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Synthesis and Oxidation Potential of 3-Ferrocenylpyrrole

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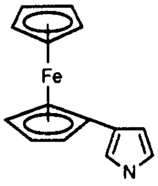
Ferrocene (Fc) is the archetypal organometallic redox compound because of its thermal and photochemical stability and reversible redox couple which can be utilized in both aqueous and nonaqueous systems. Its incorporation into conductive[1-5] and other polymer matrices[6,7] is being actively investigated for a wide range of applications including biosensors, reference electrodes, electro-optical devices, and electrocatalysts.[8,9] The redox potential of the Fc in these polymer hosts is always close to that of free or alkyl-substituted Fc. As part of a broader program to develop conductive polymers with electroactive groups,[10,11] we have recently synthesized 3-ferrocenylpyrrole, **1**, and characterized its electrochemical properties. We found **1** has the lowest oxidation potential of any ferrocene with a single organic substituent and is the first example of extensive electron delocalization between an electroactive substituent and a heterocycle commonly used to form electronically conducting polymers.



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The synthesis of **1** followed the procedure we reported recently for 3-(2,5-dimethoxyphenyl)pyrrole.[11] Ferrocenecarboxaldehyde was heated with ethyl cyanoacetate in the presence of piperidene to give the Knoevenagel condensation product, ethyl 2-cyano-3-ferrocenylacrylate,[12] which was converted to 2-ferrocenylsuccinonitrile by treatment with alcoholic KCN.[13] Reduction of the succinonitrile with diisobutylaluminum hydride, followed by hydrolysis, lead to **1**.[14] This synthesis not only leads to formation of a single product with the redox substituent at the 3-position but also allows introduction of chemically reactive species which cannot be incorporated with the more commonly used Friedel–Crafts reaction.

Figure 1 shows the cyclic voltammogram (CV) of **1** along with that for Fc.[15] The E_p^a value for Fc in our cell was 0.40 V vs SCE, in good agreement with the literature values.[16,17] The CV of **1** on a Pt electrode was reproducible with $E_p^a = 0.25$ V vs SCE and $E_p^a - E_p^c = \Delta E_p = 160$ mV. The value of i_p^a/i_p^c of 1.04 is very close to the expected value of 1.00 for a reversible reaction. Both $\Delta E_p = 160$ mV and $E_p^a - E_{p/2} = 90$ mV are larger than the expected value for a reversible reaction of 60 mV. However, since these same values were obtained with both **1** and Fc, the large value is attributed to the presence of uncompensated solution resistance between the reference and working electrode. There was no additional oxidation reaction observed as the positive limit was increased to 1.25 V vs SCE, as is customarily found with pyrrole and 3-substituted pyrroles. Repeated cycling to this upper potential limit, however, resulted in a shift of E_p^a to more positive potentials and almost complete loss of the cathodic wave indicating formation of an electroinactive film.

The E_p^a value of **1** is shifted 150 mV negative of that for Fc. We believe this is the largest negative shift observed for a ferrocene with a single organic substituent.[16,18-21] Table I lists the oxidation potential for several pyrroles and ferrocenes. The oxidation potential of the ferrocene *increased* when it was directly attached to the nitrogen in pyrrole as expected if the nitrogen lone pair is involved in the π-system of the ring giving the nitrogen a formal δ^+ charge and electron-withdrawing properties. Interestingly,

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(12) Ethyl 2-cyano-3-ferrocenylacrylate: purple crystals, mp 86–87 °C, yield 79%, IR (KBr pellet) 3106, 3025, 2990, 2926, 2215, 1719, 1586, 1273, 1248, 1190, 1092, 1047, 828 cm^{-1}.

(13) 2-Ferrocenylsuccinonitrile: orange-purple crystals, mp 89–90 °C, yield 72%, IR (KBr pellet) 3106, 3092, 2980, 2944, 2247, 1790, 1671, 1460, 1470, 1294, 1244, 1103, 1041, 1028, 1001, 824 cm^{-1}.

(14) 3-Ferrocenylpyrrole, **1**: orange crystals, mp 111–112 °C, yield of 21%, IR (KBr) 3463, 3403, 3094, 2961, 2921, 2869, 1127, 1103, 1013, 849, 818, 775, 710, 675, 646, 556, 540, 517 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.1 (b, 1H), 6.81 (d, 1H), 6.74 (d, 1H), 6.34 (s, 1H), 4.33 (t, 2H), 4.16 (t, 2H), 4.04 (s, 5H). Anal. Calcd for $C_{14}H_{13}NFe$: C, 66.96; H, 5.22; N, 5.58; Fe, 22.24. Found: C, 66.91; H, 5.50; N, 5.68; Fe, 21.80.

(15) Electrochemical measurements were done in a three-electrode cell using a Pt disk working electrode (area = 8×10^{-3} cm^2) and a Pt wire counter electrode. The reference electrode was a clean strip of Li metal in 0.1 M $LiClO_4$/propylene carbonate separated from the working and counter electrode compartment by a fine-porosity glass frit. The value of the Li^+/Li reference electrode is 3.06 V vs aqueous saturated calomel electrode (SCE) (Auborn, J. J.; Ciemiecki, K. T. *Proc. Symp. Lithium Batteries*; Day, A. N., Ed.; The Electrochemical Society: Pennington, NJ, 1984; Vol. 84-1; pp 363–373). All operations were done in a drybox filled with Ar.

