The Hydroquinone–Quinone Redox Behaviour in Acetonitrile

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Summary Cyclic voltammetry reveals the occurence of five different electrode processes during the cyclic oxidation–reduction of the hydroquinone–quinone system in acetonitrile.

THE redox behaviour of quinone–hydroquinone systems is complicated in aprotic solvents since protons are involved in the conversion of one into the other. This complexity was encountered during the study of anodic deacylation and demethylation of hydroquinone diesters and diethers in acetonitrile.[1] Thus in addition to the intrinsic interest in the classical organic redox system, a study of this behaviour is of considerable analytical importance.

Hydroquinone is irreversibly oxidized at a platinum electrode in carefully purified acetonitrile. At moderate sweep rates ($<$ 40 v/min. in this study), the single cycle voltammogram consists of a two-electron oxidation peak (P$_1$) at +1·13 v† and a two-electron reduction peak (P$_2$) at +0·12 v[2] (Figure 1). The nature of the cathodic processes was found to be highly dependent on electrode history. If the electrode was first anodized by holding at +1·50 v for 30 sec. followed by stirring the solution and allowing to stand for 30 sec., the only reduction peak observed was P$_2$. On the other hand, cathodizing the electrode at −1·50 v for 30 sec. resulted in the observation of a new peak (P$_3$) at −0·34 v and a new oxidation peak (P$_4$) at −0·16 v. Voltammograms obtained in this manner are difficult to reproduce but clearly illustrate the importance of the surface condition of the electrode.

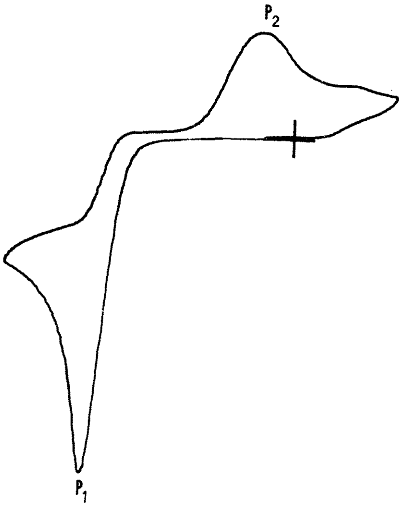

FIGURE 1. *Cyclic voltammogram of hydroquinone* (*in* MeCN, 1·0 mM, *lithium perchlorate*, 0·1 M). Sweep rate 10 v/min.

P$_1$ and P$_2$ have been characterized as oxidation to, P$_1$, and reduction of, P$_2$, the protonated quinone.[2] I was able to verify the assignment for P$_2$ by observing the effect of incremental addition of perchloric acid to a solution of benzoquinone in acetonitrile. In the absence of added acid, the voltammogram of benzoquinone shows a reduction peak (P$_3$) at −0·34 v and an oxidation peak (P$_4$) at −0·14 v. Continuous cycling of the couple (P$_3$–P$_4$) results in P$_3$ moving in the cathodic direction and becoming increasingly large. Making the solution 1·5 mM in perchloric acid resulted in the observation of P$_2$ and P$_3$ in approximately equal heights while adjusting the concentration to 3·0 mM nearly eliminated P$_3$ and P$_4$ (Figure 2).

The two-electron reduction of benzoquinone (P$_3$) is coupled with an oxidation peak (P$_4$). In the presence of protons or proton donors, the hydroquinone di-anion formed at P$_3$ is rapidly half-protonated and P$_5$ (+0·67 v) is observed on the anodic scan. P$_5$ was shown to involve the oxidation of the mono-anion of hydroquinone by observing the effect of incremental addition of 2,6-lutidine, which has been shown to have low nucleophilic reactivity in anodic processes.[3] Addition of one equivalent of 2,6-lutidine to the voltammetric solution of hydroquinone resulted in a voltammogram with P$_5$ and P$_1$ being about equal in height (Figure 3a) and the elimination of P$_2$. Two equivalents of the base completely eliminated P$_1$ (Figure 3b). P$_5$ is also observed during cyclic voltammetry of benzoquinone in acetonitrile in the presence of less than one equivalent of perchloric acid.

