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Use of Medium Effects to Tune the $\Delta E_{1/2}$ Values of Bimetallic and Oligometallic Compounds

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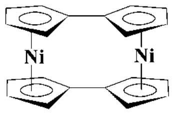
Received February 27, 2002

Differences in the formal potentials of successive one-electron redox processes play a crucial role in both the mechanistic and synthetic aspects of multielectron reactions.[1] The $\Delta E_{1/2}$ values[2] (and corresponding comproportionation constants, K_{comp})[3,4] of linked redox systems are commonly used as a guide to the extent of the electronic interaction between electron-transfer sites,[5,6] despite interpretive ambiguities.[5c,6] Although the effects of both solvents[7] and counterions[8] on $\Delta E_{1/2}$ values may be large,[9] there has been little systematic investigation of the combined medium effects in low polarity[10,11] solvents. On the basis of measurements employing large-anion supporting electrolytes, we now report that systematic alteration of medium effects can regulate the $\Delta E_{1/2}$ values in molecules having multiple redox sites.



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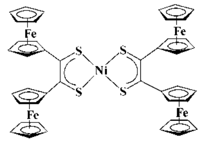

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Bis(fulvalene)dinickel, **1**,[12] is a convenient model with which to probe medium effects of anodic processes. This compound is known[13] to undergo two reversible one-electron oxidations (eqs 1 and 2)

$$\mathbf{1} \rightleftharpoons \mathbf{1}^{+} + e^{-} \qquad E_{1/2}{}^{1} \tag{1}$$

$$\mathbf{1}^{+} \rightleftharpoons \mathbf{1}^{2+} + e^{-} \qquad E_{1/2}{}^{2} \tag{2}$$

at potentials that are accessible in most electrolytes ($E_{1/2}{}^{1} = -0.708$ V, $E_{1/2}{}^{2} = -0.228$ V in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$, all potentials referenced to $Cp_2Fe^{0/+}$). Our results show that the positively charged anodic products, $\mathbf{1}^{+}$ and $\mathbf{1}^{2+}$, are sufficiently long-lived and soluble to allow facile measurement of $\Delta E_{1/2}$ values by cyclic voltammetry (CV), square wave voltammetry (SWV), and differential pulse (DP) voltammetry.[14] The mixed-valent cation $\mathbf{1}^{+}$ is intrinsically delocalized,[15] making it unlikely that any variations in $\Delta E_{1/2}$ arise from changes in the Robin/Day electronic delocalization class[16] of $\mathbf{1}^{+}$.

We have measured the $\Delta E_{1/2}$ values for **1** in representative solvents containing one of three types of anions categorized according to size and ion-pairing abilities: (i) a small, comparatively strongly ion-pairing halide (usually Cl^-), (ii) an intermediate-sized anion of the type traditionally employed[17] in nonaqueous electrochemistry (e.g., $[PF_6]^-$, $[BF_4]^-$), and (iii) a large weakly coordinating anion[18] such as $[B(C_6F_6)_4]^-$ or $[B(C_6H_3(CF_3)_2)_4]^-$. In CH_2Cl_2 using $[NBu_4]^+$ counterions (Table 1 and Supporting Information), very large increases in $\Delta E_{1/2}$ are observed as the anion is changed from category (i) to (ii) to (iii). The increases arise primarily from shifts of $E_{1/2}{}^{2}$ to more positive potentials, owing to diminishing ion-pairing of $\mathbf{1}^{2+}$ with anions of increasing size. In CH_2Cl_2, the $\Delta E_{1/2}$ value observed when using the $[PF_6]^-$ salt (480 mV) is closer to that observed using Cl^- (273 mV) than those measured with the large anions $[B(C_6F_5)_4]^-$ (753 mV) or $[B(C_6H_3(CF_3)_2)_4]^-$ (744 mV). The largest $\Delta E_{1/2}$ value (850 mV) was measured in a saturated (ca. 20 mM) solution of $Na[B(C_6H_3(CF_3)_2)_4]$ in CH_2Cl_2. The increase of this last $\Delta E_{1/2}$ value by about 100 mV over that observed in $[NBu_4][B(C_6H_3(CF_3)_2)_4]$ may be primarily traced to competition between $\mathbf{1}^{2+}$ and Na^+ for the $[B(C_6H_3(CF_3)_2)_4]^-$ anion, which further reduces the already weak ion-pairing interaction of $\mathbf{1}^{2+}$ with $[B(C_6H_3(CF_3)_2)_4]^-$. The smallest value of $\Delta E_{1/2}$ measured to date for this system is 212 mV in anisole/$[NBu_4]Cl$. The minimum and maximum observed values of 212 mV and 850 mV represent a change from 3.9×10^{3} to 2.5×10^{14} in the values of K_{comp}.

