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Preliminary communication

METALLOCENE ELECTROCHEMISTRY

I. EVIDENCE FOR ELECTRONIC STABILIZATION WITH ALKYLATED CYCLOPENTADIENE: ELECTROCHEMICAL SYNTHESIS OF DECAMETHYLFERRICINIUM DICATION

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Summary

Constant potential coulometry at −0.1 V of decamethylferrocene in a 1.5/1 aluminum chloride/1-butylpyridinium chloride melt gave a deep brown solution containing the decamethylferricinium dication.

Although highly reactive nickel(IV) species have been produced by the 2-electron oxidation of nickelocene at −40°C [1,2], we are unaware of any literature reports that show it is possible to further oxidize a ferricenium cation to a discrete iron(IV) derivative with a formal d^4 electron configuration. Other Group VIII metallocenes, of ruthenium and osmium, have a greater stability toward oxidation than ferrocene, but each is known to undergo 2-electron oxidations [3]. It has been suggested that with increasing atomic number, the stability of the half-filled d^5 configuration of the single charged cations decreases and a doubly charged 16-electron cation becomes possible for the two heavier elements [4].

Previous attempts [5] to oxidize the unsubstituted η^5-$(C_5H_5)Fe^+$ cation in acidic** $AlCl_3$/1-butylpyridinium chloride (BPC) mixtures at room temperatures led to a multielectron irreversible wave just prior to the potential at which oxidation of the solvent itself occurs. This result is reproduced by us in Fig. 1a.

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**Acidic, i.e. >1/1 mol ratio, respectively. The acid-base behavior of these melts is discussed in greater detail in ref. 6.

The value of the ferrocene oxidation potential has been found to be independent of melt acidity [7]. Because its value is positive of the aluminum electrode at all acidities, its iron(II) oxidation state is unaffected by melt acidity changes. Contrary to this, cyclic voltammetry of decamethylferrocene (synthesized by the method of Bercaw and Threlkel [8]) reveals it is oxidized reversibly in basic $AlCl_3$/1-BPC melts at −0.292 V ($E_{1/2}$ versus Al reference, 2/1 melt) as illustrated in Fig. 1b and, accordingly, the acidic molten salt can spontaneously oxidise this iron(II) complex. A negative shift of the oxidation potential from that of ferrocene, $\Delta E_p \approx 530$ mV, induced by the introduction of 10 methyl groups to ferrocene, is expected and consistent with the additivity of the electron donating effect of the substituents [9]. Straw-colored solutions of $(\eta^5\text{-}C_5(CH_3)_5)_2Fe$ in a basic melt become green when the Lewis acidity is raised beyond the neutral 1/1 condition, or when subject to exhaustive oxidative coulometry. If a solution of $(\eta^5\text{-}(CH_3)_5C_5)_2Fe$ in an 0.8/1 melt is fully oxidized by constant potential coulometry at −0.1 V to $(\eta^5\text{-}(CH_3)_5C_5)_2Fe^+$ and the melt composition is then altered to 1.5/1 by the addition of $AlCl_3$, cyclic voltammetry reveals that a further 1-electron, reversible oxidation to $(\eta^5\text{-}(CH_3)_5C_5)_2Fe^{2+}$ ion is possible, $E_{1/2}$ + 1.387 V (Fig. 1c). The extent of charge delocalization in the formal iron(IV) complex is not known, however, the large potential difference between the two oxidation states ($\Delta E_{1/2} \approx 1.68$ V) implies that a significant energy barrier exists between the two oxidation states. Constant potential coulometry has confirmed that a stable, 2-electron product is obtained as a deep brown

