The Wedge Scheme, a General Framework for Incorporating H-Bonding into Proton-coupled Electron Transfer Reaction Mechanisms

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There is a growing awareness of the important role that H-bond complexes can play in complex electron transfer mechanisms. One of the reasons for this is the current interest in the mechanism of proton-coupled electron transfer (PCET) reactions. This arises both because of the importance of PCET in biological electron transfer, but also because these reactions are central to non-thermal, fuel-consuming and producing reactions, such as those involved in fuel cells or envisioned for artificial photosynthesis. Until relatively recently it had been thought that PCET reactions always proceeded step-wise with sequential electron and proton transfer. Much of the recent fundamental interest in PCET stems from the realization that a third option is available, concerted electron and proton transfer in which the electron and proton both move in a single kinetic step. This focus on the concerted process has increased awareness of the importance of H-bonding states in PCET, since the concerted reaction occurs within a H-bonded intermediate. However, even if the proton and electron transfer is not concerted, the H-bonded complex formed in the process of proton transfer can play an important role in the PCET mechanism if it is sufficiently long-lived.

In this paper we introduce a generally useful mechanistic framework with which to include H-bonding steps within an overall PCET pathway. The development of this scheme, which for obvious reasons we call a "wedge", is outlined in Scheme 1 for the generic 1e$^-$, 1H$^+$ oxidation, $AH + B = A + HB^+ + e^-$. Such reactions are commonly described by square schemes, such as that shown in Scheme 1a, with the two possible electron transfer reactions shown on the horizontal axes and the two possible proton transfer reactions shown on the vertical axes. The *overall* concerted reaction is indicated by the diagonal. The utility of this presentation is that it clearly defines the thermodynamic relationship between the five reactions. However, while the diagonal shown in Scheme 1a indicates the overall concerted process, in fact, as noted above, the actual concerted transfer occurs through a H-bond intermediate, as do the proton transfer reactions. Therefore a more complete representation of the pathways requires another dimension to represent the H-bonding steps. This leads to the cube scheme shown in Scheme 1b. The back square represents the electron and proton transfer reactions within the H-bonding complex and thus the diagonal here would represent the true concerted step, the E° of which is affected by the magnitudes of the K's for the H-bonding reactions and, unless they are all equal (unlikely), will not be the same as the E° for the overall concerted reaction.

While the cube scheme provides a complete description of the intermediates (assuming only 1:1 H-bonding is important), from a kinetic, mechanistic point of view, it is also likely needlessly complex, since all the reactions in the back panel are unimolecular. If the proton transfers within the H-bonded complex are at

equilibrium, then the overall square behaves like a simple 1 e$^-$ transfer with an apparent E° that depends on the two component E° values, and the two K's. It seems safe to assume that the proton transfers will be at equilibrium within a H-bond complex and thus, for kinetic evaluation of the mechanism, the back square can be replaced by a single electron transfer, giving the "wedge" scheme shown in Scheme 1c.

Scheme 1

(A) The Square Scheme

(B) The Cube Scheme
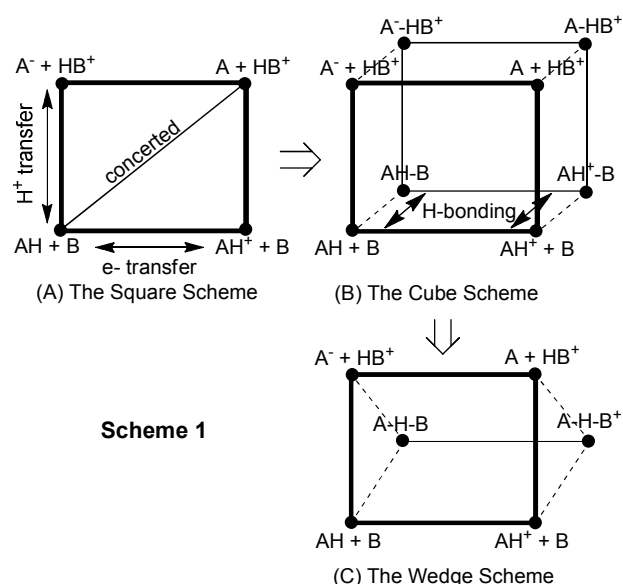
(C) The Wedge Scheme

The usefulness of the wedge scheme will be illustrated by showing its utility in explaining the voltammetric behavior of the electroactive urea U(H)H. In the presence of a suitable base B (which may be the dimethylamino group on another unoxidized urea) U(H)H undergoes an overall -2 e$^-$/-1 H$^+$ transformation to give the quinoidal cation as shown below:
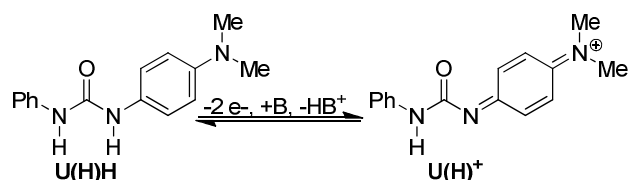
The reversibility of this reaction is strongly solvent dependent, being more reversible in less polar solvents. This and other evidence strongly suggests a H-bonded complex between U(H)$^+$ and HB$^+$ plays an important role in the mechanism. Simulations show that the observed voltammetric behavior can be quantitatively accounted for using the proposed wedge scheme.