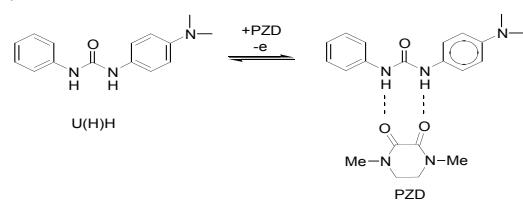


## Solvent Effects on the Oxidation of Electroactive Ureas

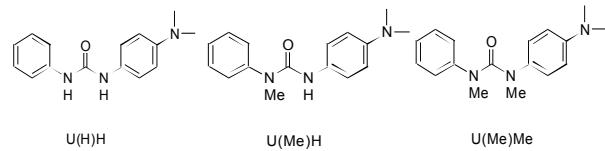
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In previous work done by our group, we reported the observation of strong oxidation-based redox dependent hydrogen bonding between an electroactive urea 1-phenyl-3-(p-N,N-dimethylaminophenyl)urea U(H)H and a cyclic diamide 1,4-dimethylpiperazine-2,3-dione (PZD) in methylene chloride.<sup>1</sup> Large negative shifts in the apparent, reversible one electron oxidation of U(H)H are observed upon addition of PZD, consistent with strong H-bonding of PZD to the radical cation of U(H)H as shown below:



However, with further study of molecules similar to U(H)H, it is clear that the electrochemistry and the mechanism is not as simple as once believed. Instead of undergoing a simple one electron oxidation, a variety of data now suggests that U(H)H actually undergoes a two electron oxidation to the quinoidal form with transfer of a proton to another U(H)H, which deactivates the second U(H)H. Thus the overall process corresponds to one electron per urea. This study is aimed to further investigate the structural and solvent effects on the oxidation mechanism of similar ureas in order to further understand the electron transfer, proton transfer, and hydrogen bonding steps involved. Besides methylene chloride, a more polar aprotic solvent, acetonitrile, is used. In contrast to the behavior observed in methylene chloride, both U(H)H and U(Me)H show irreversible behavior in acetonitrile, with a reduction peak observed on the return scan at a potential significantly more negative than the oxidation. This is to be expected for reduction of the quinoidal form. Because acetonitrile is more polar than methylene chloride, it can better solvate the quinoidal urea and the protonated, unoxidized urea to prevent them from hydrogen bonding to each other. In contrast, stronger H-bonding between the quinoidal urea and the protonated, unoxidized urea is expected in methylene chloride and we believe this is what facilitates the observed reversible electrochemistry.



1. Jessica E. Woods, Yu Ge, and Diane K. Smith, *Journal of the American Chemical Society* **2008** *130* (31), 10070-10071.