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**I G8 C9 'CZ]W'cZGWYbW'fG7 kZ
6 Ug]W9 bYf[mGWYbW'g'f6 9 GL'fG7 !&&L**

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Effects of Electrolytes on Redox Potentials Through Ion Pairing

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Abstract

Reduction potentials have been determined for two molecules, benzophenone (BzPh) and perylene (Per), effectively in the complete absence of electrolyte as well as in the presence of three different supporting electrolytes in the moderately polar solvent THF. A description of how this can be so, and qualifications, are described in the discussion section. The primary tool in this work, pulse radiolysis, measures electron transfer (ET) equilibria in solution to obtain differences in redox potentials. Voltammetry measures redox potentials by establishing ET equilibria at electrodes, but electrolytes are needed for current flow. Results here show that without electrolyte the redox potentials were 100-451 mV more negative than those with 100 mM electrolyte. These changes depended both on the molecule and the electrolyte. In THF the dominant contributor to stabilization of radical anions by electrolyte was ion pairing. An equation was derived to give changes in redox potentials when electrolyte is added in terms of ion pair dissociation constants and activity coefficients. Definite values were determined for energetics, ΔG_d° , of ion pairing. Values of ΔG_d° for pairs with TBA⁺ give some doubt that it is a “weakly-coordinating cation.” Computations with DFT methods were moderately successful at describing the ion pairing energies.

I. Introduction

Redox potentials determined by voltammetric measurements are of tremendous value for determination of energetics of electron transfer in photochemistry, photosynthesis, dye-sensitized solar cells and organic photovoltaics, although none of those energy conversion systems contain the high concentration of electrolytes needed for the electrochemical measurements. We may ask: What is the effect of the electrolyte on the measured potentials? Several distinguished electrochemists have sought to use microelectrodes¹ to answer this question,^{2,3,4} but importantly in one of these Pendley and coworkers³ concluded that when the supporting electrolyte concentration is low shifts of $E_{1/2}$ may arise principally from ionic impurities, ohmic effects and migration of ions due to electric fields. None of these contribute to the sought after potentials. Similar conclusions come from theory of Smith and White⁵ and Amatore.^{4,6} They may thus not provide quantitative measurements of redox potentials that determine free energies of reduction or oxidation. Bao and coworkers⁷ measured half-wave potentials over a wide range of electrolyte concentrations. They applied a model using an effective dielectric constant. Here we seek to measure the free energy changes for converting neutrals to radical anions at high, low and zero concentrations of supporting electrolyte, applying techniques not used traditionally. Central to measurement of these thermodynamic redox potentials is understanding of ion pairing, so improving knowledge of ion pairing will be a goal of this work.

Ion pairing between positive and negative ions in solution was studied intensively about 50 years ago,⁸ but interest decreased partly because the field matured. Understanding of ion pairing will be essential to our goals here. It will also be key to improved voltammetry using electrolytes containing “weakly-coordinating anions” (WCAs) and cations, and for the goal, also somewhat elusive, of obtaining an internal standard redox couple having little dependence on solvent or electrolyte. Hill et. al.⁹ and Geiger et. al.^{10,11} showed how and why WCA electrolytes can improve cyclic voltammetry and related electrochemical methods. They noted that tetrabutylammonium (TBA⁺) behaves analogously to WCAs. A goal of the present work will be to learn how weakly coordinating TBA⁺ is. Knowledge of ion pairing received a boost from Fry who has shown insights into how ion pairing works using computational chemistry.¹² Guijarro¹³ noted the importance of pairing in understanding of lithium batteries. Both Guijarro¹³ and Wu¹⁴ applied DFT and Schwartz¹⁵ used simulation to develop computational pictures of ion pairing by alkali metal ions, highlighting the role of specific solvent molecules.

The method traditionally used to explore ion pairing, DC conductivity, has remained almost exclusively confined to the investigation of salts composed of two stable ions, like (TBA⁺,PF₆⁻), or a radical anion paired with an alkali metal cation like (Per^{•-},Na⁺). Experimental methods are not readily available to examine ion pairing of radical anions with tetrabutylammonium cations (TBA⁺) widely used in electrochemistry experiments along with other tetraalkylammonium cations, although very recently Mani has applied transient mid-IR detection with pulse radiolysis to characterize free nitrile radical anions and their pairs with TBA⁺.¹⁶

This work will begin by using pulse radiolysis to examine electron transfer in solution between radical anions of perylene (Per) and benzophenone (BzPh), which have similar reduction potentials, but distinct characters. Perylene forms a delocalized radical anion in which the electron is spread almost evenly over perylene’s twenty carbon atoms. In contrast, a large fraction of the negative charge in BzPh^{•-} is localized on the carbonyl. Pulse radiolysis enables measurement of the equilibrium between Per^{•-} and BzPh^{•-} free ions (eq 1), which favors Per^{•-}. Results reported below will show that addition of Na⁺ in eq 2 reverses the direction of the electron transfer reaction from that in (eq 1)

and changes its energetics by more than 300 meV. In the presence of tetrabutylammonium (TBA⁺), on the other hand, the energetics changes by only 113 meV, possibly supporting the idea the idea that TBA⁺ is a weakly-coordinating cation (WCC), which interacts weakly with all anions. Results described below will determine the presently unknown free energy changes for ion pairing, $\Delta G_d^\circ(\text{A}^{\bullet-}, \text{M}^+)$ for (BzPh^{•-},Na⁺), (BzPh^{•-},TBA⁺) and (Per^{•-},TBA⁺). The results along with that known for (Per^{•-},Na⁺) will support a different picture in which pairing with TBA⁺ stabilizes both anions strongly, but by different magnitudes.

Goals of this work will be to 1) demonstrate methods that can determine redox potentials in the absence of electrolyte, 2) gain insight into the nature of ion pairing and 3) examine the feasibility of a solvent-independent redox couple to serve as a standard.¹⁷ We further hope to 4) evaluate TBA⁺ as a non-coordinating cation, 5) determine dissociation constants for ion pairs of radical anions with TBA⁺, and 6) evaluate use of computational chemistry for estimates of ion pairing in a low-polarity solvent like THF.