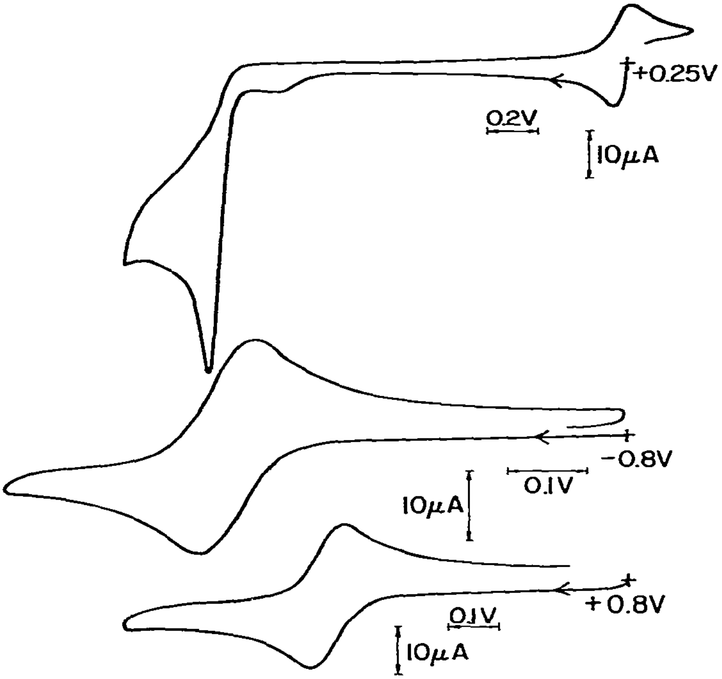

Fig. 1. Cyclic voltammograms of 9.5 mM $(\eta^5\text{-}C_5H_5)_2Fe$ in 1.5/1 melt, ν 50 mV/S (upper); 2.7 mM $(\eta^5\text{-}(CH_3)_5C_5)_2Fe$ in 0.95/1 melt, ν 200 mV/S (middle); and 2.7 mM $(\eta^5\text{-}(CH_3)_5C_5)_2Fe^+$ in 1.05/1 melt at 200 mV/S (lower); vitreous C electrode, reference Al wire in 2/1 melt.

solution, which retains its color for days under an argon atmosphere. Figure 2 illustrates electronic spectra of solutions of $(\eta^5\text{-}(CH_3)_5C_5)_2Fe$, the monocation, and dication. Addition of dried, redistilled acetonitrile to the brown solution of the dication in the drybox destroyed the color. It has been suggested that strong Lewis acid $AlCl_3$-based molten solvents can stabilize cation radicals [10] and in this case, too, it seems probable that the absence of a solvent nucleophile enables the dication species to exist.

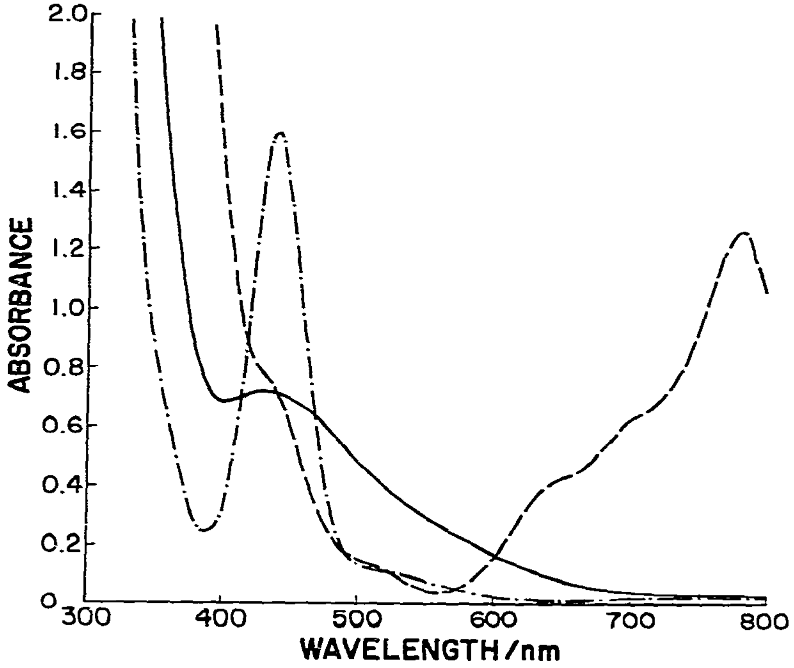

Fig. 2. Spectrum of 3.8 mM $(\eta^5\text{-}(CH_3)_5C_5)_2Fe$ in 0.8/1 melt (solid line); nominal 2.2 mM $(\eta^5\text{-}(CH_3)_5C_5)_2Fe^+$ in 1.5/1 melt from chemical oxidation (broken line); and nominal 0.3 mM $(\eta^5\text{-}(CH_3)_5C_5)_2Fe^{2+}$ in 1.5/1 melt after two $1\bar{e}$ coulometric oxidations (dot-dash line).

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