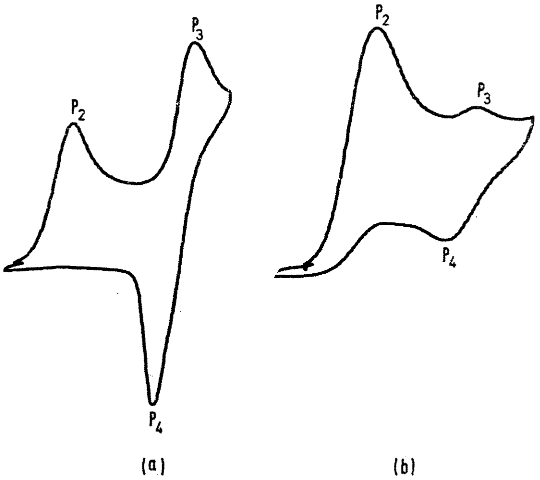

FIGURE 2. *Cyclic voltammogram of benzoquinone* (*in* MeCN, 1·0mM, *lithium perchlorate*, 0·1 M), *in the presence of perchloric acid.* [HClO$_4$]: (a) 1·5 mM; (b) 3·0 mM. Sweep rate 10 v/min.

The process involved at each of the voltammetric peaks are summarized in the Scheme.

In order to explain the observation of P$_3$ at high scan rates and P$_2$ at low scan rates, Eggins and Chambers[2] postulated that quinhydrone was formed at P$_1$ and was short-lived in the electrolysis medium. Their assignment of −0·56 v for the peak potential of benzoquinone reduction is questionable in the light of this work. Intuitively, one

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† All potentials refer to the saturated calomel electrode.

would expect methyl-substituted hydroquinones to be oxidized more easily and the corresponding quinones to be reduced with more difficulty than the unsubstituted compounds. Indeed, this was found to be the case for oxidation, the peak potentials for hydroquinone, 2,5-dimethylhydroquinone, and 2,3,5,6-tetramethylhydroquinone were found to be +1·12 v, +0·99 v, and +0·83 v, respectively.[2] 2,3,5,6-Tetramethylquinone was reduced at −0·69 v and 3,5-dimethylquinone at −0·54 v, and one would predict that benzoquinone would reduce at about −0·40 v, much closer to the value reported for P_3 (−0·34 v) than that assigned for the quinone (−0·56 v).[2] It should be emphasized that the assignment for P_3 as reduction of benzoquinone does not rule out quinhydrone formation as proposed by Eggins and Chambers.[2] However, it makes this postulate unnecessary. The failure to observe P_2 at high scan rates could possibly be due to slow protonation of the anodically generated quinone (Equation). This would require that benzoquinone is first generated and then protonated. The fact that P_3 is observed after pretreatment of the electrode suggests that the availability of protons at the electrode surface may be less after pretreatment making protonation of the quinone slower. Addition of small amounts of water causes P_3 to appear on the first scan. This could be due to competition between the quinone and water for the protons released in the oxidation. Thus, the complexity in the hydroquinone–quinone redox system in acetonitrile can be explained by the deficiency of protons.

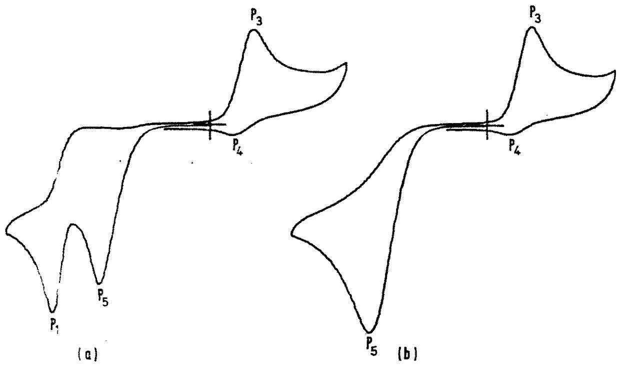
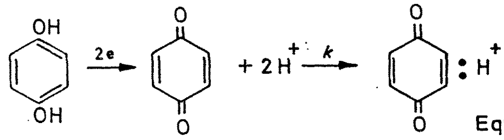


FIGURE 3. *Cyclic voltammogram of hydroquinone* (*in* MeCN, 1·0 mM, *lithium perchlorate*, 0·1 M), *in the presence of* 2,6-*lutidine*. [2,6-Lutidine]: (a) 1·0 mM; (b) 2·0 mM. Sweep rate 10 v/min.

	E_P
P_1 $QH_2 \rightarrow Q + 2H^+ + 2e$	+1·13
P_2 $QH^+ + 2e + H^+ \rightarrow QH_2$	+0·12
P_3 $Q + 2e \rightarrow Q^{2-}$	−0·34
P_4 $Q^{2-} \rightarrow Q + 2e$	−0·14
P_5 $QH^- \rightarrow Q + H^+ + 2e$	+0·67

SCHEME



Equation

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[1] V. D. Parker, *Chem. Comm.*, 1969, 610;

[2] The number of electrons transferred at peaks 1 and 2 has been determined to be equal to 2. B. R. Eggins and J. Q. Chambers, *Chem. Comm.*, 1969, 232.

[3] V. D. Parker and L. Eberson, *Tetrahedron Letters*, in the press.