II. Methods

Tetrahydrofuran (THF) was distilled from sodium benzophenone or was purified by a Vacuum Atmospheres purifier. Perylene, benzophenone, and tetrabutylammonium tetraphenylborate (TBABPh₄) from Aldrich and the 222 cryptand (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, C222) from Merck or Aldrich were used as received; 7,16-Dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane ($\phi[\cdot]\phi$) was synthesized by the nucleophilic substitution reaction of 1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane (Aldrich) and benzylchloride with excess triethylamine in benzene,¹⁸ was purified twice with column chromatography and characterized by ¹H-NMR and elemental analysis. Sodium tetraphenylborate (NaBPh₄) from Aldrich was recrystallized.

Pulse radiolysis used <50 ps pulses of high energy electrons from accelerators at Argonne (ANL) or Brookhaven (BNL) as described previously¹⁹ to ionize the solvent. Ionization produced solvated electrons in THF which attached to the solute molecules. Measurements were made in deaerated solvents in 0.5 or 2 cm cells. Transient absorption was detected using probe light from a pulsed xenon arc lamp.

Chemical reductions and spectrophotometric measurements were performed under Ar in a glove box. Details are in supporting information below Figure S3.

Cyclic voltammetry was performed in THF with a CH Instruments 600E potentiostat using a glassy carbon working electrode and an Ag/Ag⁺ (0.01 M) reference electrode. Scans were at 100 mV/s. Ferrocene was used as an internal standard.

DC conductivity measurements used a YSI 3200 conductivity meter that had been calibrated with KCl in water. Measurements with radical anions reduced the molecules e.g. BzPh with Na in THF under Ar in a glove box and added varied concentrations to the conductivity cell. This method does not control adventitious water and other impurities as well as that of Szwarc who used an evacuated, sealed glass apparatus which had been flamed to remove traces of water adsorbed to the glass. The present system can measure K_d 's for radical anions, which react with traces of water, down to $\sim 1 \times 10^{-9}$ M.

Computations were performed with Gaussian 09.²⁰

III. Results

A principal theme of this paper will be formation of ion pairs of radical anions with inert counter ions such as Na^+ and TBA^+ . Sometimes ion pairing is accompanied by substantial spectral shifts. Figure 1a shows the absorption spectrum of $\text{BzPh}^{\bullet-}$ free ions measured by pulse radiolysis in THF solution along with spectra in the presence of 10 mM NaBPh_4 , or TBABPh_4 . Addition of a crown or cryptand altered the nature of Na^+ and the strength of ion pairing. In each case >99% of $\text{BzPh}^{\bullet-}$ were paired based on dissociation constants of $\text{BzPh}^{\bullet-}$ pairs of the salts given in Table 4 below. Without counter ions the spectrum peaks near 800 nm. The spectrum shifts upon pairing with the different counter ions. A peak at 530 nm due to ketyl radicals, $\text{BzPhH}^{\bullet}$, formed when $\text{BzPh}^{\bullet-}$ reacts with solvated protons, might be considered an extremely strongly-bound ion pair. Similar, but smaller, shifts are seen for biphenyl $^{\bullet-}$ (Figure S1). Figure 1b summarizes spectral shifts for six different radical anions along with shifts^{21,22} for the fluorene carbanion. Spectral shifts for perylene $^{\bullet-}$ were not detectable.

Because ion pairing induces large spectral shifts for $\text{BzPh}^{\bullet-}$ and very small spectral shifts for $\text{Per}^{\bullet-}$, we might expect that ion pairing stabilizes $\text{BzPh}^{\bullet-}$ more than $\text{Per}^{\bullet-}$. Measurement of the equilibrium constant for the electron transfer (ET) reaction $\text{Per}^{\bullet-} + \text{BzPh} \rightleftharpoons \text{Per} + \text{BzPh}^{\bullet-}$ can determine this difference in stabilization. The free energy change for this reaction in THF without electrolyte was measured by pulse radiolysis. Example data are pictured in Figure S2. The results find $K_{\text{eq}} = (1.3 \pm 0.24) \times 10^{-3}$, $\Delta G^\circ = 171$ meV: the equilibrium of free ions in reaction 1 strongly favors $\text{Per}^{\bullet-}$, as does even more

Figure 1 a) Normalized transient absorption spectra of $\text{BzPh}^{\bullet-}$ in THF for free ions (FI) and ions paired with counter ions, Na^+ , TBA^+ (tetrabutylammonium), $\{ \text{Na}^+ \}$ where $\{ \}$ refers to encapsulation in the 222 cryptand, and $\phi[\text{Na}^+]\phi$, $\square\square\square\square$ encapsulation in this crown ether. b) Spectral shifts in THF as a function of the size of the counter ion for solvated electrons ($e_s^{\bullet-}$) and anions of triptycene ($\text{Trip}^{\bullet-}$), paracyclophane ($p\text{Cp}^{\bullet-}$), benzophenone ($\text{BzPh}^{\bullet-}$), fluorene carbanion ($\text{FICa}^{\bullet-}$), biphenyl ($\text{Bip}^{\bullet-}$) and perylene ($\text{Per}^{\bullet-}$).

strongly the free energy difference determined in vacuum.²³ K_{eq} and free energy changes are reported in Table 1 for this reaction and with the addition of electrolytes. Table 1 Equilibrium constants and free energy changes for reaction (1)-(2) in THF with different cations, M^+ , no cation, and comparison to vacuum.

M^+ ^a	K_{eq}	ΔG° (meV) ^b
Vacuum	6×10^{-6}	304 ²³
Free ions	$(1.3 \pm 0.3) \times 10^{-3}$	171
Na^+	$(4.2 \pm 0.7) \times 10^2$	-155
TBA^+	$(1.2 \pm 0.2) \times 10^{-2}$	113
$\{Na^+\}$	$(2.0 \pm 0.7) \times 10^{-2}$	101
TBA^+ DMF		94 ^c

^a In the presence of either no electrolyte, 10 mM of $NaBPh_4$, $TBABPh_4$ or $NaBPh_4$ + 14.1 mM C222.

^b From $RT \ln(K_d)$ with $T=296$ K; uncertainties are ± 10 meV.

