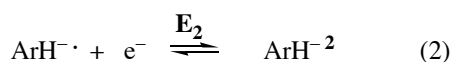
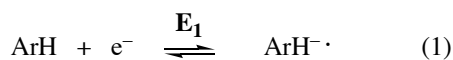


Ion Pair Formation Between Organic Cations and Nitrobenzene and Nitrosobenzene Redox Species and its Effects upon Voltammetric Behavior

Albert J. Fry

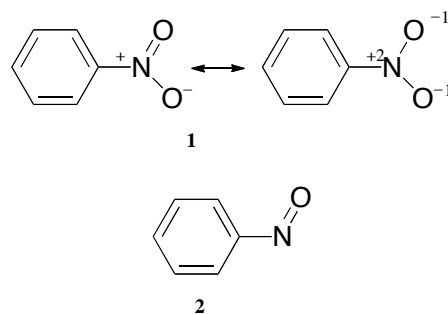
Chemistry Department, Wesleyan University
Middletown, Connecticut, 06459, U.S.A.

It has been known for many years that the voltammetric behavior of polycyclic aromatic hydrocarbons (PAHs) in aprotic solvents is dependent upon the nature of the supporting electrolyte.^{1,2} We have shown that this is due to ion pairing of the PAH dianion to the cation of the supporting electrolyte, which has the effect of moving the second voltammetric wave to more positive potentials.³ That is, one cannot describe the system simply by equations 1 and 2 in Scheme 1; one must include the effect of ion-pair association between the cation of the electrolyte and the dianion of the PAH (Equation 3). We have shown that the ion-pairing association constant K_{assoc} between the two species can be computed to excellent accuracy by a density functional theory (DFT) quantum chemical technique and that the cyclic voltammogram of several PAHs in the presence of several tetraalkylammonium ions can be simulated⁴ very closely when the computed K_{assoc} for each particular cation is included in the simulation.^{5,6}



Scheme 1

We have now examined a more challenging situation, the ion pairing of tetraalkylammonium cations to nitrobenzene (**1**) mono- and di-anions, which should form stronger ion pairs than PAH's because the negative charge should be localized on the nitro group instead of being spread over a large ring as it is in PAH dianions. It is also well established that nitrosobenzene (**2**) is an intermediate in nitrobenzene because it is produced at the second 1-electron reductive wave of **1** and is easier to reduce than **1**.⁷ Because the charge will be localized on a single oxygen atom in the anions, it would be expected that nitrosobenzene anions should form even stronger ion pairs than those from nitrobenzene. Computations confirm this expectation. This should result in significant shifts of the second voltammetric waves of these compounds from their intrinsic position in the absence of ion-pairing.



The computations show that the anion radicals from **1** and **2** should also form ion pairs with tetraalkylammonium ions, though not as strongly as the corresponding dianions. We will discuss the effects on the voltammetry expected **1** and **2**, including whether digital simulation of their voltammograms should include further terms, including additional equations analogous to Equation 4, to account for ion-pairing to the neutral compounds and to the anion radical(s).

References

1. Fry, A. J.; Hutchins, C. S.; Chung, L. L. *J. Am. Chem. Soc.* **1975**, *97*, 591.
2. Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.
3. Fry, A. J. *Electrochem. Commun.* **2005**, *7*, 602
4. Rudolph, M.; Reddy, D. P.; Feldberg, S. W., *DigiSim 3.0, Bioanalytical Systems, West Lafayette, IN.*
5. Fry, A. J. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14775.
6. Fry, A. J. *Tetrahedron* **2006**, *62*, 6558.
7. Fry, A.J. in "The Chemistry of Nitro and Azo Compounds," S. Patai, ed., Wiley-Interscience, London, 1982.