

The Anomalous Electrochemistry of the Ferrocenylamines

Wayne E. Britton,* Ram Kashyap, Maher El-Hashash, and Mohammed El-Kady

Programs in Chemistry, The University of Texas at Dallas, P.O. Box 830688, Richardson, Texas 75083-0688

Max Herberhold*

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 3008, D-8580 Bayreuth, West Germany

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The electrochemistry of the ferrocenylamines has been studied and compared with a number of other substituted ferrocenes. The amine substituent acts as an unusually potent activating group for ferrocene oxidation, as shown by various Hammett-type correlations, with ferrocenylamine oxidizing at a potential 0.37 V more negative than ferrocene itself. Included in this study is triferrocenylamine, a compound with a nearly planar nitrogen. It produces three reversible oxidation waves, the first of which is 0.31 volts negative of ferrocene's oxidation. These and other data suggest that resonance interaction between ferrocene and the nitrogen lone pair is an important factor in ferrocene oxidation. This contrasts with conclusions of earlier studies in which ferrocenes, with primarily electron-withdrawing groups, were examined.

Introduction

During the last 25 years numerous studies have been reported concerning the effects of substitution on the properties of ferrocenes.¹⁻¹⁴ Correlations of ferrocene oxidation potentials with various Hammett-type σ constants suggest that the primary mode of interaction is inductive rather than through resonance.^{7,15} For example, phenyl-substituted ferrocenes do not correlate well with Brown's σ^+ values, which measure primarily resonance effects,¹⁶ but good correlations with Hammett's σ_p (derived from the dissociation of para-substituted benzoic acids) or Taft's σ_p^o values¹³ are found, which measure more of the inductive component.¹⁷ The latter constants are determined from systems in which the substituent and reaction site resonance interaction is prevented by the introduction of an insulating methylene group.

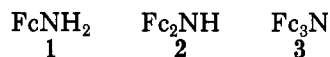
Several studies have included ferrocene derivatives in which nitrogen is bonded directly to the cyclopentadienyl ring and have found anomalous results^{7,13} for these com-

Table I. Measured E^o Values and σ Constants

ferrocene subst	$E^o,^a$ V	Hammett σ_p^b	Taft $\sigma_p^o,^c$	Brown $\sigma^+,^d$
(CH ₃) ₁₀	-0.566	-1.7	-1.5	-3.1
OEt	-0.01	-0.24		
OPh	-0.01	-0.320		-0.5
I	0.155	0.18	0.27	0.135
Cl	0.165	0.227	0.27	0.114
Br	0.168	0.232	0.26	0.150
CO ₂ H	0.235	0.45		0.421
H	0	0	0	
COPh	0.245	0.429		
COCH ₃	0.248	0.502	0.40	
CN	0.365	0.660	0.63	0.659
Ph	0.025	-0.01	0.04 ^e	-0.179
1,1'-diphenyl	0.04	-0.02	0.08 ^e	-0.358
CHO	0.283			
NH ₂	-0.37	-0.66	-0.38	-1.3
OCH ₃	-0.01 ^f	-0.268	-0.16	-0.778

^a Measured in Baker HPLC acetonitrile containing 0.1 M sodium perchlorate. Potentials vs. oxidation potential of ferrocene.
^b Reference 29. ^c Reference 17. ^d Reference 16. ^e Reference 30.
^f Assumed to be equal to ethoxy.

pounds. However, a recent paper by Stahl, Boche, and Massa¹² on the oxidation of 1,1'-bis(dimethylamino)-ferrocene found that the oxidation potentials correlate reasonably well with Hammett's σ_p parameters. We wish to report our results on the three ferrocenylamines 1-3 and compare their electrochemistry with other substituted ferrocenes. Of particular interest is the unusual triferrocenylamine (3)¹⁸ which contains an almost planar nitrogen and whose oxidation potential is more positive than expected from that of the other two ferrocenylamines 1 and 2.



Results

The series of substituted ferrocenes¹⁹ (Table I) investigated is shown in Figure 1, which is a plot of their E^o

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(19) Compounds were prepared according to literature procedures and gave analytical data and spectra in agreement with published data. The synthesis of the ferrocenylamines 1-3 is described in ref 31.

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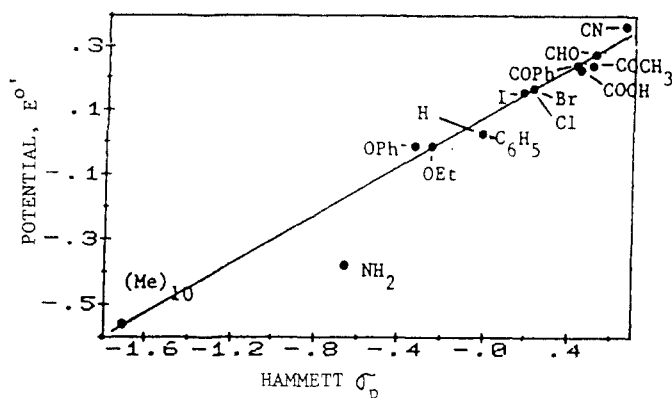


Figure 1. Oxidation potential of substituted ferrocenes vs. Hammett constant, σ_p .