^c From redox potentials in DMF with 0.1 M $TBAPF_4$.²⁴

Reduction potentials measured by cyclic voltammetry in THF containing 100 mM of supporting electrolyte are reported in Table 2. The voltammograms were reversible, except for $BzPh$ in $NaBPh_4$ where no reoxidation wave was evident. We will see below that this reduction of $BzPh$ leads to the formation of an extremely strongly-bound ion pair, $(BzPh^{\cdot-}, Na^+)$. The Discussion section will note the connection of the nearly-missing reverse wave to this very strong ion pairing, where it can be understood to provide support for the very small K_d deduced through other methods.

Table 2 Reduction potentials measured in THF by cyclic voltammetry (CV) with 100 mM of $NaBPh_4$ or $TBAPF_6$, reported as V vs. $Fc^{+/0}$.^a

	Per	BzPh	E^0 (Per)- E^0 (BzPh)
Na	-2.271	-2.155 ^b	-0.116
TBA	-2.244	-2.361 ^c	0.118
Na-TBA	-0.028	0.206	

^a $E^0(Fc^{+/0})$ vs. Ag/Ag^+ was 0.266 V in $TBAPF_6$ and 0.232 V in $NaBPh_4$. The reported potentials are the mid point between the forward and reverse peaks.

^b The reoxidation portion of CV wave for $BzPh$ in $NaBPh_4$ was barely visible or absent (see Figure S8), so the potential was estimated using the forward (reduction) peak only resulting in an uncertainty estimated as ± 0.05 V.

^c Shalev and Evans²⁵ reported -2.32 V under similar conditions.

The free energy change for reaction (2), ΔG°_2 , in THF determined from equilibrium constants (K_{eq}) in

Table 1 with TBAPF_6 , is 113 meV. From the difference of redox potentials (from CV), ΔG°_2 is 118 meV, (Table 2) which is almost identical. Here we convert from mV to meV with the Faraday constant = 1.0 eV/V. When the electrolyte is changed to NaBPh_4 both estimates of the free energy change become substantially more negative $\Delta G^\circ_3 = -268$ meV (from K_{eq}) and -234 meV (from CV). The 34 meV difference may reflect uncertainties in both measurements, especially those from the poor reoxidation wave noted in the CV of BzPh with NaBPh_4 in Table 2. The small reoxidation wave is consistent with a small K_d and may point to the possibility to determine K_d using voltammetry, which has been done for ion association and other reversible follow-up reactions.²⁶ Corrections were not made for the difference in electrolyte concentration, 10 mM in Table 1 and 100 mM in Table 2, but these are small as will be discussed below. At the bottom of each panel in Figure 2 are the standard states with 1 M of *free* Na^+ or TBA^+ , which makes a large difference. The large spectral shifts for $(\text{BzPh}^{\bullet\bullet}, \text{Na}^+)$ and chemical intuition suggest that the ~ -251 meV difference arises from strong ion pairing of $\text{BzPh}^{\bullet\bullet}$ with Na^+ . Results below will seek to assess these and other energies for ion pairing in a quantitative way and relate them to the results in the absence of electrolyte.

Reactions 1-3 (signed) can be added together to give reaction 4, so their free energy changes, given in Table 1, can be evaluated in a cycle. The free energy change for reaction 1 without electrolyte, $\Delta G^\circ = 171$ meV, is the top segment in a free energy cycle in Figure 2a. This and the value with 10 mM electrolyte are directly determined from

equilibria; these direct values are shown in blue in Figure 2. Free energy changes for a 1 M standard state require corrections that will be described below. Figure 2 shows that with addition of 10 mM sodium tetraphenylborate (NaBPh_4) K_{eq} becomes 420 ± 70 ($\Delta G^\circ = -155 \pm 10$ meV): addition of Na^+ changed K_{eq} by a factor of 3.2×10^5 . The dissociation free energy $\Delta G^\circ_d(\text{Per}^{\bullet\bullet}, \text{Na}^+)$ reported by Slates and Szwarc²⁷ forms the left hand segment in Figure 2a. Simply adding segments in the cycle, which we might call the naïve estimate, yields $\Delta G^\circ_d(\text{BzPh}^{\bullet\bullet}, \text{Na}^+) = 600$ meV. The results of the cycle with this naïve estimate say that 600 meV is the difference between the reduction potential of BzPh without electrolyte and that with $[\text{Na}^+] = 1$ M due to ion pairing. Analysis below will show that this difference is smaller with more realistic electrolyte concentrations, but will then include an additional, smaller contribution from activity coefficients. An improved estimate, described below, yields the almost identical value

$\Delta G_d^\circ(\text{BzPh}^\bullet, \text{Na}^+) = 602 \text{ meV}$ ($K_d = 6.75 \times 10^{-11} \text{ M}$). Both the K_d of Slates²⁷ for Per and our values for BzPh are in molar concentrations and refer to a hypothetical standard state with $[\text{Na}^+] = 1 \text{ M}$ but with properties of dilute solutions. The choice of 1 M as the standard concentration means that our K_d values have units of M, but they are numerically equal to the dimensionless K_d that is defined in terms of activities using a 1 M standard state. The naïve estimate makes an error of only 2 meV out of 602. This is surprisingly accurate given that the experiments for the bottom segment used 10 mM of NaBPh₄, which does not seem compatible with the 1 M standard state for K_d . Discussion below will give a quantitative description that includes ion pair formation and the effects of ionic atmospheres that alter activity coefficients, which will also explain why the naïve estimate works so surprisingly well. The cycles shown here omit one step which is included in Figure S3, where we argue that the omitted energies are small and contributions from BzPh and Per cancel accurately.

Addition of an electrolyte shifts the redox potentials of BzPh[•] and Per[•] to become more positive. Denoting the redox potential for BzPh in the absence of electrolyte and in the 1 M standard state as $E^0(\text{BzPh}^{0/-})$ and $E^0(\text{BzPh}^{0/-}, \text{Na}^+ = 1.0)$ the difference is 602 meV. But the corresponding difference caused by addition of 10 mM of NaBPh₄, $E^0(\text{BzPh}^{0/-}, \text{Na}^+ = 0.01)$, in which the concentration of free Na⁺ is just 0.7 mM, is 420 mV for BzPh and is only 94 mV for Per as shown in Figure 2a. The discussion section will show how these differences can be approximately understood solely on the basis of the differences in K_d 's but will be more accurately understood using both K_d 's and activity coefficients. Before that discussion we describe more experimental results that will enable a more complete picture.

