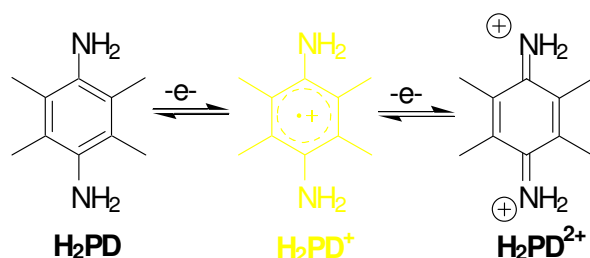


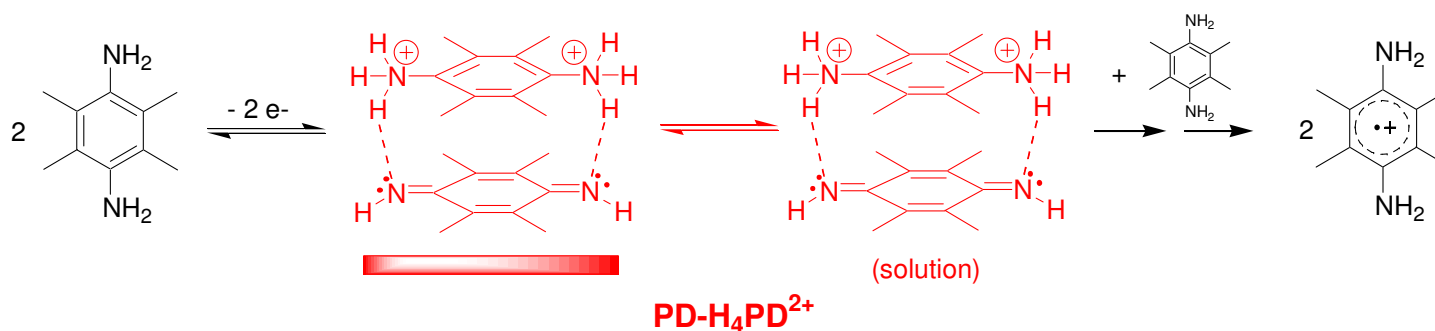
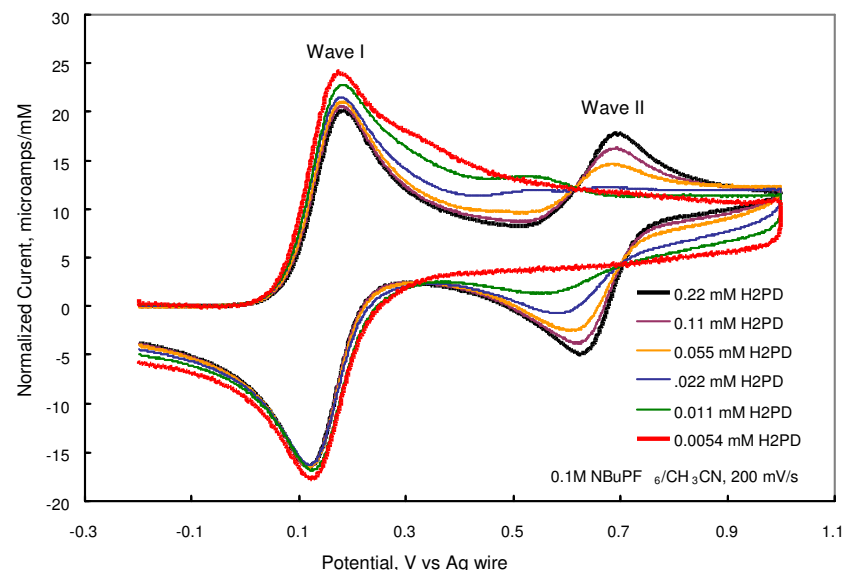
Electrochemical Studies on the Effect of H-Bonding and Proton Transfer on the Electron Transfer Reactions of Organic Redox Couples

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THE MYSTERY OF THE MISSING RADICAL CATION



Oxidation of H₂PD in aprotic solvents is expected to occur in two 1 e⁻ steps, giving two CV waves of equal height....but wave II is already too small at mM concentrations (black curve)....and disappears entirely at μM concentrations (red curve). Spectro-electrochemistry shows wave II is clearly due to oxidation of dissolved radical cation H₂PD^{•+}.....so, no wave II means no radical cation....where did it go?



The best explanation that is consistent with all our data so far is that it is locked up in the form of the H-bonded, pi dimer, PD-H₄PD²⁺ that is formed on the electrode surface upon H⁺ and e⁻ exchange between 2 radicals. The dimer is thermodynamically stable at the effective high concentration of a monolayer, but gradually reverts back to the radical cation in solution. This reaction is catalyzed by reaction with bulk H₂PD, which explains why wave II is relatively larger at slower scan rates [more time for decomposition] and higher H₂PD concentration [faster decomposition rate].