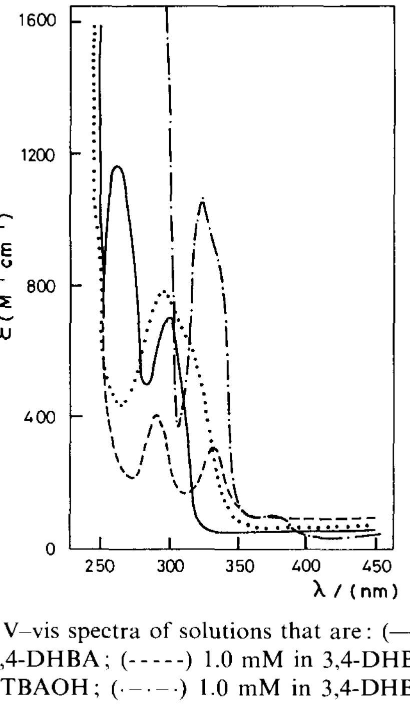


Fig. 2. UV–vis spectra of solutions that are: (——) 1.0 mM in 3,4-DHBA; (-----) 1.0 mM in 3,4-DHBA plus 1.0 mM TBAOH; (·—·—·) 1.0 mM in 3,4-DHBA plus 2.0 mM TBAOH; (·····) 1.0 mM in 3,4-DHBA plus 3.0 mM TBAOH.

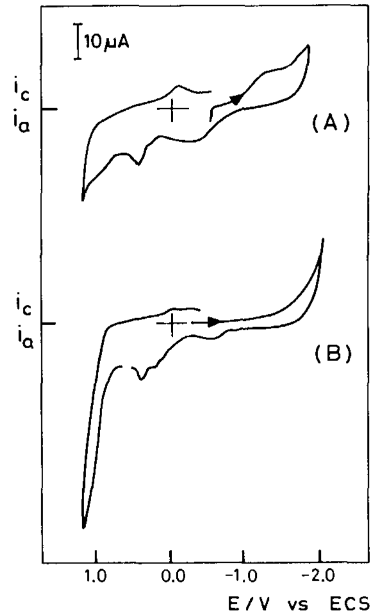


Fig. 3. Cyclic voltammograms of solutions in DMSO that are: (A) 3.0 mM in $Mn^{II}(DMU)_6(ClO_4)_2$, 3.0 mM in 3,4-DHBA and 6.0 mM in TBAOH; (B) 1.5 mM in $Mn^{II}(DMU)_6(ClO_4)_2$, 3.0 mM in 3,4-DHBA and 6.0 mM in TBAOH. The supporting electrolyte is 0.1 M TEAP and the scan rate is 0.1 V s^{-1}.

The magnetic susceptibility of a solution of manganese(II) with the dianion of the ligand in a 1 : 2 metal-to-ligand mole ratio is 5.42 B.M., which is indicative of the presence of manganese(II).

The voltammetric behaviour of a solution of the manganese(II) complex indicates that the oxidation of the ligand to the semiquinonic form produces another stable complex with the dimer of the oxidized ligand:

$$Mn^{II} + 2[SQ]_2^{2-} \longrightarrow \{Mn^{II}[(SQ)_2]_2\}^{2-}$$

If the semiquinone of the ligand is generated by controlled-potential electrolysis at 0.00 V vs SCE and this species is made to react with manganese(II), a complex forms whose UV–vis spectrum is illustrated in Fig. 4. An absorption band appears between 450 and 700 nm. Initially, the solution turns blue, probably by the formation of a 1 : 2 complex between the metal ion and the monomeric semiquinone. After some time the solution turns green, indicating that a new species is probably formed by the dimerization of the semiquinone. In this case a 1 : 4 complex would be stable in solution.

Analogous behaviour is observed with manganese(III), where a 1 : 1 complex is finally obtained between the metal ion and the dimer of the semiqui-

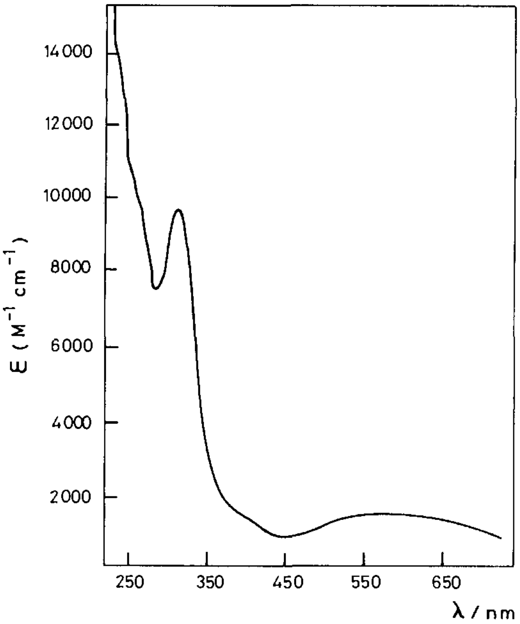


Fig. 4. UV–vis spectrum of a solution of the semiquinone complex of manganese(II) obtained by controlled-potential electrolysis of a solution of the manganese(II)–dianion complex.

none. The voltammetric behaviour of the solutions indicates the presence of free manganese(III) when the amount of metal ion is more than 0.5 times the amount of semiquinone originally present in the solution. The magnetic susceptibility of this solution is 4.73 B.M., indicating the presence of manganese(III).

The formation of this complex can be described by the following process:

$$\mathrm{Mn^{III}} + (\mathrm{SQ})_2^{2-} \longrightarrow [\mathrm{Mn^{III}}(\mathrm{SQ})_2]^+$$

On the other hand, the combination of manganese(III) with the dianion of the ligand forms a 1 : 2 complex as indicated by the voltammetric behaviour of the corresponding solutions:

$$\mathrm{Mn^{III}} + 2\,\mathrm{DA} \longrightarrow \{\mathrm{Mn^{III}}(\mathrm{DA})_2\}$$

Therefore, we can conclude from this work that this ligand can be oxidized to the corresponding semiquinone at a potential more positive than that found for other catechols (i.e. 3,5-di-tert-butyl-catechol),[19] due to the presence of a deactivating group on the aromatic ring. The semiquinone dimerizes and the resulting dimer presents good coordination characteristics due to the *ortho* position of the hydroxy groups. This can be inferred from the formation of stable complexes with both manganese(II) and manganese(III).

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