The dissociation constant $K_d = 6.75 \times 10^{-11} \text{ M}$ for (BzPh[•], Na⁺) pairs is very small, even smaller than that reported for (Benzene[•], Na⁺), $K_d = 4.5 \times 10^{-10} \text{ M}$.²⁸ An attempt to check this very low K_d by DC conductivity of (BzPh[•], Na⁺) in THF gave only an upper limit, $K_d \leq 1.0 \times 10^{-9} \text{ M}$. Conductivity could not confirm that it is as small as the value deduced from the free energy cycle because of uncertainties due to residual conductivity arising from traces of water. Support for this value will come from measurements on the effects of other ions and computed values of ΔG_d° reported below. The CV data, with modeling, can provide another estimate that will be described in the Discussion section along with additional notes about the meaning of the free energy cycles.

A similar free energy cycle constructed for Per[•] + BzPh without and with pairing with TBA⁺ is shown in Figure 2b. Here addition of TBA⁺ does not change K_{eq} by a factor of 3.2×10^5 , as with Na⁺, but only a factor of 9.2, so ΔG° changes by only 58 meV. To construct the cycle in Figure 2b the equilibrium in the presence of 10 mM TBABPh₄ determined the bottom segment, while the top segment was identical to that in Figure 2a. Dissociation free energies for ion pairing of radical anions with TBA⁺ are almost unknown, except for recent determinations for nitrile anions by Mani.^{16,29} None are known for Per[•] or BzPh[•]. Here we evaluate equilibria using two additional methods to obtain new determinations (Figures 3, S4).

The first additional method utilizes the large spectral shifts of BzPh[•] seen in Figure 1a. The spectral shifts themselves do not determine K_d 's, but their distinct spectra enable us to determine the ratio, $K_d(\text{BzPh}^\bullet, \text{TBA}^+)/K_d(\text{BzPh}^\bullet, \text{Na}^+)$ in the salt metathesis reaction $(\text{BzPh}^\bullet, \text{Na}^+) + (\text{TBA}^+, \text{PF}_6^-) \rightleftharpoons (\text{BzPh}^\bullet, \text{TBA}^+) + (\text{Na}^+, \text{PF}_6^-)$. This method can be called chemical equilibria of ion paired species (ceip). Like the method

described above using reaction 1, the ceip method is based on equilibria, but here in ceip the equilibrium involves competition to pair the same radical anion with two different cations. Varied

concentrations of TBAPF₆ or TBABPh₄ were added to a solution of (BzPh[•], Na⁺) while absorption spectra were recorded. Sample absorption spectra are shown in Figure S4 along with details of the experimental procedure. The spectra were well-described as sums of the spectra of (BzPh[•], Na⁺) and (BzPh[•], TBA⁺). Figure 3 shows fits to the fraction of TBA⁺ pairs as a function of the concentration of added salts. The fits required knowledge of the concentration of free TBA⁺ ions which were calculated using LeSuer's measurement of K_d(TBA⁺, PF₆⁻),¹¹ or Szwarc's for K_d(TBA⁺, BPh₄⁻).³⁰ The fits determined that the ratio of dissociation constants K_d(BzPh[•], TBA⁺)/K_d(BzPh[•], Na⁺) = 930±40. With K_d(BzPh[•], Na⁺) = 6.75×10⁻¹¹ M, K_d(BzPh[•], TBA⁺) = (6.3 ± 0.6)×10⁻⁸ M. This K_d was also unknown, but can now be used to form the right hand side of the energy cycle in figure

2b, which in turn gives us K_d(Per[•], TBA⁺).

A similar experiment determined K_d(BzPh[•], {Na⁺})/K_d(BzPh[•], TBA⁺)=344, where {} denotes encapsulation in the C222 cryptand, yielding K_d(BzPh[•], {Na⁺})=2.2×10⁻⁵ M. Thus in the same reaction K_d is changed by a factor of 3.3 ×10⁵ by encapsulating Na⁺ in C222. Similarly with C222 K_d(BzPh[•], {Na⁺}) could be measured directly by dc conductivity to be 3.6×10⁻⁶ M with an uncertainty of a factor of 2. The rough agreement of the two values, the former of which utilized K_d(BzPh[•], Na⁺)=6.75×10⁻¹¹ M gives support to this very small K_d.

The equilibrium of reaction 2 was also determined with {Na⁺}. Figure S4 shows an energy cycle like those in Figure 2. With these results dissociation constants, which will be seen to be responsible for most of the effect of electrolytes on redox potentials, in THF are now reported in Table 3 for several ion pairs.

Table 3 Dissociation Free Energies of Ion Pairs in THF. Values are determined here except those indicated by references in the method column. The last column contains computed estimates described below.

Pair	K_d (M^{-1})	Method ^a	ΔG°_d (meV)	Comp. ΔG°_d
(Na^+ , Per^+)	2.3×10^{-5}	dcc ²⁷	272 ²⁷	301, ^b 1967
($\{Na^+\}$, Per^+)	$(6.3 \pm 3) \times 10^{-5}$	dcc	244	241
($\{Na^+\}$, $BzPh^+$)	$(3.6 \pm 2) \times 10^{-6}$	dcc	320	243
($\{Na^+\}$, $BzPh^+$)	$(2.2 \pm 1) \times 10^{-5}$	Fec, ceip	274	243
(Na^+ , $BzPh^+$)	$(6.75 \pm 0.3) \times 10^{-11}$	Fec, ceip	598	952, ^b 1812
(TBA^+ , Per^+)	$(5.91 \pm 2) \times 10^{-7}$	fec	364	369
(TBA^+ , $BzPh^+$)	$(6.3 \pm 0.6) \times 10^{-8}$	ceip, Fec	424	467, ^b 579
($\{Na^+\}$, BPh_4^-)	9.3×10^{-5}	dcc	237	
(Na^+ , BPh_4^-)	4.8×10^{-5}	dcc	254	
(Na^+ , BPh_4^-)	8.52×10^{-5}	dcc	293 ³⁰	
(TBA^+ , BPh_4^-)	4.32×10^{-5}	dcc	265 ³⁰	
(Na^+ , PF_6^-)	2.0×10^{-7} ^c	dcc, ceip	393	
(TBA^+ , PF_6^-)	2.68×10^{-6}	dcc	328 ¹¹	684 ^b
(Na^+ , Bip^+)	1.15×10^{-6}	dcc	349 ²⁷	394 ^b

