

A computational study of solution effects on the disproportionation of electrochemically generated polycyclic aromatic hydrocarbon radical anions. Thermodynamics and structure

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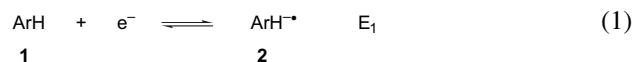
Abstract—Density functional quantum chemical methods are used to predict the thermodynamics of disproportionation of electrochemically generated polycyclic aromatic hydrocarbon radical anions (**2**) into the corresponding neutral species (**1**) and dianions (**3**). The computations reveal the overwhelming influence of solvation effects upon the disproportionation equilibrium. By comparison, the effect of ion pairing between **3** and the cation of the supporting electrolyte (R_4N^+) is modest but real. The computational results can be combined with a variety of entropy effects to calculate the spacing ΔE between the first and second reduction potentials of **1** within 100–150 mV. The highly asymmetric structures of the ion pairs between **3** and R_4N^+ show little evidence for steric hindrance to ion pairing, yet the computations do show that the strength of the ion pairs does appear to diminish with increasing size of the R group. The strength of the ion pairs with small cations appears to arise out of the large charge-to-size ratio in such cations.

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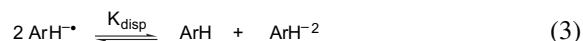
1. Introduction

The most fundamental process in electrochemical reduction of organic substrates, and indeed most reduction and oxidation processes in organic chemistry in general, is injection of an electron into the LUMO orbital of an organic substrate. For most substances, especially those containing heteroatoms, the initial electron transfer is quickly followed by a rapid chemical reaction, indeed often by a cascade of coupled chemical processes initiated by the electron transfer. This makes it quite difficult to study the nature and characteristics of the initial step itself. It has been recognized for many years that reductions of polycyclic aromatic hydrocarbons (PAH's) in aprotic media offer the best opportunity to study such processes: (a) PAH's contain no heteroatoms; (b) electron transfer to the PAH affords long-lived anion radicals, which can be studied by a variety of spectroscopic methods, and (c) a wide variety of PAH's are available, which permits, inter alia, studies of the correlation of redox potentials and electrochemical reactivity with structure.¹ Many such substances also undergo further addition of a second electron at more negative potential to afford a dianion. Dianions are much more reactive toward trace electrophilic impurities in the solvent than the corresponding radical anions, but reversible behavior can be observed in highly

purified media,^{2–5} permitting acquisition of thermodynamically valid data. A particularly significant property of the PAH in such media is the difference in ΔE (in volts) between the first and second reduction potentials (E_1 and E_2 , respectively) of the hydrocarbon. It is readily shown that ΔE is a measure of K_{disp} , the equilibrium constant for disproportionation of the arene radical anion (**2**) into the neutral (**1**) and dianion (**3**) species (Scheme 1). The three species are interrelated via the disproportionation equilibrium (Eq. 3); thus, the study of processes involving the dianion can be used to obtain information about the properties of the radical anion itself. Ion pairing can be accommodated within this schema by incorporating an additional equation (Eq. 4) representing formation of the ion pair between the dianion and the cation of the supporting electrolyte (Scheme 2).



Subtracting Eq 1 from Eq 2, one has:

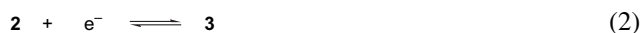


$$\Delta G_{\text{disp}} = -nF\Delta E = -nF(E_2 - E_1) = -RT \ln K_{\text{disp}}$$

Scheme 1.

Keywords: Radical anions; Ion pairing; Polycyclic aromatic hydrocarbons; Density functional computations; Electrochemically generated dianions.

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Scheme 2.

