Inverted and Amplified Waves in Cyclic Voltammograms of [PtH(PEt₃)₃]⁺; Catalytic Production of Hydrogen at a Mercury Electrode

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Cyclic voltammograms of solutions of $[PtH(PEt_3)_3]^+$ in phosphate buffer (pH 6.88) at mercury electrodes show large reduction waves on all forward and reverse scans except the first negative scan, which are interpreted in terms of catalytical hydrogen production; sustained hydrogen production occurs at -1.7 V vs. standard calomel electrode after initiation.

We have recently shown[1] that $[MH(PEt_3)_3]^+$ (M = Pt or Pd) produces hydrogen and $[M(PEt_3)_3]$, on reduction in non-aqueous solvents, but that hydrogen is not produced on irradiation of solutions containing $[Ru(bipy)_3]^{2+}$, $[MH(PEt_3)_3]^+$, and ethylenediaminetetra-acetic acid (bipy = 2,2′-bipyridyl). Since this failure to produce hydrogen photochemically probably arises because $[Ru(bipy)_3]^{2+*}$ is an insufficiently strong reducing agent to reduce $[MH(PEt_3)_3]^+$ we have carried out cyclic voltammetric studies on $[PtH(PEt_3)_3]^+$.

Cyclic voltammograms for $[PtH(PEt_3)_3]^+$ (1.5×10^{-4} mol dm⁻³ in 0.5 mol dm⁻³ phosphate buffer, pH 6.88) at a mercury drop electrode are shown in Figure 1. In the first negative scan (1), very small reduction features, A and B, are observed before breakdown of the solvent. Since reversing the scan before wave B gives subsequent scans containing waves C and D, wave B will not be considered further. On all subsequent positive (2 and 4) and negative scans (3) large *reduction* waves, C and D, are observed. Hydrogen gas can be observed to evolve during passage of waves C and D.

Inverted waves have been described before[2—4] and have usually been attributed to formation of adsorbed species or amalgams. However, Ginsburg[5] has suggested that all distorted or inverted waves can be attributed to oscillation of the mercury drop. Clearly this cannot be the case in the recently reported oxidations of methanol, formaldehyde, and formic acid on platinum,[6,7] and we do not believe it to be the case for $[PtH(PEt_3)_3]^+$ since identical voltammograms are observed using a mercurised copper wire electrode, which has been shown[8] to be quantitatively equivalent to a mercury drop. It could be argued that the suspended wire might accumulate a mercury drop (or at least thickening of the layer) at the bottom and that oscillation of this may account for the observed inverted waves, but we can rule this out as doubling the length of wire electrode in the solution doubles the height of the waves. We therefore offer the following chemical explanation of what occurs.

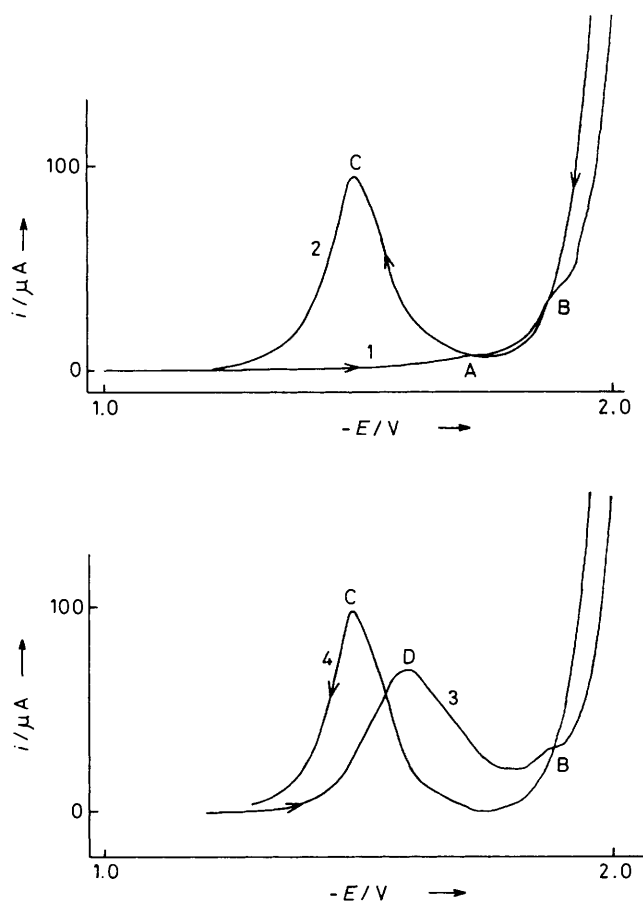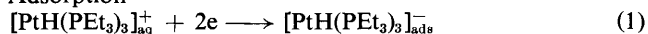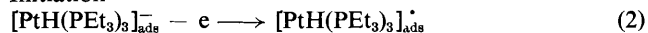The species generated during passage of wave A cannot be

