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Improved Electrochemistry in Low-Polarity Media Using Tetrakis(pentafluorophenyl)-borate Salts as Supporting Electrolytes[**]

Robert J. LeSuer and William E. Geiger[*]

The widespread nature of electron-transfer reactions provides an impetus to extend electrochemical experiments to new matrix conditions (solvents, temperatures, electrolytes).[1] The choice of supporting electrolyte is crucial in that the "indifferent salt" affects not only mass transport and solution resistance, but possibly determines the chemical fate of the electrolysis products.[2, 3] Mann and co-workers have shown, for example, that the oxidation of ruthenocene is a reversible one-electron process when the electrolyte anion is $[B\{C_6H_3(CF_3)_2\}_4]^-$, whereas an irreversible two-electron process is found when the more traditional anions $[ClO_4]^-$, $[BF_4]^-$, or $[PF_6]^-$ are used.[3] We now bring attention to several electrochemical advancements that are possible when tetraalkylammonium salts of the weakly coordinating[4] anion tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$, are employed in solvents of low dielectric strength. Our results establish that these electrolytes are greatly advantageous for the investigation of electrode processes in such solvents. Voltammetry can now be more accurately performed at conventionally sized electrodes under demanding conditions (e.g., at low temperatures and/or high scan rates) in solvents of very low polarity. The improvements arise from the increased solubilities and dissociation tendencies of cations having a $[B(C_6F_5)_4]^-$ counterion, phenomena that have received attention in the area of homogeneous catalysis.[4, 5]

We show here that 1) the $[B(C_6F_5)_4]^-$ anion is extremely effective in solubilizing positively charged species produced in anodic reactions and 2) voltammetric measurements are now possible in solvents having very low dielectric constants, including aliphatic ethers.

Addressing the first point, we note that, although dichloromethane is a preferred solvent for oxidation reactions, the precipitation of polycationic products at the electrode often complicates voltammetric scans in this solvent. As a result, studies are often performed in a more polar (but usually more reactive) solvent such as CH_3CN. Examples of this strategy may be found in the study of polyferrocenyl compounds, where precipitation of multiply charged species frequently passivates electrode surfaces in low-polarity solvents.[6] Product precipitation is avoided with a $[B(C_6F_5)_4]^-$-containing electrolyte. Figure 1 compares cyclic voltammetry (CV) scans of the triferrocenyl compound **1** in CH_2Cl_2 containing 0.1 M $[NBu_4][PF_6]$ with those of the same system

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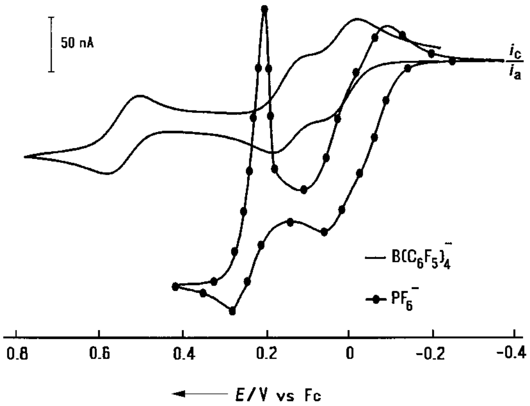
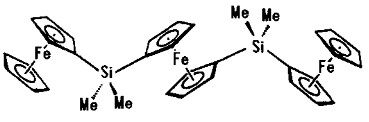


Figure 1. Comparison of cyclic voltammograms (scan rate 0.2 V s^{-1}) of 1.0 mM **1** in CH_2Cl_2 (Pt electrode, 0.5 mm diameter) at ambient temperature with different supporting electrolytes. •–•– 0.1M $[NBu_4][PF_6]$; —— 0.1M $[NBu_4][B(C_6F_5)_4]$. Fc = Cp_2Fe^+/Cp_2Fe^0.

with 0.1M $[NBu_4][B(C_6F_5)_4]$. The diffusion-controlled shapes of all three waves for the experiment with $[B(C_6F_5)_4]^-$ media attest to the fact that even the trication $\mathbf{1}^{3+}$ is soluble, in contrast to the clear evidence of precipitation of the trication and subsequent cathodic stripping wave on the return sweep (ca. 0.2 V) in $[PF_6]^-$-containing media. We have experienced a number of such situations, which will be discussed in more detail in subsequent papers, and it appears that the simplification of anodic processes through solubilization of polycations in $[B(C_6F_5)_4]^-$-containing media is quite general. We strongly urge the adoption of this or a related anion for voltammetry and electrolyses that must be conducted in low-polarity solvents.