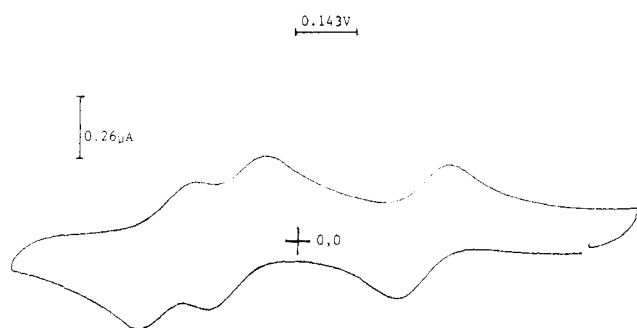


Figure 2. Cyclic voltammogram of triferrocenylamine in acetonitrile containing 0.1 M NaClO_4 (scan rate is 100 mv/s; potential vs. ferrocene).

values (measured vs. ferrocene oxidation) against the Hammett substituent constant, σ_p . The equation for the regression line (aminoferrocene not included) is $E^{\circ'} = 0.38 (\sigma_p) + 7.0 \times 10^{-2} \text{ V}$, with a correlation coefficient of 0.990. Correlations with Brown's σ^+ values are significantly poorer, indicating less importance for resonance effects. However, σ^+ values were not available for all compounds (see Table I). Tables I and II summarize our electrochemical data on a number of ferrocene compounds.

The cyclic voltammogram for triferrocenylamine, Fc_3N (3) (Figure 2), shows three reversible oxidation waves. (All potentials in this paper are reported as $E^{\circ'}$ values vs. the oxidation potential of ferrocene. To convert to the SCE scale one adds 0.35 V to the values given here, which is the value we will use for the oxidation potential of ferrocene vs. SCE in acetonitrile.) The oxidations of the ferrocenylamines all appear to be diffusion controlled, since a plot of the peak current vs. the square root of the voltage scan rate is linear.²⁰

Discussion

The Anomalous Behavior of Ferrocenylamine, FcNH_2 (1). Figure 1 indicates that the correlation between $E^{\circ'}$ and σ_p is quite good for most of the substituted ferrocenes. Noteworthy are the results for the ferrocenyl ethers, as others had difficulties with these compounds.⁴ Decamethylferrocene also falls on the line while one might expect to find a deviation due to buttressing of adjacent methyl groups on the rings. The crystal structure shows that the methyl groups are bent away from the iron atom by an angle of 3.4° with respect to the ring planes. This would result in a different σ value for this methyl group. Apparently these structural perturbations have small effects on the oxidation potential, or there is some cancel-

lation of effects, since the oxidation potential correlates nicely with the other data.

In contrast with these and the other substituents examined, the amino group is clearly a bad actor here, as others have found for N-containing substituents.^{7,21} It is interesting that the $E^{\circ'} = -0.37 \text{ V}$ for ferrocenylamine intersects the correlation line of Figure 1 at $\sigma = -1.25$, which is very close to Brown's σ^+ value of -1.3 (Table I). This suggests that for the amine group resonance may be important in stabilizing the ferrocenium ion. (*N,N*-Dimethylamino)ferrocene also deviates from the correlation line ($E^{\circ'} = -0.36 \text{ V}$;²² $\sigma_p(\text{NMe}_2) = -0.83$), but less so than for the unmethylated amine.)

If such a picture is acceptable, it would also be expected to hold for the ethers, but as seen in Figure 1, they conform reasonably well to the other compounds in the series. It may be that the energy gained through resonance cannot pay back the energy cost for any restructuring or rehybridizing required. The nitrogen may overcome this threshold value and therefore find a unique stabilization pathway.

A system which also belongs in this discussion is 1,1'-bis(*N,N*-dimethylamino)ferrocene, whose electrochemistry was reported recently by Boche and co-workers.¹² This compound was oxidized reversibly in acetonitrile at -0.23 V vs. SCE (which corresponds to -0.63 V vs. ferrocene²²). If we include this in our correlation (Figure 1), the oxidation potential falls right on the line. (The correlation coefficient with this data point added is 0.994). Why this compound should fit with the other ferrocenes and the simple ferrocenylamine does not is unclear. A possible explanation follows.

