THE FATE OF ELECTROCHEMICALLY GENERATED ARENE DIANIONS

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It has been known for many years that electrochemical reduction of a polycyclic aromatic hydrocarbon (PAH; **1**) in a dipolar aprotic solvent containing a tetraalkylammonium salt as electrolyte takes place in two 1-electron steps to afford in turn the corresponding radical anion 1^{-1} and dianion 1^{-2}, respectively. The radical anions are relatively stable and can readily be studied by *in situ* ESR techniques. The dianions are more reactive but are stable on the cyclic voltammetry (CV) time scale in rigorously purified solvents.[1] Yet, essentially nothing is known about the nature of these species in solution, and there are even problems with interpretation of the voltammetry itself. Low-level quantum chemical calculations many years ago indicated that the spacing (ΔEp) between the first and second voltammetric waves should be approximately 5V,[2] yet ΔEp is actually close to 0.5V for almost all PAH's in solvents such as DMF, DMSO, and acetonitrile.[2,3] It is generally agreed that this discrepancy lies in the fact that the calculations are essentially for the gas phase whereas in solution ion-pairing and perhaps solvation must be important. Furthermore, while ion pairing is almost certainly a significant factor, nothing is known about the actual structure of the ion pairs of PAH dianions with organic cations. In the present study high-level *ab initio* quantum chemical computations have been shown to shed considerable light for the first time upon both the reported ΔEp discrepancy and the structure of arene dianion ion-pairs. Computations have also demonstrated that some dianions react with the counterion and that the nature of the reaction depends upon the structure of both the dianion and the cation.

Computations. Several aromatic species were examined, including anthracene, pyrene, chrysene, and 1,2-, 1,3-, and 1,4-dinitrobenzene. The reduction of anthracene to its radical anion and dianion was the prototype for these calculations. The energy of each of the three species was computed (with full geometry optimization for each) by density functional theory (DFT) using the B3LYP functional and the large 6-311+G* basis set, which includes diffuse orbitals and polarization functions on the first-row (carbon) atoms. [This level of computation has been shown to give highly reliable structures and energies for aromatic species.[4]] The optimized structures were corrected for zero-point energies and thermal corrections to 298 °K were computed by frequency calculations on the optimized structures. The computations, including geometry optimization) were then repeated, including computation of solvation energies (in acetonitrile) using the SCF-polarized continuum model (SCF-PCM), which has been shown to afford solvation energies with an accuracy of about 2 kcal/mol, or 0.1 eV.[5] Energies of several organic cations, including both tetraalkylammonium and substituted imidazolium ions, were computed, as were the energies and structures of the resulting adducts, both in the absence and presence of solvent. The differences between the two calculations correspond to the solvation energy of each species.

These computations have lead to a number of conclusions:

1. Surprisingly, solvation is much more important than ion pairing in stabilizing arene dianions. For example, SCF-PCM solvation energies for anthracene, anthracene radical anion, and anthracene dianion are 8, 47, and 163 kcal/mole respectively. Solvation in itself is important enough to reduce ΔEp from 4.22 V in the gas phase to about 1 V.

2. The geometry of ion pairing of these species has been established for the first time. In tetraalkylammonium ion-arene dianion ion pairs, the cation is located above the center of the arene plane. In the 1,2,3-trimethylimidazolium ion-arene dianion ion pair, the two species lie in parallel planes.

3. Me_4N^+ ion acts as an acid toward anthracene and tetracene dianions but not toward pyrene dianion. The difference seems to be due to high degree of charge localization, i.e., higher basicity, in the anthracene and tetracene species. Proton transfer does not take place between anthracene dianion and Et_4N^+ ion, nor between anthracene radical anion and Me_4N^+ ion. These differences have been clarified by thermochemical calculations. On the other hand, 1,3-dimethylimidazolium ion, in which C-2 is relatively acidic, undergoes proton transfer with a wide range of arene species. Interestingly, in the resulting ion pairs the resulting two species do not lie in parallel planes; in fact, they are perpendicular.

4. The previously reported[6] strong ion pairing between 1,4-dinitrobenzene dianion and 1,3-dimethylimidazolium ion is actually a proton-transfer process, requiring reinterpretation of the cyclic voltammetric results. It is concluded that proton transfer between the imidazolium ion and dianion is fast and irreversible on the cyclic voltammetric time scale. 1,3-dinitrobenzene dianion does not undergo transfer but instead forms an ion-pair of unusual structure with the same imidazolium ion. 1,2-dinitrobenzene dianion is found to chemically bind to 1,3-dimethylimidazolium ion.

Summary. High level quantum chemical calculations have afforded a great deal of information about the interaction between organic cations and organic dianions, permitting a better understanding of the processes which accompany electrochemical reduction of organic species to dianions.

References

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