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Because the thermodynamic potentials of all three ferrocenyl-centered oxidations of **1** are now directly accessible from the CV scans, the influence of possible ion-pairing interactions on the potentials of the three successive couples may be probed. Observed shifts of $\Delta E_{1/2} = 46$ mV and 116 mV for the 0/1+ and 1+/2+ couples, respectively, when going from $[PF_6]^-$ to $[B(C_6F_5)_4]^-$ media are consistent with increasingly *reduced* ion pairing of the Fe^{III} centers with the borate anion (compared to hexafluorophosphate) as the ferrocenyl groups are progressively oxidized.[7]

An example of newly useful electrochemical solvents can be taken from the aliphatic ether family. Diethyl ether is an important reaction medium, but its low dielectric constant (4.3) has severely restricted its use in electrochemistry.[8] However, $[NBu_4][B(C_6F_5)_4]$ gives modestly conducting solutions[9] in this solvent, even at subambient temperatures. Figure 2 shows a CV scan (scan rate 0.005 V s^{-1}, $T = 210$ K) of decamethylferrocene at a Pt disk 125 μm in diameter. Under these slow scan conditions a quasi-steady-state voltammogram is obtained with $E_{1/2} = -0.60$ V versus Cp_2Fe^+/Cp_2Fe^0. Although there is ohmic distortion[10] in this wave, thermodynamic information about the decamethylferrocene/decamethylferrocenium couple is clearly accessible in Et_2O.

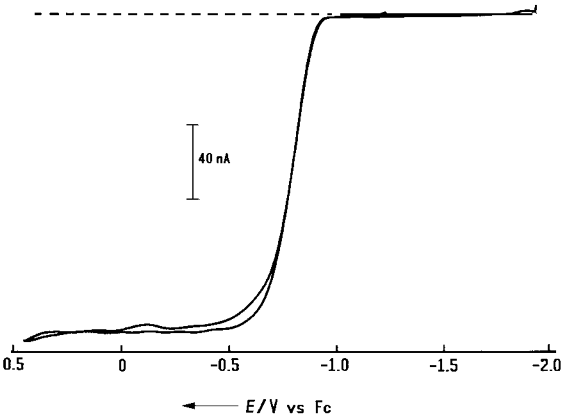

Figure 2. "Steady-state" CV scan (scan rate 0.005 V s^{-1}) of the oxidation of 1.1 mM decamethylferrocene in Et_2O saturated with $[NBu_4][B(C_6F_5)_4]$ (< 25 mM) at 210 K (Pt disk, 0.125 mm diameter). The dashed line gives the zero current value. Fc = Cp_2Fe^+/Cp_2Fe^0.

Greatly improved performance is achieved in *tert*-butyl methyl ether, in which $[NBu_4][[B(C_6F_5)_4]$ displays an increased solubility, which leads to a lower solution resistance.[9] For example, a CV scan of 9,10-anthroquinone in this solvent (Figure 3) exhibits respectable ΔE_p values (ca. 130 mV, scan rate 0.2 V s^{-1}, 2-mm Pt electrode) and clearly demonstrates the generation of both the semiquinone species and the anthroquinone dianion with approximate $E_{1/2}$ values of −1.51 and −1.99 V, respectively, versus Cp_2Fe^+/Cp_2Fe^0.[11]