We pointed out a number of years ago that it ought to be possible to obtain an estimate of ΔE and thus, K_{disp} by computation of the energies of species 1–3.⁶ We found in fact, however, that estimates of ΔE using energies computed by a semi-empirical quantum mechanical method differed by almost an order of magnitude from the experimentally measured values; the theoretical values lie in the range of 4–5 V in contrast to the typical experimental values of 0.5–0.7 V.⁶ While appreciating that part of the discrepancy might have been due to the relatively primitive computational method available at that time, we suggested it to be much more likely that the principal contributors are solvation and ion pairing effects, which were not included in the computations. Because of the high degree of charge on the dianion 3, it should be stabilized substantially more than either 1 or 2 by these effects. Both effects would have the effect of displacing E_2 to more positive potentials and thus reducing ΔE to the experimental value. This interpretation is now generally accepted. Several laboratories have made further inroads into understanding the significance of the value of ΔE for several systems. Evans and Hu assumed a series of PAH's to be approximately spherical and estimated the spherical radius of each PAH.⁷ They then estimated the corresponding values of ΔG_{disp} from Born theory, considering the hydrocarbons simply as structureless chargeable spheres. Values of ΔG_{disp} for a series of PAH's calculated from the corresponding enthalpies of 1–3 by the AM1 semi-empirical method agreed closely with those calculated from Born theory, suggesting that (in vacuum) ΔE is 'almost entirely electrostatic in origin'.⁷ Kubota et al. reached similar conclusions, again using Born theory to estimate the solvation energies.⁸ Both groups were aware of the fact that ion pairing and solvation act in the same way upon ΔE . However, a problem arises when one wishes to dissect the discrepancy between theory and experiment further into the individual contributions of solvation and ion pairing. No experimental method can do so. Even the magnitude of this discrepancy is not known with certainty for *any* PAH because of the rather low accuracy of the semi-empirical methods that have been generally applied to this problem. Development of sufficiently fast computers in recent years has permitted the use of an ab initio theory with rather large basis sets in structure calculations even for molecules as large as these. This, together with the development of DFT (density functional) theory, which permits inclusion of electron correlation into the calculations at reasonable computational cost, has permitted the application of quantum chemical methods to relatively large molecular systems with excellent accuracy.⁹ In addition and of critical importance to studies such as these, the development of good methods for computing solvation energies within the ab initio framework permits the extension of computational methods to experimental situations in solution. The polarized continuum model (PCM), for example, though grounded in Born theory, discards the assumption of a molecule as a sphere (ill-founded in the case of PAH's)

in favor of a more realistic model consisting of a series of spheres centered on each nonhydrogen atom.¹⁰ We recently reported¹¹ a study in which ΔE 's for reduction of the PAH's anthracene (4) and perylene (5) in dimethylformamide (DMF) in the presence of tetraethylammonium ion were computed to surprisingly good accuracy (100–200 mV) by a DFT method, including estimation of solvation energies by the PCM procedure. The calculations showed that at least 98% of the difference between the computed (essentially gas phase) and experimental values of ΔE is due to differential solvation effects favoring the dianion 2. A corollary of this result is that ion pairing plays a very modest role in such systems. Still, it is known that ΔE is sensitive to the size of the electrolyte cation, suggesting that ion pairing does make a real contribution in these systems.^{2,6,12,13} A number of investigators, including our group, have found that the value of ΔE for any particular hydrocarbon depends on the nature of the cation of the supporting electrolyte.^{2,6} The data of Jensen and Parker for the reduction of 4 and 5 in the presence of a series of tetraalkylammonium ions illustrate the phenomenon clearly (Table 1).² A regular pattern can be noted in which ΔE is relatively large for Me_4N^+ ion, reaches a minimum for Et_4N^+ , and increases again as the size of R increases. The effect of increased ΔE for large tetraalkylammonium ions has been observed with hydrocarbons other than PAH's, including cyclooctatetraene⁶ and a series of 15,16-dialkyl-15,16-dihydropyrenes.^{14,15} The increase has been interpreted by all commentators on this effect as arising from steric hindrance to ion pairing of R_4N^+ to the hydrocarbon dianion (3) as R increases in size. It was not possible in our previous work to address the dependence of ΔE upon electrolyte size for electrolytes larger than tetraethylammonium because the calculations on ion pairing of cations larger than Et_4N^+ to large arene dianions such as 4 or 5 would have been impractical with our previous resources. However, recent acquisition of a multiprocessor parallel computer in this laboratory has now permitted an attack on such problems. We report herein the results of such a study. The present study has two aims: (a) to define more closely the thermodynamics, both enthalpy and entropy, of ion pairing and solvation interactions between the larger tetraalkylammonium ions and arene dianions and (b) to develop a clearer picture of the structure of such ion pairs through DFT computations. The computational results provide a number of new insights into the phenomena that operate in these systems.

Table 1. Experimental first and second voltammetric reduction potentials of some polycyclic aromatic hydrocarbons (0.001 M) in dimethylformamide solution containing various tetraalkylammonium supporting electrolytes (0.1 M)

Arene	Electrolyte cation	$-E_1$ (V) ^{a,b}	$-E_2$ (V) ^{a,b}	ΔE (V) ^c
4	Me_4N^+	1.920	2.650	0.730
4	Et_4N^+	1.915	2.585	0.670
4	Pr_4N^+	1.910	2.650	0.740
4	Bu_4N^+	1.905	2.655	0.750
5	Me_4N^+	1.620	2.230	0.610
5	Et_4N^+	1.635	2.180	0.545
5	Pr_4N^+	1.625	2.205	0.580
5	Bu_4N^+	1.610	2.205	0.595

^a Potential versus SCE.

^b See Ref. 2.

^c $\Delta E = -(E_2 - E_1)$.

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