^a Methods, dcc=dc conductivity, fec=free energy cycle, ceip=chemical equilibrium of ion paired species. Sometimes more than one method was used as described in the text, e.g. ceip determined a ratio of two K_d 's which could be applied with a value from Fec. References to published work are given.

^b Four explicit THF molecules were added to Na^+ . Without the THF molecules the computed ΔG°_d 's for binding to bare Na^+ were 1967 meV (Per) and 1812 (BzPh) meV.

^c Determination by dc conductivity is shown in Figure S5.

Another method created $BzPh^+$ free ions in THF using pulse radiolysis and added $TBAPF_6$ in concentrations between 1 μM and 300 mM. These additions produced time-dependent mixtures of the spectra of $BzPh^+$ free ion and ($BzPh^+$, TBA^+) ion pairs. The mixtures evolved to contain no detectable contribution from $BzPh^+$ free ions even at the lowest, 1 μM , concentration of $TBAPF_6$. Therefore fits to these composite spectra did not obtain a value, but found the limit $K_d(BzPh^+, TBA^+) < 1 \times 10^{-7}$ M, which does support the small value, 6.8×10^{-8} M reported in Table 2. The spectrum of the ($BzPh^+$, TBA^+) ion pair did not change with a three decade increase in $TBAPF_6$ concentration from 5 μM to 10 mM, but a small blue-shift occurred at 100 mM. This observation may point to an additional mechanism for stabilization of $BzPh^+$ ions at high $TBAPF_6$ concentrations. Such additional stabilization could come from triple ion formation (e.g. (TBA^+ , $BzPh^+$, TBA^+), which could change the redox potential at 100 mM $TBAPF_6$, but the data do not yield a quantitative estimate.

Computed Dissociation Energies We computed dissociation energies for ions pairs following methods similar those used by Fry.¹² Dissociation energies were estimated as the difference between an optimized pair, e.g. (Per^{•-},TBA⁺) and the energies of the two components optimized separately. Optimizations were at the b3lyp/6-31g* level with the SMD³¹ solvation model for THF. Diffuse functions were not added because they can lead to spurious results for radical anions. These results are included in Table 3 along with a summary of experimental results for ion pair energetics in THF. For pairs with the small cation, Na⁺, DFT optimized structures sometimes greatly overestimated the dissociation energies. In some such cases four explicit THF molecules were included around Na⁺, following Guijarro¹³ and Wu¹⁴ who found four to be the optimal number. Their DFT calculations yielded a plausible picture of “loose” or solvent-separated ion pairs that is qualitatively similar to that in Figure 4. In their picture and in Figure 4, explicit solvent molecules cause the Na⁺ counter ion to move further from the anions so Na⁺ is less tightly paired to the anions. For perylene the inclusion of the explicit THF molecules caused the Na⁺ to sit almost 5.9 Å from the perylene plane, although, unlike the classical picture of solvent-separated ion pairs, no THF solvent molecule lies directly between the two ions. The present work thus supports this revised picture^{13,14} of loose or solvent-separated ion pairing. In this perylene case the computed dissociation energy (Table 3) is only slightly larger than experiment, although the error is much larger for benzophenone. Explicit solvent molecules have much less effect on ion pairing of BzPh^{•-} and Per^{•-} to TBA⁺, and in most cases were not included.

Figure 4 Optimized (b3lyp/6-31g* SMD for THF) structures for ion pairs of Na⁺ with anions of perylene (upper) or benzophenone (lower), where Na⁺ is solvated by four THF molecules. The Na⁺ ions

(purple) lie near the center of each picture. They are 2.19 Å from the carbonyl oxygen of BzPh vs. almost 5.9 Å from the perylene plane.

IV. Discussion

Electron Transfer Equilibria We framed the description of the electron transfer equilibria, reactions 1-4, in terms free energies of ion pairing to focus attention on the dominant contribution to free energies of radical ions in electrolytes in moderately polar THF. This can simplify the discussion, but it is an approximation. Addition of electrolyte also causes smaller contributions to the free energy of each ion in reactions 1-4 arising from electrical attractions of the radical ions to their ionic atmospheres described by the Debye-Hückel theory, and expressed in terms of activities. In more polar media the contributions from ion pairing are smaller. In highly polar media the contributions of activities are relatively more important and can even become the dominant effect on energies of ions. In addition to ion pairing and activity “triple ions,” which can be formed by association of redox-active ion with an ion pair of the electrolyte or with two counter ions, may contribute at high concentrations of electrolyte. Contributions from triple ions seem required to explain some conductivity data in low-polarity solvents and their effects on optical electron transfer transitions have been noted,³² but their actual role remains controversial.³³

Eq 5 is a simple, quantitative description for redox potentials underlying these equilibria, taking account of ion pairing and changes in activity coefficients γ for the redox-active ions. It omits the possible role of triple ions.

$$E^{0'} = E^0 + \frac{RT}{F} \ln \left(\frac{1}{\gamma_{\pm}} + \frac{\gamma_{\pm}[X^+]}{K_d} \right) \quad (5)$$

E^0 is the redox potential without electrolyte where the activity coefficients γ of the reduced and oxidized forms are both 1.0. Here we define standard conditions as the *absence* of electrolyte, which enables a particularly simple definition of E^0 since there is no electrolyte to create notable alteration of activities. $E^{0'}$ is the redox potential for the same species in a given concentration of electrolyte. The derivation of eq 5 is described in the section called “Derivation of Eqs 5-6” in supporting information (SI). It is used along with eq 6 which calculates activity coefficients using the Bjerrum approach³³ where the distance of closest approach, R , is set equal to the Bjerrum distance, q ; ions that get any closer would be considered paired and not contribute to the activity coefficient. This use of the Bjerrum distance is slightly arbitrary, but changing the distance to a different value makes little difference to the end result.

$$\ln \gamma_{\pm} = -\frac{\kappa q}{1+\kappa R} = -\frac{\kappa q}{1+\kappa q} \quad (6)$$

In eq 6 κ is the Debye inverse screening length (m^{-1}), described in eq S11. An iterative procedure used to calculate the activity coefficients is also described in the SI. Eq 5 can readily account for the changes in redox potentials that underlie all the shifts in equilibria due to addition of electrolyte.