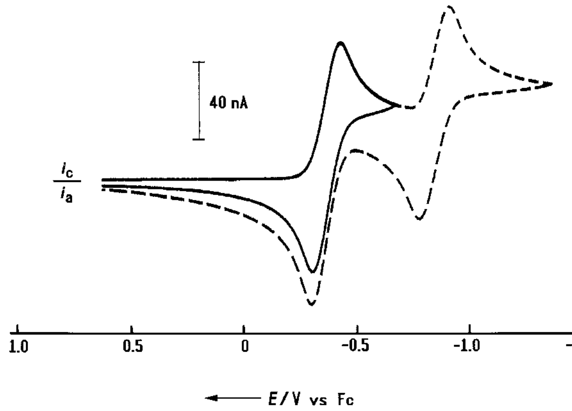

Figure 3. CV scans (scan rate 0.2 V s^{-1}) of 1 mM anthroquinone in *tert*-butyl methyl ether/0.075 M $[NBu_4][B(C_6F_5)_4]$ at ambient temperature (Pt electrode, 2 mm). The dashed line is obtained when the scan is extended to more negative potentials. Fc = Cp_2Fe^+/Cp_2Fe^0.

The decreased resistivities of low-polarity solvents containing $[NR_4][B(C_6F_5)_4]$ salts and the concomitant lowering of iR_u (ohmic) losses[12] also allow voltammograms of greater accuracy to be recorded at conventional electrodes, compared to analogous solutions with the traditional anions. The resistivity of 0.10M $[NBu_4][B(C_6F_5)_4]$ in THF at 295 K is 490 Ω cm, compared to 2300 Ω cm for the same concentration of $[NBu_4][ClO_4]$.[9] At a 2-mm Pt disk electrode, the Cp_2Co^+/Cp_2Co^0 couple showed a peak separation of 158 mV in $[ClO_4]^-$-containing media (scan rate 0.2 V s^{-1}, 1 mM Cp_2Co^+) compared to a separation of 78 mV in $[B(C_6F_5)_4]^-$-containing media under identical conditions (0.1 M supporting electrolyte). The latter more closely approaches the value of 61 mV[13] expected for this system.[14] The new family of electrolytes raises expectations that faster heterogeneous electron transfer rates may be measured in low-polarity media,[15] in addition to aiding mechanistic studies through increased accuracy of diagnostic parameters such as peak potentials and voltammetic wave shapes.[16]

There is no reason to think that $[NBu_4][B(C_6F_5)_4]$ is the optimum supporting electrolyte for all electrochemistry in low-polarity media, and analogues specifically designed to meet the needs of other redox systems are easily envisioned. When combined with ultramicroelectrode technology,[17] which already minimizes problems of ohmic loss, and advances in the use of very small concentrations of supporting electrolytes,[18] this family of salts holds significant promise in aiding further advances in applications of electrochemistry.[19]

Experimental Section

Experiments were carried out under a nitrogen atmosphere using Schlenk or dry-box conditions, and solvents were dried and distilled, except for *tert*-butyl methyl ether, which was used as received (Aldrich, anhydrous). $[NBu_4][B(C_6F_5)_4]$ was prepared by metathesis of an aqueous solution of $Li[B(C_6F_5)_4] \cdot n Et_2O$ ($n = 2-3$) (Boulder Scientific Co.) with a solution of $[NBu_4]Br$ in methanol. The precipitate was washed with water, dried under vacuum, and recrystallized several times from CH_2Cl_2/Et_2O (purified yield ca. 70%). Conductance values were obtained with a YSI Model 3200 conductance meter and a conductivity cell with a cell constant of 0.1 cm^{-1}. Voltammetry was performed using a Princeton Applied Research Model 273 potentiostat without ohmic compensation. A standard three-electrode cell configuration was employed using working electrodes composed of polished disks (Pt or glassy C), a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode.

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Combinatorial Synthesis of Four-Helix Bundle Hemoproteins for Tuning of Cofactor Properties**

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The aim of protein design is to create novel proteins with tailored structural and functional properties. Besides a rational approach by site-directed mutations of known proteins, a general strategy is to generate a large pool of different molecules and to screen this library for single substances with the desired properties. This goal is realized by phage display

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