A similar strategy may be employed to increase the sequential K_{comp} values for a complex containing a larger number of electronically interacting redox sites. The tetrakis(ferrocenyl)−nickel dithiolene complex **2**[19] may display up to six one-electron features arising from four ferrocenyl-based oxidations and two Ni dithiolene-based[20] reductions (eq 3). In CH_2Cl_2 containing the traditional salt $[NBu_4][PF_6]$,

$$\mathbf{2}^{4+} \xrightleftharpoons{E_{1/2}{}^{4}} \mathbf{2}^{3+} \xrightleftharpoons{E_{1/2}{}^{3}} \mathbf{2}^{2+} \xrightleftharpoons{E_{1/2}{}^{2}} \mathbf{2}^{+} \xrightleftharpoons{E_{1/2}{}^{1}} \mathbf{2} \xrightleftharpoons{E_{1/2}{}^{1-}} \mathbf{2}^{-} \xrightleftharpoons{E_{1/2}{}^{2-}} \mathbf{2}^{2-} \tag{3}$$

($E_{1/2}$ values of 0.29 V, 0.23 V, 0.12 V, 0.0 V, −0.68 V, and −1.46 V for $E_{1/2}{}^{4}$ through $E_{1/2}{}^{2-}$, respectively) the four one-electron oxidations are closely spaced, with a total of ca. 292 mV separating the first and fourth anodic processes (adsorption of $\mathbf{2}^{4+}$ tends to occur at Pt electrodes). As shown in Figure 1, the total spread of the four ferrocenyl-based $E_{1/2}$ potentials increases to 510 mV in CH_2Cl_2/$[NBu_4]$ $[B(C_6F_6)_4]$ and then to 682 mV in CH_2Cl_2/$Na[B(C_6H_3(CF_3)_2)_4]$. All four oxidation processes give stable and soluble cations and polycations when the large fluoroarylborate anionic electrolytes are used, making it feasible now to perform spectral characterization of the sequential oxidation products of **2** and its analogues.[21]

The factors which *maximize* the $\Delta E_{1/2}$ values for the *oxidation* processes of **2** (principally, solvent of low polarity and low donor number,[22] large anion and small cation supporting electrolyte) are expected to *minimize* the $\Delta E_{1/2}$ values for its *reduction* processes, owing to preferential and increasingly stronger ion pairing of a small cation such as Na^+ with the dianion $\mathbf{2}^{2-}$. Indeed, we observe a lowering of $E_{1/2}{}^{1-} - E_{1/2}{}^{2-}$ from 770 mV in CH_2Cl_2/$[NBu_4][B(C_6H_3(CF_3)_2)_4]$ to 472 in THF/$Na[B(C_6H_3(CF_3)_2)_4]$, and then to 183 mV

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10.1021/ja020309d CCC: $22.00 © 2002 American Chemical Society

Table 1. $E_{1/2}$ Values (Volt vs $Cp_2Fe^{0/+}$) for Two One-Electron Oxidations of Bis(fulvalene)dinickel, **1** (Precision ±5 mV)

