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Substituent effects on alkylferrocenes in molten salt mixtures

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Abstract

The reduction potentials of five alkyl-substituted ferrocenes were determined in an *N*-(n-butyl)pyridinium chloride/aluminum chloride molten salt. By varying the substituent(s) on the cyclopentadienyl ring(s) of ferrocene, the reduction potential was caused to range over approximately 1.6 V. These changes are greater than have been observed for similar ferrocenes in other nonaqueous solvents. A close correlation of σ_p^0 constants with reduction potentials was observed for these compounds.

Introduction

Redox couples of certain ferrocenes in low temperature molten salts possess possible application as photoelectrochemical cells [1]. Both the potential of the redox couple as well as the solubilities of the various species in the melt are essential considerations in the design of such cells.

The following properties render $AlCl_3$/*N*-(n-butyl)pyridinium chloride (BuPyCl) mixtures ideal for specific electrochemical investigations: (1) they possess a voltage window of 2 V [2], (2) they are ionic conductors and (3) they are liquid below 30 °C over a range of compositions [3]. In addition, such melts possess variable acid–base properties which enhance their versatility as solvents [4].

Herein are described the results of electrochemical measurements of five alkyl-substituted ferrocenes in the 2/1 $AlCl_3$/BuPyCl melt. This is an acidic melt where $AlCl_4^-$, Cl^- and $Al_2Cl_7^-$ are in equilibrium [5]. Semi-quantitative correlation of the observed reduction potentials with σ_p^0 constants is found, in spite of the complexity of the substitution patterns of the five ferrocenes. Such substitution offers a convenient and effective method of controlling the redox potential of ferrocene; an impressive range of reduction potentials is available with this system (Table 1) [6*].

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* Reference number with asterisk indicates a note in the list of references.

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Table 1

Reduction potentials of certain alkylferrocenes

Substituted ferrocene	Reduction potential (±0.02 V) vs. Al
Decamethylferrocene (1)	−0.40
1,1′-Dimethylferrocene (2)	0.16
Ferrocene	0.28
2-Methyldimethylaminomethylferrocene methiodide (3)	0.37
2-Chlorodimethylaminomethylferrocene methiodide (4)	0.57
α,α-diphenylhydroxymethylferrocene (5)	1.23

Experimental

BuPyCl was prepared in 3-mole batches from pyridine and n-butyl chloride (Matheson, Coleman and Bell) [7]. Equimolar mixtures of the reactants were gently refluxed in the absence of light in an apparatus equipped with a drying tube. The product appears as long white crystals. When the reaction was about 70% complete, the mixture was cooled and the excess reactants decanted. The product was slurried in approximately 10% by volume of ethyl acetate, isolated on a Büchner funnel with suction, washed again with ethyl acetate and transferred moist to a vacuum oven. After drying at 70 °C for 48 h, the material was transferred to a glovebox for storage until use.

The molten salts were prepared by mixing weighed amounts of BuPyCl and aluminum chloride (Fluka) in a Vacuum Atmospheres glovebox under an argon atmosphere in which the moisture content was typically less than 1 ppm. The pre-electrolysis step generally removed most of the pale yellow color of the melt. Current-voltage curves were obtained using a potentiostat (Princeton Applied Research, Model 173) equipped with a plug-in coulometer unit (Model 179). A scan rate of 100 mV/s was utilized. Working and indicator electrodes were either glassy carbon (Tokai Electrode Manufacturing Co.) or tungsten rods (Materials Research Corporation). Reduction potentials were calculated using the formula $E^0 = 1/2(E_{pa} + E_{pc})$ [8].

Some of the ferrocenes listed in Table 1 were ordered from supply houses. In addition, the following ferrocenes were prepared by procedures described in the literature: 2-methyldimethylaminomethylferrocene [9], 2-chlorodimethylaminomethylferrocene [10], and α,α-diphenylhydroxymethylferrocene [11].

The methiodides of the two amines were prepared by conventional techniques.