The description of eqs 5-6 let us understand how the addition of 10 mM NaBPh₄ produced a shift $E^{0'} - E^0 = 420$ mV for BzPh but only 94 mV for perylene (Figure 2a). The formal potential $E^{0'}$ increases (becomes less negative) as electrolyte is added. The shift is 4.4 (420/94) times larger for BzPh, which may seem surprising, but is readily understood in terms of the 602 and 274 meV standard dissociation free energies (ratio 2.2). Figure 5 shows how the formal reduction potentials, $E^{0'}$, for BzPh and Per change as functions of concentration of Na⁺. With the far smaller $K_d(\text{BzPh}^{\bullet-}, \text{Na}^+) = 6.75 \times 10^{-11}$ M, $E^{0'}(\text{BzPh})$

Figure 5 The change in reduction potentials $E^{0'}$ of BzPh and Per with increasing concentration of free Na⁺ either due solely to ion pairing from eqs 5-6 with γ fixed to 1.0 (—) or with ion pairing and activity corrections (---). The two vertical lines mark the free Na⁺ concentrations at 10 and 100 mM of NaBPh₄ in THF.

begins rising near 6.75×10^{-11} M while with $K_d(\text{Per}^{\bullet-}, \text{Na}^+) = 2.3 \times 10^{-5}$ M, $E^{0'}(\text{Per})$ does not increase appreciably until the Na⁺ concentration increases another five decades. For γ set constant to 1.0 in Figure 5 (solid lines) both lines increase with the same 59 mV/decade slope after onsets near their respective K_d 's. So viewed as functions of Na⁺ concentration the redox potentials for Per and BzPh differ only by where they begin rising. At 10 mM NaBPh₄ $E^{0'}$ has increased by 85 mV for Per and 409 mV for BzPh; the experimentally determined differences, 94 and 420 meV, in Figure 2a are slightly larger. With changes in γ included by eq 6 the behavior is qualitatively similar (dashed lines in Figure 5). For an extreme example if $[\text{Na}^+] = 1 \mu\text{M}$ $E^{0'}(\text{BzPh})$ would increase by 274 mV while $E^{0'}(\text{Per})$ would increase by only 2 mV.

Figure 5 also explains why the “naïve” method to estimate K_d worked reasonably well in Figure 2a. That method used the reported $K_d(\text{Per}^{\bullet-}, \text{Na}^+)$ ²⁷ as one segment of the free energy cycle to determine to opposite segment, $K_d(\text{BzPh}^{\bullet-}, \text{Na}^+)$. The top segment was the free energy change for the free ions, but the bottom was for 10 mM NaBPh₄, not for free $[\text{Na}^+] = 1.0$ M. This method makes only a small error because the slopes of the two solid lines in Figure 5 are parallel, so K_{eq} for the electron transfer from $\text{Per}^{\bullet-}$ to BzPh remains almost constant even as the electrolyte concentration increases by a few decades.

How can we Measure Redox Potentials without Electrolyte? Three steps obtain redox potentials without electrolyte:

1. Electron transfer (ET) equilibria with no electrolyte added in electrolyte free. Pulse radiolysis creates solvated electrons and radical cations ($\text{RH}^{\bullet+}$) of THF; $\text{RH}^{\bullet+}$ rapidly transfers a proton to become RH_2^+ , a solvated proton. RH_2^+ is thus the counter ion. About 75% of the radical anion - RH_2^+ pairs are formed <7.5 nm (the Onsager radius) apart and annihilate in geminate recombination, leaving less than $1 \mu\text{M}$, measured by transient absorption, of ion pairs that are free of each other. These free anions established electron transfer equilibria in $< 2 \mu\text{s}$ (see Figure S2). While we used well purified THF the presence of impurity electrolyte cannot be ruled out. Pendley and coworkers,³ found their E° 's to be dominated by unknown impurity electrolyte hypothesized to be present at 40 or 10 nM. With these estimates and the $1.5 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ of Beaumont and Rodgers³⁴ for diffusion-controlled combination of $\text{BzPh}^{\bullet-}$ with Na^+ in THF we estimate $166 \mu\text{s}$ for the time required for combination of $\text{BzPh}^{\bullet-}$ or $\text{Per}^{\bullet-}$ with plausible impurity electrolyte. The impurity electrolyte would not have time to reach the reactive ions before electron transfer equilibrium is established. As a result the equilibria without added electrolyte can be considered to be electrolyte-free.
2. The ET equilibria give differences of reduction potentials without and with electrolyte. The free energy cycles, used to determine reduction potentials, required knowledge of dissociation constants for ion pairs, which by definition include counter ions. The conductivity measurements focus on very low concentrations and carefully model behavior at higher concentrations.^{11,27}
3. The final step is the assumption of eq 5. If effects not included are important to the energetics in the presence of electrolyte, then difference $E^{\circ'} - E^{\circ}$, determined herein, will be an underestimate.

