# Electrochemical Oxidation of Hydroquinone in Acetonitrile

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WE have characterised the oxidation of hydroquinone (QH_2) in acetonitrile by using electrochemical techniques over a wide time scale. The products and an intermediate have been detected by cyclic voltammetry.[1] At fast sweep rates (10 v/sec.) a wave is observed which is assigned to the reduction of a quinhydrone intermediate. This is significant in understanding quinone–hydroquinone redox behaviour[2] which has been regarded as the classical organic reversible redox system.

The oxidation of hydroquinone at platinum electrodes in acetonitrile is irreversible, producing the protonated quinone (QH^+) in a two-electron step.

$$QH_2 \rightarrow QH^+ + H^+ + 2e^- \qquad (1)$$
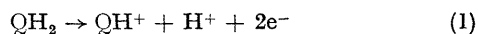
Cyclic voltammograms of QH_2 [Figure, (a)] show one irreversible two-electron oxidation wave (I) followed by one irreversible two-electron reduction wave (II) on the cathodic sweep. The number of electrons involved in each wave was determined by double potential step chronoamperometry[3]. With increasing sweep rate the current functions (i peak/ $Acv^{\frac{1}{2}}$: A = electrode area, c = concentration, v = sweep rate) for waves (I) and (II) decrease and a new wave (III) appears as shown in the Figure, (a)—(c). Similar behaviour is observed for 2,5-dimethyl- and 2,3,5,6-tetramethyl-hydro-quinones except that wave (III) appears at more negative potentials and slower sweep rates. Peak potentials for waves (I)—(III) are given in the Table.

Waves (volts vs. *S.C.E.)*

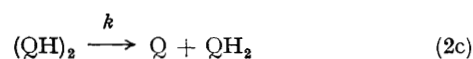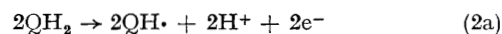| Compound	(I)[a]	(II)[a]	(III)	Q reduction
Benzohydroquinone	$+1 \cdot 12$	$+0 \cdot 13$	$-0 \cdot 34^{b}$	$-0 \cdot 56^{b}$
2,5-Dimethylhydroquinone	$+0 \cdot 99$	$+0 \cdot 10$	$-0 \cdot 59^{c}$	$-0 \cdot 54^{c}$
2,3,5,6-Tetramethyl-hydroquinone	$+0 \cdot 83$	$-0 \cdot 04$	$-0 \cdot 83^{b}$	$-0 \cdot 69^{b}$
Quinhydrone			$-0 \cdot 35^{b}$	
H^+ ($HClO_4$)			$-0 \cdot 54^{b}$	

Sweep rates: [a] 2 v/sec., [b] 20 v/sec., [c] 60 v/sec.
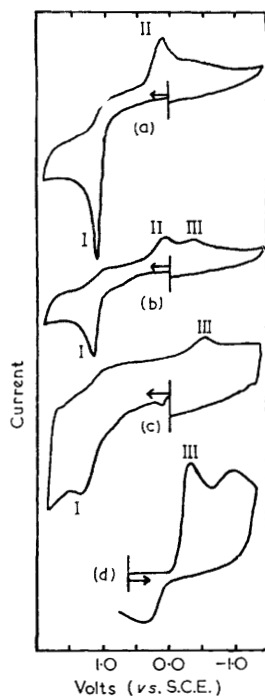
FIGURE

Cyclic voltammograms of hydroquinone (2·1 × 10⁻³ M in MeCN *with* 0·1 M-*tetraethylammonium perchlorate*) (a—c) *and quinhydrone* (d) (*see text*) *in the same solution. Sweep rates*: (a) 2·02 v/sec., (b) 20·2 v/sec., (c) 2020 v/sec., (d) 19·1 v/sec.

Wave (II) can be assigned to reduction of QH^+, as reduction of a 2:1 mixture of perchloric acid to quinone (Q) gave a cyclic voltammogram identical with that in the Figure, (a).

Wave (III) is assigned to the reduction of quinhydrone on the following grounds: (*a*) the cyclic voltammogram of quinhydrone in equilibrium with 10^{-2}M-Q and an excess of QH_2 gave a wave, (d) in the Figure, with properties similar to wave (III) (quinhydrone has a formation constant in acetonitrile of 0·083 ± 0·004 l.mole⁻¹; *cf.* ref. 4); and (*b*) other possible intermediates do not explain all the properties of wave (III); H⁺ waves would not vary with the nature of the hydroquinone, semiquinone ($QH\cdot$) would be too short lived, $QH_2^{\ddagger}$ would be reduced at a more positive potential, and waves (III) do not match quinone reduction potentials.

We suggest the following oxidation scheme for hydroquinone [wave (I)]:

$$2QH_2 \rightarrow 2QH\cdot + 2H^+ + 2e^- \qquad (2a)$$

$$2QH\cdot \rightarrow (QH)_2 \qquad (2b)$$

$$(QH)_2 \xrightarrow{k} Q + QH_2 \qquad (2c)$$

$$Q + H^+ \rightarrow QH^+ \qquad (2d)$$

The slow process which permits the observation of the dimer wave is step (2c); dissociation of the dimer. This mechanism does not attempt to distinguish between homogeneous and heterogeneous coupled chemical reactions.

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[2] K. J. Vetter, "Electrochemical Kinetics", Academic Press, New York, 1967, p. 483; J. M. Hale and R. Parsons, *Trans. Faraday Soc.*, 1963, **59**, 1429; P. H. Given and M. E. Peover, *J. Chem. Soc.*, 1960, 385; M. E. Peover, *ibid.*, 1962, 4540.
[3] T. Kanbara, *Bull. Chem. Soc., Japan*, 1954, **69**, 30.
[4] R. E. Moser and H. G. Cassidy, *J. Amer. Chem. Soc.*, 1965, **87**, 3463.