Results and discussion

Cyclic voltammograms were measured for the ferrocenes listed in Table 1. The reduction potentials refer specifically to the 2/1 $AlCl_3$/BuPyCl molten salt versus an aluminum wire reference electrode immersed in the same electrolyte. The potential difference between anodic and cathodic current peaks was approximately 150 mV at 100 mV/s scan rate. While this is considerably greater than the 60 mV difference usually associated with a reversible electron transfer, ohmic losses in the

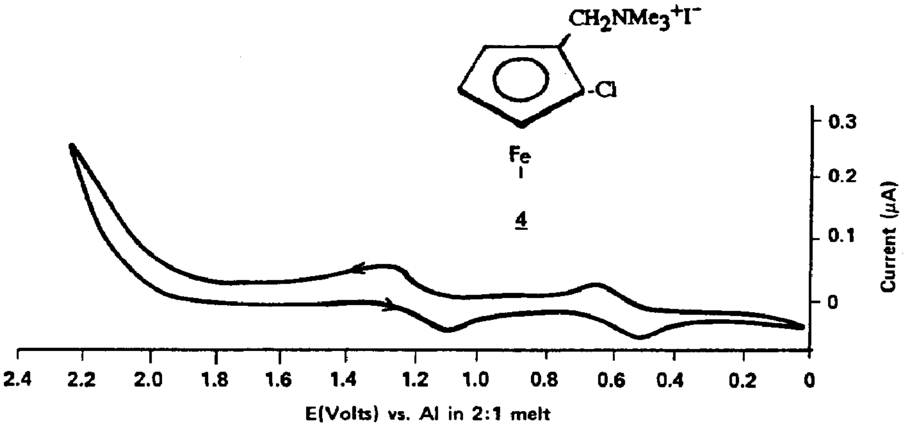

Fig. 1. Cyclic voltammogram of 2-chlorodimethylaminoferrocenemethiodide (4) on a tungsten electrode at 100 mV/s.

molten salt can account only to some extent for this apparent deviation from reversibility [12*].

Of particular interest was the effect on the redox potential of an electron-withdrawing trimethylammonium group. For methiodide **3**, the negative shift in redox potential associated with the methyl substituent was more than compensated for by the positive shift associated with the trimethylammonium group, despite the presence of an interspersing methylene. A slightly more positive potential was observed for methiodide **4**, which is consistent with the presence of both a moderate [$CH_2NMe_3^+$] and a weak [Cl] electron-withdrawing group on one ring (Fig. 1). Although this work was carried out using methiodide salts because of their ease of preparation, the chloride or bromide analogues would serve to avoid the undesirable feature of the proximity of the iodide/iodine and ferrocene/ferrocenium potentials in these melts. In Fig. 1, the more anodic wave is assigned to the iodide/iodine transition.

As has been observed for ferrocenes in other nonaqueous solvents [6], the electron-donating methyl substituents shift the reduction potential to values negative to that of ferrocene. Interestingly, the result is essentially cumulative; the two methyl groups in **2** shift the potential by -0.12 V whereas the ten methyl groups in **1** shift the potential by -0.68 V which is approximately five times as much. The low oxidation potential of decamethylferrocene is in accord with the concept of the pentamethylcyclopentadienyl ligand as a strong σ donor [13*].

The observation that the $CH_2NMe_3^+$ substituent more than offsets the electron-donating ability of the methyl group in **3** suggests that the $CH_2NMe_3^+$ group is a moderately strong electron-withdrawer. No σ or σ^0 constants for this substituent could be found in the literature. From the dimethyl compound **2**, the effect of a single methyl group can be calculated as -0.06 V; the fact that **3** has been shifted $+0.09$ V relative to ferrocene suggests that the overall effect of the $CH_2NMe_3^+$ group on the reduction potential of ferrocene is $+0.15$ V. This would translate into a σ_p^0 value of $+0.35$ and a σ_m^0 of $+0.15$ for this substituent [14*].

