On the Anodic Oxidation of Hydroquinone in Acetonitrile

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Summary Rotating-disc electrode voltammetry provides evidence for a two-electron oxidation of hydroquinone in acetonitrile.

THE suggestion[1] from this laboratory that the complexity of the hydroquinone–quinone redox behaviour in acetonitrile could be explained by protonation effects without invoking the one-electron dimerisation scheme[2] has been questioned by Eggins.[3] Eggins[3] correctly pointed out that lithium perchlorate is not a suitable supporting electrolyte to be used in comparisons of reduction behaviour of quinones, due to the occurrence of ion pairing when lithium ion is used.[4] However, the oxidation behaviour of hydroquinone is independent of the supporting electrolyte.

We now present evidence that the dimerisation scheme[2,3] is not correct. A rotating-disc electrode (RDE) study of the anodic oxidation of hydroquinone in acetonitrile in the presence and absence of 2,6-lutidine using several different supporting electrolytes, shows that under all conditions studied the anodic oxidation in acetonitrile occurs by a two-electron process. The quantity, $i_L/\omega^{1/2}C$ (where i_L is the limiting current in μA and ω is the angular rotation of the electrode in radians/sec and C is the concentration), is constant with a value close to 30 in every case (see Table).

RDE data for the anodic oxidation of hydroquinone in acetonitrile[a]

	$i_L/\omega^{1/2}C$			
$(\omega^{1/2})$[b]	($LiClO_4$)	(Bu_4NClO_4)	(Bu_4NBF_4)	(Bu_4NClO_4)[c]
2·5	29·4	30·8	30·8	30·4
5·0	29·0	30·4	30·4	30·4
7·5	28·7	30·2	30·8	30·1
10·0	28·2	29·8	30·0	30·0
12·5	28·2	29·8	29·9	30·0
15·0	28·2	29·6	29·9	29·6
17·5	28·2	29·6	30·0	29·6
20·0	28·1	29·8	30·0	29·7
22·5	28·0	29·5	29·7	29·6

[a] Substrate concentration = 1·0 mM, supporting electrolyte concentration = 0·1 M.

[b] Data obtained at a Beckman RDE.

[c] Solution contained 2,6-lutidine (10 mM).

Under the same conditions, two compounds which undergo one-electron oxidation to give stable cation-radicals, 9,10-diphenylanthracene and thianthrene, exhibited constant $i_L/\omega^{1/2}C$ values of 12·2 and 15·5, respectively. When rapid chemical reactions are coupled between the electron transfers for a two-electron oxidation process, at low rotation rates $i_L/\omega^{1/2}C$ corresponds to the transfer of two electrons and if the chemical reaction can be "outrun" in the range of accessible rotation rates, one-electron behaviour will be observed at higher rotation rates.[5] The range of rotation rates used was such that coupled chemical reactions having rate constants ranging from 0 to 1000 sec^{-1} would have readily been detected. The constant values observed for $i_L/\omega^{1/2}C$ corresponding to a two-electron process show that there are no detectable complications prior to or between the two charge-transfer steps.

The voltage sweep rates necessary to detect the transient intermediate during the oxidation of hydroquinone[2] predicts a rate constant for the chemical step well within the range detectable by RDE voltammetry. In fact, the cyclic voltammetric data has been interpreted in terms of formation of a one-electron oxidation product, a quinone hemiacetal, which has a half-life of about 0·1 sec.[6] In the presence of 2,6-lutidine[1] or pyridine,[6] the reduction wave assigned[2,3] to this intermediate can be detected at slow sweep rates. The latter observation has been interpreted[6] to indicate that the quinone hemiacetal is stable under the more basic conditions. If this interpretation is correct, the RDE behaviour in the absence of the base would be two-electron at low rotation and approach one-electron behaviour at high rotation rates. In the presence of the base, one-electron behaviour would be expected at all rotation rates. Since two-electron behaviour was observed at the RDE under all conditions, we conclude that the reduction peak observed[2] and interpreted as reduction of one-electron oxidation products, quinhydrone[2] or a quinone hemiacetal,[3,6] is due to some form of quinone as previously suggested.[1] Our data do not distinguish between possible ECE and EEC mechanisms for the generation of the two-electron oxidation product if the chemical step, deprotonation, is extremely rapid.

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