Redox Potentials Without Electrolyte Table 4 reports the changes in reduction potentials of benzophenone and perylene in THF when 100 mM of electrolyte is added, from results in Figures 2, 4 and S4. With the assumption that changes of the redox potential, $E^{\circ'}$, follow the form of eq 5, the results find that addition of 100 mM of NaBPh_4 makes $E^{\circ'}(\text{BzPh}^{0/-})$ 0.451 V more positive: BzPh is easier to reduce principally due to stabilization of $\text{BzPh}^{\bullet-}$ by strong ion pairing with Na^+ . By contrast addition of NaBPh_4 makes $E^{\circ'}(\text{Per}^{0/-})$ only 0.124 V more positive, while TBAPF_6 has a larger effect. These differences begin to provide answers to the question: what is the effect of the electrolyte on redox potentials, and shows contrasts for anions with two different natures. The present data finds large differences in redox potentials due to effects of ion pairing specific to molecules like BzPh . Such effects would not be predicted by the effective dielectric constant approach of Bao.⁷

The treatment described here omits effects other than ion pairing and activity coefficients. If some additional factor(s) is significant and contributes equally to stabilization of BzPh and Per anions, then their effects will simply be missed in our treatment, which is based on the free energy cycles of Figure 2.

Table 4 I) Changes in reduction potentials when electrolyte is added, $\Delta E^0 = E^0(M^{0/-}, 100 \text{ mM electrolyte}) - E^0(M^{0/-})$, for benzophenone (BzPh) and perylene (Per) in THF and II) reduction potentials of BzPh and Per in THF with 100 mM of TBAPF₆, NaBPh₄, {Na}BPh₄ or without electrolyte, all vs. Fc^{+/0} in 100 mM of TBAPF₆.

	$\Delta E^0(M^{0/-}) \text{ (V)}^a$			
I	TBAPF ₆	NaBPh ₄	{Na}BPh ₄ ^b	No electrolyte
BzPh ^{•-}	0.232	0.451	0.173	n/a
Per ^{•-}	0.174	0.124	0.100	n/a
II	$E^0(M^{0/-}) \text{ (V) vs. Fc}^{+/0}{}^c$			$E^0(M^{0/-}) \text{ (V)}^c$
BzPh ^{•-}	-2.32	-2.10	-2.38	-2.55
Per ^{•-}	-2.21	-2.26	-2.28	-2.38

^a $E^0(\text{BzPh}^{0/-}) - E^0(\text{Per}^{0/-}) = -171 \text{ mV}$ (see Figure 2).

^b {} refers to encapsulation in the 222 cryptand.

^c The reference is based on measurements of Shalev and Evans giving $E^0(\text{Bzph}^{0/-}) = -0.989 \text{ V}$ vs. $\text{Cocp}_2^{+/0}$ in THF with 100 mM TBAPF₆²⁵ and $E^0(\text{Fc}^{+/0}) = 1.332 \text{ V}$ vs. $\text{Cocp}_2^{+/0}$. Note that the reference redox couple, Fc^{+/0}, is always in THF with 100 mM TBAPF₆ even when Per or BzPh is in THF without electrolyte or with a different electrolyte.

Another reference for redox potentials is the electron in vacuum. Figure 6 uses this reference, graphing free energy changes for formation of BzPh^{•-} and Per^{•-} in vacuum, in THF without electrolyte and in THF with the three electrolytes in Table 4, but with the standard condition of 1 M counter ion. Without electrolyte in THF computed solvation energies (SMD/6-31g*) are -2.02 eV for both Per and BzPh anions, so the computations do not reproduce the change in K_{eq} and ΔG° reported in Table 1.

Figure 6 Electron attachment free energy changes, which may be regarded as redox potentials vs. the reference of electron in vacuum, using Kebarle's gas phase electron affinities determined by equilibria,²³ computed solvation energies in THF (b3lyp/6-31g*/SMD) and the relative redox potentials determined as in Table 4 but for the 1 M standard state. Redox potentials with Na⁺ are distinguished with a dark line.

Redox potentials, sometime called half-cell potentials, are usually reported with respect to a reference electrode or another half cell, often reduction of ferrocenium, Fc^{+/0}. The reduction potential of BzPh reported by Shalev and Evans vs. Fc^{+/0} in THF, or the very similar potential reported here in Table 2 lets us give the potentials vs. Fc in the lower part of Table 4. Frequently experiments determine the empirical formal potential, E^{0'}, which often does not correct for the, usually small,^{25,35} effects of activity coefficients or the effect of ion pairing, which is larger in the present experiments. In this work the effects of both are always included, although some additional effects of large concentrations of electrolytes may still be missing. The expression we have derived (see supporting information) is given in equation 5 and enables us to recover the standard, electrolyte-free, redox potentials E⁰ in Table 4.

Dissociation Constants The dissociation constants and dissociation free energies in Table 3 measure how strongly two ions of opposite charge bind to each other. We first note the effects of Na⁺ and TBA⁺ on reaction (1). While electron transfer from Per[•] to BzPh is uphill (unfavorable) by 171 meV in THF without electrolyte, and even further uphill in vacuum, it is exoergic, ΔG°=-155 meV, when Na⁺ is added. Results in Table 3 show that this is mainly due to strong ion pairing. The central feature is the strong pairing of the negative charge localized on C=O in BzPh[•] with Na⁺.

The near-absence of a return wave for reduction of BzPh in NaBPh₄, described in connection with Table 2, supports the strong ion pairing ΔG_d°(BzPh[•],Na⁺)=602 meV, K_d=6.75x10⁻¹¹. With this very small K_d simulations by DigiSim³⁶ (Figure S6) predict the absence of a return wave seen in the experimental CV (Figure S7). Return waves are noticeable only in simulations with K_d≥2x10⁻¹⁰, leading to the conclusion that K_d is smaller than 2x10⁻¹⁰.