This result can be checked using compound **4**. The chlorine substituent has a σ_p^0 of 0.34 and a σ_m^0 of 0.37. Assuming a proportional relationship of the substituent constants, the contribution of a chlorine substituent to the reduction potential of

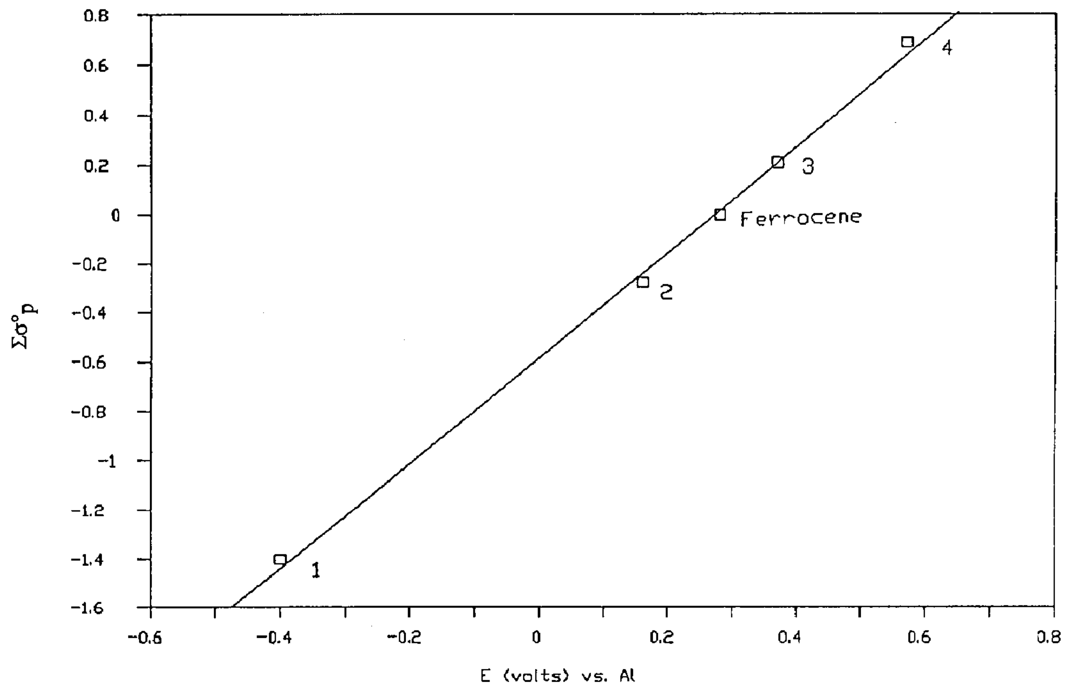

Fig. 2. Summation for multisubstituted ferrocenes of the Hammett σ_p^0 constants plotted against the reduction potential; $\Sigma\sigma_p^0 = 2.13 \pm 0.06E - 0.57 \pm 0.04$.

ferrocene is (0.34/0.35) × 0.15 V = 0.15 V. This coupled with the contribution of the $CH_2NMe_3{}^+$ group (0.15) yields a total effect of the two substituents of 0.30 V. The calculated reduction potential of **4** is thus 0.28 V + 0.30 V = 0.58 V which agrees well with the observed value for compound **4** of 0.57 V. A similar calculation utilizing the value for σ_m^0 provides poor agreement.

The correlation of σ_p^0 with the observed reduction potentials in these molten salts is impressive, particularly in view of the diversity of substitution patterns examined. Figure 2, a plot of σ_p^0 vs. reduction potential possesses a correlation coefficient of better than 0.99, which nicely illustrates the point. A much more detailed account of such correlations will be examined in our companion paper describing results for ferrocenes containing electron-withdrawing substituents in these molten salt mixtures [15].

For ferrocene substituted with a diphenylcarbinol substituent (compound **5**) a significant anodic shift was observed. It is likely that under these acidic conditions, the ferrocenylcarbinol has ionized to form $FcCPh_2{}^+$, where Fc stands for $C_5H_5FeC_5H_4{}^-$. The stability of α-ferrocenyl carbonium ions is well established [6]. Such a cationic species would be expected to have a much higher oxidation potential.

From this preliminary study it is apparent that these substituted ferrocenes meet many of the requirements for a redox couple in molten salts in that they exhibit quasi-reversible charge transfer characteristics, possess good solubilities in the melt (particularly the ammonium salts) and exhibit significant variation in their redox potentials. The effect of ring substitution on the stability of the ferrocenium ions cannot be accurately assessed at this point. It is pertinent to note, however, that no instability was noted in the cyclic voltammograms although at a scan rate of 100 mV/s only gross effects are expected to be observed [16*].

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