Figure 1. Cyclic voltammograms of $[PtH(PEt_3)_3]^+$ at a mercury drop electrode. 1 and 2 first scan; 3 and 4 second and subsequent scans. For peak assignments, see text. Scan rate 100 mV s⁻¹; potentials vs. standard calomel electrode.
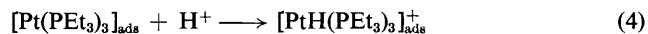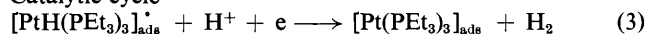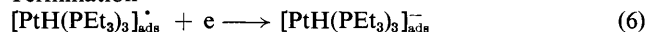
Adsorption
$$[PtH(PEt_3)_3]^+_{aq} + 2e \longrightarrow [PtH(PEt_3)_3]^-_{ads} \qquad (1)$$

Initiation
$$[PtH(PEt_3)_3]^-_{ads} - e \longrightarrow [PtH(PEt_3)_3]^{\cdot}_{ads} \qquad (2)$$

Catalytic cycle
$$[PtH(PEt_3)_3]^{\cdot}_{ads} + H^+ + e \longrightarrow [Pt(PEt_3)_3]_{ads} + H_2 \qquad (3)$$

$$[Pt(PEt_3)_3]_{ads} + H^+ \longrightarrow [PtH(PEt_3)_3]^+_{ads} \qquad (4)$$

$$[PtH(PEt_3)_3]^+_{ads} + e \longrightarrow [PtH(PEt_3)_3]^{\cdot}_{ads} \qquad (5)$$

Termination
$$[PtH(PEt_3)_3]^{\cdot}_{ads} + e \longrightarrow [PtH(PEt_3)_3]^-_{ads} \qquad (6)$$

Scheme 1

present in the catalytic cycle which is responsible for hydrogen production and for waves C and D; however, it is clear that adsorption must occur, probably of the species produced during wave A since the area of waves C and D is essentially constant over a wide range of concentrations of $[PtH(PEt_3)_3]^+$. We propose that wave A corresponds to the two-electron reduction of $[PtH(PEt_3)_3]^+$ to give $[PtH(PEt_3)_3]^-_{ads}$ [equation (1) in Scheme 1].† This anionic species remains on the surface until on the first positive scan the catalytic reductive cycle represented by equations (3)—(5) is initiated by the one-electron oxidation of $[PtH(PEt_3)_3]^-_{ads}$ [equation (2)]. The cycle ceases when the potential becomes insufficiently negative for one of the reductive processes [equations (3) or (5)] to occur, but recommences on the next negative scan once the potential is again sufficiently negative to drive both reductions. Finally, termination of the catalytic cycle occurs on the negative scan once the potential is sufficiently negative for reduction of $[PtH(PEt_3)_3]^{\cdot}_{ads}$ to $[PtH(PEt_3)_3]^-_{ads}$ to occur [equation (6)].

Two important features are implicit in the reaction scheme. Firstly, the species $[PtH(PEt_3)_3]^+_{ads}$ is not equilibrated with

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† The area of this peak (measured from voltammograms of more concentrated solutions, where it is sharper) is consistent with a 2 e reduction producing a monolayer of adsorbed $[PtH(PEt_3)_3]^-$.

the solution species at potentials less negative than that necessary for reac ion (1) to occur. Secondly, it is apparent that $[PtH(PEt_3)_3]_{ads}$ can exist at potentials less negative than that necessary for the reduction of $[PtH(PEt_3)_3]^+_{aq}$. That $[PtH(PEt_3)_3]^{\cdot}_{ads}$ survives here without further oxidation implies electrochemical irreversibility in the reduction of $[PtH(PEt_3)_3]^+_{aq}$ and/or the oxidation of $[PtH(PEt_3)_3]^{\cdot}_{ads}$. We have evidence[9] that at > -1.2 V the major species on the surface is derived from $[PtH(PEt_3)_3]^{\cdot}_{ads}$.

By scanning to -1.9 V and then returning to -1.7 V it is possible to observe sustained catalytic hydrogen production [both visibly (bubbles) and by monitoring current flow]. This will proceed for at least 16 h at a catalytic turnover rate of *ca.* 2×10^5 h^{-1}, testifying to the efficiency of the catalytic process.

Variations of the shapes, intensities, and positions of the catalytic waves with scan rate and concentration of [PtH(PEt_3)_3]$^+$ are the subject of continuing studies but appear to arise from adsorption–desorption phenomena.

References

1 R. F. Jones, J. R. Fisher, and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1981, 2550.
2 P. Margaretha and P. Tissot, *J. Electroanal. Chem.*, 1979, **99**, 127.
3 E. A. H. Hall and L. Horner, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 1145.
4 D. A. Tysee, *J. Electroanal. Chem.*, 1971, **30**, 14.
5 G. Ginsburg, J. Y. Becker, and E. Lederman, *Electrochim. Acta*, 1981, **26**, 851.
6 B. Beden, F. Kadirgon, C. Lamy, and J. M. Leger, *J. Electroanal. Chem.*, 1983, **142**, 171.
7 R. R. Adzic, A. V. Tripkovic, and W. E. O'Grady, *Nature*, 1982, **296**, 137.
8 P. J. Daly, D. J. Page, and R. G. Compton, *Anal. Chem.*, in the press.
9 J. R. Fisher, G. R. Sealy, R. G. Compton, and D. J. Cole-Hamilton, unpublished results.