The effect of TBA⁺ on reaction (1) is dramatically different from the effect of Na⁺. TBA⁺ stabilizes BzPh[•] and Per[•] by reasonably large, but similar magnitudes: $\Delta G_d^\circ(\text{BzPh}^\bullet, \text{TBA}^+) = 424 \text{ meV}$, which is only 58 meV greater than $\Delta G_d^\circ(\text{Per}^\bullet, \text{TBA}^+) = 368 \text{ meV}$. Both are larger than $\Delta G_d^\circ(\text{Per}^\bullet, \text{Na}^+) = 272 \text{ meV}$. For Per[•] the somewhat stronger binding to TBA⁺ than to the smaller ion, Na⁺ might seem surprising, but stronger binding to TBA⁺ was confirmed by a second method (ceip, Table 3) and by computed values, with four explicit THF molecules coordinated to Na⁺. Both support stronger binding of Per[•] to TBA⁺ (Table 3). The weaker binding to Na⁺ is an example of the well-known behavior that the “small ion,” Na⁺, can act like a larger ion in solvents like THF that coordinate well to Na⁺. Computed results in Table 3 further support this picture giving far stronger binding (larger ΔG_d°) without inclusion of explicit THF molecules. Similar behavior, with ΔG_d larger for TBA⁺ than for Na⁺ was reported by Szwarc for pairing with the large anion, tetraphenylborate (BPh₄⁻) as noted in Table 3. Fry found similar behavior for pairing to tetramethylammonium cations in some solvents. The computed structure for (BzPh[•], TBA⁺) in Figure 4 supports the interpretation that the C=O of BzPh[•] cannot closely approach the nitrogen of TBA⁺. The distance between oxygen of BzPh[•] and the nitrogen of TBA⁺, 0.357 nm, seems consistent with steric interference by the butyl groups in TBA⁺. Fry has also presented computational evidence that partial delocalization of positive charge from the nitrogen to adjacent methylenes weakens ion pairing to TBA⁺. Nevertheless the present experiments show that TBA⁺ forms the stronger pairs with Per[•] than does Na⁺.

V. Conclusions

The present experiments examined the effects of electrolytes on reduction potentials of a delocalized radical anion, Per[•], and a more localized one, BzPh[•]. In moderately polar THF the dominant effect was from ion pairing. Here we applied experimental techniques not previously used for investigations of ion pairing, along with the traditional techniques of dc conductivity and cyclic voltammetry. The techniques newly applied to this question include measurement of equilibrium constants by pulse radiolysis along with measurements of equilibria from chemical reduction. Free energy changes from these equilibrium constants could be used in free energy cycles along with two additional methods based on equilibria. These techniques, with the assumptions of eq 5, enabled determination of several previously unknown dissociation free energies for ion pairs. One other new method is promising, but was able only to obtain limits. The new methods and eq 5 enabled clear determinations of how two redox couples, Per^{0/-} and BzPh^{0/-}, change when electrolyte is completely absent. Without electrolyte the potentials become more negative by 100 to 451 mV (see part I of Table 4). While the present results did so for only two molecules, they pave the way for expansion to many molecules. The present experiments obtained electrolyte-free potentials in a solvent of moderately low polarity, THF, $\epsilon = 7.6$, where such a determination is moderately difficult. In the past it has been challenging to obtain redox potentials without electrolyte even in the much easier cases of high polarity solvents like acetonitrile. Further the present results obtained definite, and often quite different, values for redox potentials and dissociation constants with different electrolytes. The present results thus represent a good start on this important, outstanding problem. The present results also imply that determination of redox potentials without electrolyte may become reasonably straightforward in media with $\epsilon = 7.6$ and higher. A remaining challenge will be to determine them in media of lower polarity.

Somewhat surprising findings of this work are that free energies for ion pairing of TBA^+ to the localized $\text{BzPh}^\bullet$ is only 14% larger than ion pairing to the delocalized $\text{Per}^\bullet$, (Table 4) while TBA^+ binds more strongly to $\text{Per}^\bullet$ than does the small Na^+ ion. Computations are in at least qualitative agreement with these findings and several others. A few tries at the more challenging question of computing ion pairing by Na^+ found moderate success, but overall the computed results here supported Fry's proposal that computation can contribute to understanding ion pairing, while the experiments provided new ways to determine ion pairing and to test computed results. We could hope that computation will be able to accurately predict dissociation constants for ion pairing and redox potentials with and without electrolyte in media of both low and high dielectric constants. The present computed results provide only partial support to this hope. The measurements do provide benchmarks that can be used in future computational work that may improve on computational methods used here.

TBA^+ has been considered a weakly-coordinating cation (WCC), hence useful for determining electrochemical potentials with minimal effects from the electrolyte. Table 3 gives quantitative values for K_d and ΔG_d° , the most important descriptors, which show that while TBA^+ binds less strongly than Na^+ to some anions, this is true in only some cases and that TBA^+ is often fairly strongly coordinating to radical anions. TBA^+ may be considered to be a WCC in polar solvents like acetonitrile, but it seems not to be in less-polar THF. Hupp showed that ion pairing to ferrocenium weakens the "ferrocene hypothesis" that its redox potential may be solvent-independent, the present work shows that ion pairing by TBA^+ makes it not a good WCC. $\{\text{Na}^+\}$ was found to be a somewhat better WCC for both delocalized $\text{Per}^\bullet$ and more localized $\text{BzPh}^\bullet$. A general message from the present work, seen in Table 4 and visualized in Figure 4, is that the dominant effects of ion pairing often vary substantially with the individual natures of both partners.

These individual variations are somewhat successfully described by simple computations. While Fry successfully computed energetics for ion pairing in acetonitrile, comparison of results for computation of ion pairing energetics in THF produced some successes, but also failures. The failures may reflect the interplay of tight and solvent-separated ion pairs of Na^+ with arene radical anions discussed by Szwarc.²² They found strong effects of the size of the arene anion in THF. But the sensitivity to anion size nearly disappeared in DME (dimethoxyethane) or in THF at low temperature.

The current work finds clear experimental answers to several questions about ion pairing. It provides promise that future experiments and hopefully computation will broadly answer these questions. The differences in redox potentials with and without electrolyte, $E^{0'} - E^0$, are a few hundred mV in moderately polar THF. Their determination in less polar media will be more important, but much more difficult; determinations in more polar media will be easier. The results for $E^{0'} - E^0$ include effects of ion pairing and activity coefficients, but exclude effects, such as contributions from triple ions, that may be significant in high concentrations of electrolyte. Redox potentials are usually measured in solutions containing 100 mM of electrolyte. We suspect that at this typical electrolyte concentration ion pairing and activity coefficients capture almost all of $E^{0'} - E^0$, but cannot offer clear evidence to support this suspicion. We hope to find experiments that can yield reliable answers in the future.

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