Evidence for a One-electron Intermediate in the Anodic Oxidation of Hydroquinone in Acetonitrile

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Summary The oxidation of hydroquinone at rotating-disc electrodes clearly indicates a one-electron, not a two-electron, process when the diffusion coefficients of the species compared are taken into account.

In our previous work we have presented cyclic voltammetric evidence for two-electron oxidation of hydroquinone(QH_2) in acetonitrile at long times, but involving a one-electron intermediate detectable at short times.[1] Parker and Eberson[2] dispute the existence of the one-electron intermediate on the evidence of a rotating-disc electrode (RDE) study. They[2] measured the function $i_L/\omega^{\frac{1}{2}}C$ (where i_L is the limiting current in μA, ω is the angular rotation of the electron in radians/s, and C is the concentration) which for their electrode (area 0·2 cm^2 [3]) gave values between 28 and 30. These values are compared with $i_L/\omega^{\frac{1}{2}}C$ values of 12·2 and 15·5 for 9,10-diphenylanthracene and thianthrene, respectively, both of which are known to undergo one-electron oxidations to give cation radicals.

However, the complete Levich equation[4] is $i_L/\omega^{\frac{1}{2}}C = 0{\cdot}62\, nFAD^{\frac{2}{3}}\nu^{-\frac{1}{6}}$ where A is the area of the electrode in cm^2, D is the diffusion coefficient of the electro-active species in cm^2 s^{-1}, and ν is the kinematic viscosity of the solution (viscosity ÷ density) in cm^2 s^{-1}. If one substitutes the appropriate values for QH_2 in acetonitrile into this equation, using $i_L/\omega^{\frac{1}{2}}C = 30$; $A = 0{\cdot}2$ cm^2,[3] $\nu = 0{\cdot}00360$poise $\div\ 0{\cdot}7828$ gm/cm^3;[5] $D = 3{\cdot}16 \times 10^{-5}$ cm^2 s^{-1},[1c] one obtains a value for n of 1·02.

The explanation for the discrepancy between this value and that indicated by Parker and Eberson[2] lies in their neglect of differences in D values, which are inversely related to the sizes of the molecules. We have determined the D values for 9,10-diphenylanthracene ($8{\cdot}18 \pm 0{\cdot}04 \times 10^{-6}$ cm^2 s^{-1}) and for thianthrene ($1{\cdot}31 \pm 0{\cdot}01 \times 10^{-5}$ cm^2 s^{-1}) by chronoamperometry[6] at a stationary platinum electrode ($A = 0{\cdot}351$ cm^2) at 1·3 and 1·4 V *vs.* aqueous S.C.E., respectively.

As a check we oxidised QH_2 and 9,10-diphenylanthracene at a Beckman RDE ($A = 0{\cdot}331$ cm^2) in acetonitrile containing 0·1 M-tetra-n-butylammonium perchlorate at a range of rotation rates. The results obtained for $i_L/\omega^{\frac{1}{2}}CA$ agreed with those of Parker and Eberson.[2,3]

Using these results[2] plus the D values obtained, the ratios of $i_L/\omega^{\frac{1}{2}}CD^{\frac{2}{3}}$ for QH_2 to those for 9,10-diphenylanthracene and thianthrene are found to be 0·99(8):1 and 1·08:1, respectively. Thus the oxidation process observed is clearly one-electron. This gives further support to our suggested mechanism.[1] This work was supported by a grant from the S.R.C.

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