solvent–electrolyte[a]	$E_{1/2}{}^1$	$E_{1/2}{}^2$	$\Delta E_{1/2}$ (mV)	K_{comp}
anisole- $[NBu_4]Cl$	−0.561	−0.773	212	3.9×10^3
CH_2Cl_2-$[NBu_4]Cl$	−0.460	−0.733	273	4.1×10^4
DMF-$[NBu_4]Cl$	−0.435	−0.733	298	1.1×10^5
CH_3CN-$[NBu_4][PF_6]$	−0.223	−0.682	459	5.8×10^7
CH_3CN-$[NBu_4][B(C_6F_5)_4]$	−0.203	−0.683	480	1.3×10^8
CH_2Cl_2-$[NBu_4][PF_6]$	−0.228	−0.708	480	1.3×10^8
CH_2Cl_2-$[NBu_4][B(C_6F_5)_4]$	+0.026	−0.727	753	5.4×10^{12}
anisole-$[NBu_4][B(C_6F_5)_4]$	0.00	−0.736	736	2.8×10^{12}
$CH_2Cl_2-Na[B(C_6H_3(CF_3)_2)_4]$	+0.120	−0.730	850	2.5×10^{14}

[a] Concentration of supporting electrolyte was 0.10 M except for CH_2Cl_2-$Na[B(C_6H_3(CF_3)_2)_4]$, (saturated solution, ca. 0.02 M).

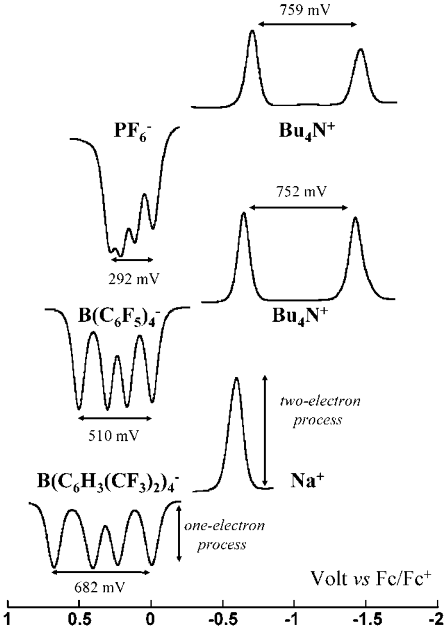

Figure 1. Differential-pulse voltammograms (pulse height 25 mV) of **2** in CH_2Cl_2: (top) 1 mM **2** and 0.1 M $[NBu_4][PF_6]$; (middle) 1 mM **2** and 0.1 M $[NBu_4][B(C_6F_5)_4]$; (bottom) 0.6 mM **2** and 0.02 M $Na[B(C_6H_3(CF_3)_2)_4]$.

in anisole/$Na[B(C_6H_3(CF_3)_2)_4]$. Finally (Figure 1), a *single* reversible wave of two-electron height[23a] ($E_{1/2} = -0.60$ V) is observed in $CH_2Cl_2/Na[B(C_6H_3(CF_3)_2)_4]$, nominally arising from nearly coincident values for the first and second one-electron reductions of **2**.[23b] There are precedents for strong ion pairing (or solvation) changes leading to two-electron waves through an EE mechanism with "potential inversion".[1] However, the organic or organometallic redox systems so studied generally undergo electron-transfer-induced structural changes which give rise to inherently modest $\Delta E_{1/2}$ values even in the absence of ion-pairing effects(e.g., $C_8H_8{}^{0/2-}$,[24] 1,1′-dinitrobiphenyl$^{0/2-}$,[25] lucigenin$^{2+/0}$,[26] $[(C_6Me_6)_2Ru]^{2+/0}$ [27]). We are unaware of similar findings for metal dithiolenes or analogous systems which begin with very large $\Delta E_{1/2}$ values (770 mV in the present case). Further investigations as to the scope and value of using combined solvent/electrolyte effects to control the electron-transfer stoichiometries (i.e., one- vs two-electron processes) of square planar complexes are in progress.

The present demonstration of very large medium effects on the separation of sequential $E_{1/2}$ values of the above two disparate compounds suggests that the use of $\Delta E_{1/2}$ measurements to assess the degree of electronic interaction between metal or other linked redox centers must be approached very judiciously.

Acknowledgment. Research at the University of Vermont was supported by the National Science Foundation (CHE 00-92702). We thank Dr. Eckhardt Schmidt for an initial sample of **1**.

Note Added after ASAP: Figure Caption 1 was incorrect in the version posted May 31, 2002; the corrected version was posted June 4, 2002.

Supporting Information Available: Square-wave voltammograms of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA020309D