Interpretation of Electrochemical Reduction and Oxidation Waves of Quinone–Hydroquinone System in Acetonitrile

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Summary When tetraethylammonium perchlorate is used as the supporting electrolyte, benzoquinone is reduced in two reversible one-electron waves, but with lithium perchlorate ion pairing can occur and the behaviour is more complex.

THERE appears to be some controversy between our work[1] and that of Parker[2] concerning the cyclic voltammetric reduction waves for quinone in acetonitrile. The difference is that we[1] used tetraethylammonium perchlorate as the supporting electrolyte whereas Parker[2] used lithium perchlorate with which ion pairs can be formed.[3]

In accordance with Peover's polarographic experiments in acetonitrile using tetraethylammonium perchlorate,[4] two reversible one-electron waves are seen on platinum as shown in Figure 1 (a) and the Table. The first wave involves the $Q \rightleftharpoons Q^{\dot{-}}$ couple as confirmed by identification of the semiquinone radical anion by e.s.r.[3a,4] The second wave is $Q^{\dot{-}} \rightleftharpoons Q^{2-}$ as can be shown by oxidising hydroquinone dianion, formed from hydroquinone and an excess of tetra-n-butylammonium hydroxide, *cf.* ref. 5, as shown in Figure 1 (b). The reversible one-electron waves are essentially unchanged with increasing sweep rate, except

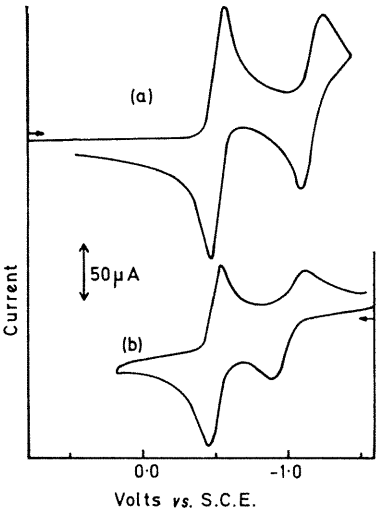

FIGURE 1. *Cyclic voltammograms in* MeCN *with* 0·1M-*tetraethylammonium perchlorate of* (a) $2{\cdot}20 \times 10^{-3}$M-*benzoquinone at* 120 mv/*sec.* (b) $1{\cdot}82 \times 10^{-3}$M-*hydroquinone plus* $1{\cdot}97 \times 10^{-3}$M-$\mathrm{Bu^n_4NOH}$ *at* 60 mv/sec.

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that they tend to broaden, indicating less reversible character, as would be expected.

Cyclic voltammetry parameters for quinone reduction waves ($2·35 \times 10^{-3}$M-*benzoquinone in* MeCN *with* 0·1-M-*tetraethylammonium perchlorate. Sweep rate* 30 mv/sec. *All potentials are in volts* vs. *S.C.E.*)

Wave	E_p	$E_{p/2}$	$E_p - E_{p/2}$*	$E_{1/2}$†	$E_{1/2}$ (ref. 4)	$i_p/ACv^{1/2}$ =	$268n^{3/2}D^{1/2}$‡
1	−0·544	−0·481	0·063	−0·512	−0·51	1·31	1·31
2	−1·095	−1·030	0·065	−1·062	−1·14	0·93	1·31

* Theoretically for a reversible wave $E_p - E_{p/2} = 0·056/n$.
† Theoretically for a reversible wave $E_{1/2} = E_p - 0·0285/n = E_{p/2} + 0·028/n$.
‡ Randles–Sevcik equation using $n = 1$; $D = 2·4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for Q.

In contrast to these results, when lithium perchlorate is used as the supporting electrolyte a reduction wave (I) with two-electron character ($E_p - E_{p/2} = 24$ mv) is seen in the region reported by Parker,[2] followed by a second smaller wave (II). On the reverse scan, one or two broad waves (III and IV) are seen, depending on the sweep rate (Figure 2). As the sweep rate is increased wave (I) shifts in the negative direction from −0·25 v at 2 mv/sec. till it merges with wave (II) at 20 v/sec. Wave (II) also shifts in the negative direction from −0·46 v till wave (I) merges with it at −0·5 v. With increasing sweep rate, wave (III) becomes more prominent and wave (IV) disappears. A yellowish blue film is deposited on the electrode surface during the scanning of wave (I).

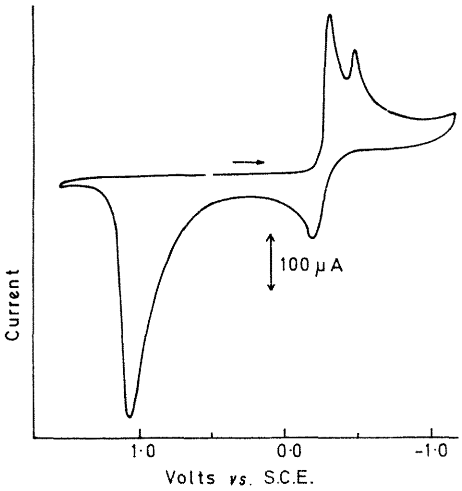

FIGURE 2. *Cyclic voltammogram of* $2·15 \times 10^{-3}$M-*benzoquinone in* MeCN *with* 0·1M-*lithium perchlorate at* 120 mv/sec.

The system is very much analogous to the behaviour of quinone in the presence of an excess (0·1—0·5M) of weak proton-donors such as phenol or hydroquinone.[6] The Li^+ ion is a moderately strong Lewis acid and may be hydrated with residual water from the acetonitrile, in which case the hydrated ion could act as a proton-donor. Wave (I) may be due to a pre-protonation process[7] (or pre-charge-transfer between Q and Li^+) giving as a product Li^+QH^- which is precipitated as a film and is oxidized in wave (IV). This former mechanism is supported by the fact that when hydroquinone is added to lithium hydroxide in acetonitrile the same yellowish blue colour is seen, *cf.* ref. 5. Wave (II) and the combined waves at fast sweep rates may involve a post ion-pair formation[3] (or post-protonation step[7]).

$$Q + e^- \rightleftharpoons Q^{\overline{\cdot}}$$

$$Q^{\overline{\cdot}} + Li \rightarrow Q^{\overline{\cdot}} \cdots Li^+$$

Then wave (III) may be oxidation of the radical ion pair. A decisive interpretation of the behaviour is not possible at present as there is no theoretical model for a system involving kinetics of this type combined with adsorption and electrode filming effects.

We have also observed the formation of QH^- by the addition of a strong-hydroxylic base to hydroquinone.[2] We used pyrrolidine,[6] a stronger base than 2,6-lutidine,[2] and in consequence the QH^- oxidation wave was seen at less-positive potentials than observed by Parker[2] *i.e.* +0·28—+0·45 v depending on the amount of base added.

In all our experiments, a reproducible platinum surface was obtained by polishing the electrode with 0·3 μ lapping compound.

Parker[2] also suggests that our intermediate wave observed at fast sweep rates during the oxidation of hydroquinone[1] might be due to slow protonation of the quinone. The properties of the wave are not in accordance with this idea, but indicate that it is due to reduction of a dimer of the one-electron oxidation product, possibly a quinone hemiacetal[6] rather than quinhydrone.[1]

This work was supported by a grant from the U.S. Public Health Service. The author thanks Dr. James Q. Chambers for helpful discussions.

(*Received, August 5th,* 1969; *Com.* 1203.)

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