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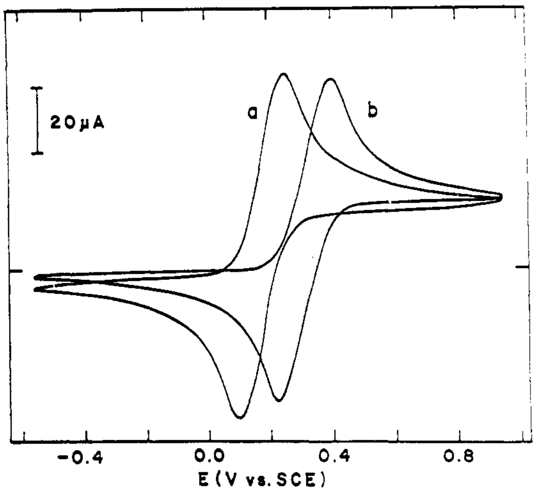


Figure 1. Cyclic voltammograms for (a) 3-ferrocenylpyrrole (0.04 M) and (b) ferrocene (0.04 M) in 0.1 M $LiClO_4/CH_3CN$ at a Pt disk electrode (area = 8 × 10^{-3} cm^2) at 25 °C and a sweep rate of 0.1 V/s.

Table I. Peak Potentials of Ferrocene and Pyrrole Derivatives[a]

compd	E_p^a (V vs SCE)	ref
1,1'-terferrocene	0.22[b]	22a
3-ferrocenylpyrrole, **1**	0.25	this work
terpyrrole	0.26	24
biferrocene	0.31[b]	22
(*p*-aminophenyl)ferrocene	0.32[c]	18
ferrocene	0.40	this work
N-ferrocenylpyrrole	0.45	3b
bipyrrole	0.55	24
pyrrole	1.2	this work

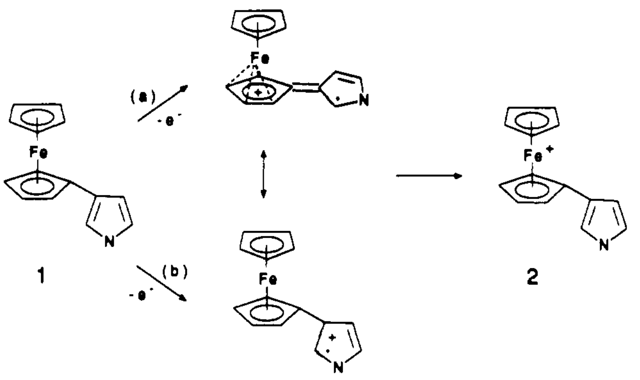
[a] Potential vs SCE measured in acetonitrile. [b] First oxidation potential. [c] Calculated from the shift in the reported $E_{1/4}$ value.

the oxidation potential of **1** is intermediate between that of biferrocene and 1,1'-terferrocene.[22] A reduction in the oxidation potential in ferrocene derivatives is generally associated with the electron-donating property of the substituent. In bi- and terferrocene each ferrocene acts independently as an electron donor with a "substituent" effect of -90 mV.[22]

We propose that the low oxidation potential of **1** results from the resonance through the π-conjugated system of the oxidized intermediate as shown in Scheme I. We are unable to distinguish if the electron is initially removed from the ferrocene (path a) or the pyrrole (path b). **1** is much more easily oxidized than pyrrole, itself, and most other pyrroles substituted at the 3-position.[23] For terpyrrole, however, where delocalization of the radical cation formed by the oxidation can be spread over the three-ring system, the oxidation potential is reduced by 904 mV.[24] If **1** is considered comparable to a "bipyrrole"-substituted pyrrole, the pyrrole could be the site of the initial oxidation.

Regardless of the mechanism of the initial electron transfer, the electron delocalization in the intermediate can be considered as a planar "fulvalene" resonance structure shown in Scheme I.

Scheme I



Such a resonance structure is sterically allowed for **1** where two five-membered rings are joined. A similar bicyclic planar resonance structure was recently proposed to explain the stability of the 1-ferrocenyl-1-cyclopropyl cation.[25] On the other hand, for the 3-hydroquinonylpyrrole system we studied previously,[11] eclipsing strain between the hydroxy group on the hydroquinone ring and the hydrogen on the 2-position of the pyrrole hinders formation of the analogous planar structure. Thus we did not observe a negative shift in the oxidation potential of 3-hydroquinonylpyrrole compared to either hydroxyquinone or pyrrole.

The para position of analine will have an enhanced electron density as is expected for the 3- and 4-positions of pyrrole. As seen in Table I, the oxidation potential for (*p*-aminophenyl)ferrocene is shifted negatively by 70 mV, which is the largest negative shift reported for a para-substituted phenylferrocene.[26] The factor of two larger shift for **1** thus indicates that more than just an inductive effect is involved and supports the importance of resonance in the intermediate leading to the ferrocenium product, **2**. The absence of a second anodic wave in the cyclic voltammogram even at potentials up to 1.25 V vs SCE is consistent with cation species **2** being more difficult to oxidize than neutral 3-substituted pyrroles. However, both the shift of the anodic peak to more positive potentials and the reduced current in the cathodic peak with successive scans indicate a homogeneous follow-up chemical reaction of **2** leading to species which passivate the electrode.

Thus far we have been unable to make homopolymers or copolymers of **1**. The formation of polymeric films was also not observed in the electrochemical oxidation of terpyrrole although there was some oligomer formation.[27] Since polymer films have been electrochemically formed from monomers with substituents even larger than ferrocene, we suspect that the failure to grow films from **1** is due to electronic, rather than steric, effects. For example, the absence of film formation from terpyrrole was attributed to the stability of the radical cation which moved away from the electrode rather than being "trapped" by another radical cation on the electrode surface. We are continuing our attempts to electropolymerize **1** to form poly(3-ferrocenylpyrrole) and characterize its expected interesting spectral and electrochemical properties.

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