Most of the substituents studied can interact with the ferrocene system via resonance, but most are electron-withdrawing groups. Resonance interaction would destabilize the oxidized species, therefore making conformations with significant resonance energies less important. In the past, almost all of the groups which were examined happened to be electron-withdrawing groups, giving one the impression resonance interactions were not important. It appears resonance can be important when it is stabilizing through electron donation to the oxidized iron center as is shown for the amine group. This explanation may allow us to rationalize the data of Boche et al. for 1,1'-bis(dimethylamino)ferrocene. Steric effects associated with methyl/cyclopentadienyl interactions may destabilize a structure in which the nitrogen lone pair was efficiently overlapped with the π system. Resonance would then not be as important a factor here in stabilizing the cation. As noted above, *N,N*-dimethylamino gives a better fit to the correlation than ferrocenylamine, which also supports this steric argument.

Comparison of the Electrochemistry of Ferrocenylamine (1), Diferrocenylamine (2), and Triferrocenylamine (3). Triferrocenyl (3) is an unusual molecule, as shown by its molecular structure.¹⁸ It contains three ferrocenyl groups surrounding an almost planar nitrogen atom. The N atom is 6 pm out of the plane, and the C_5 axes of the three ferrocenyl ligands point into different directions. One of the ferrocenyl groups has its C_5 axis nearly perpendicular to the plane defined by the three nitrogen carbon bonds. The short C(ring)-N bonds (average 141.4 pm) indicate some double-bond character between the nitrogen and the cyclopentadienyl ring.²³

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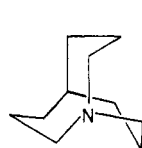
Table II. Comparison of the Oxidation Potentials of Ferrocenylamines^a

compd	E° , V	compd	E° , V
FcNH ₂ (1)	-0.37	Fc ₂ NH (2)	-0.36
FcNMe ₂	-0.36 ^b	Fc ₂ NPh	-0.28
FcNPh ₂	-0.23	Fc ₂ PPh	+0.16
Fe(C ₅ H ₄ -NMe ₂) ₂	-0.63 ^{b,c}	FcNH ₂ (1)	-0.37
Fe(C ₅ H ₄ -NPh ₂) ₂	-0.40	Fc ₂ NH (2)	-0.36
		Fc ₃ N (3)	-0.31

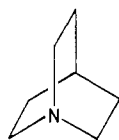
^a Conditions as in Table I. ^b Reference 22. ^c Cf. reference 12.

Apparently the steric effect associated with the three bulky ferrocenyl groups and/or π interaction between the nitrogen and the cyclopentadienyl rings along with crystal packing forces are responsible for this structure. That Fc₃N (3) is an unusual amine is shown by its lack of basicity in solution. (It should be possible for nitrogen to become tetrahedral in this system as the existence of tetraferrocenyl complexes such as Li[BFC₄]²⁴ and TiFC₄²⁵ has been reported, but the energy cost for a suitable tetrahedral structure with the amine is not known.)

We were interested in the possibility that nitrogen may be easier to oxidize than ferrocene in Fc₃N (3), since it is known that flat nitrogens are easy to oxidize.²⁶ For example, 1-azabicycloundecane contains a flat nitrogen and is almost as easy to oxidize as ferrocene, while oxidation of pyramidal nitrogen in the bicyclooctane example is much more difficult.



$E^{\circ} = 0.03$ V vs. ferrocene



$E^{\circ} = 0.61$ V vs. ferrocene

Another reason nitrogen may be easier to oxidize here is the well-known ability of ferrocene to stabilize positive charge on α -carbon atoms,²⁷ possibly through direct orbital interaction with iron. The corresponding aminium radical might be stabilized in a similar manner. However, the cyclic voltammetry data for the three ferrocenylamines 1-3 seem to indicate that the ferrocene system is undergoing the oxidation in all cases. Each system gives one reversible oxidation per number of ferrocenes in the molecule, and each has one irreversible oxidation typical in potential and reversibility for amines. In ferrocenylamine (1), this irreversible wave appears at ca. 1 V, and it moves positively for diferrocenylamine (2; 1.34 V) and again for triferoenylamine (3; 1.47 V), presumably because of the electron-withdrawing behavior of the ferricenium ions. To assign the first reversible oxidation to the amine group and the irreversible oxidation at such positive potentials to ferrocene is not reasonable. For example, Boche et al. find

(23) An even shorter C(ring)-N bond (134.7 pm) is found in TiCl₂(C₅H₄NMe₂)₂.¹²

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that the 1,1'-bis(dimethylamino)ferrocene gives a reversible oxidation for the ferrocene at only 0.9 V, yet it contains two positively charged α -substituents.

Our data for the oxidation of the substituted ferrocenes shown in Table II indicate that triferoenylamine (3) is significantly more difficult to oxidize than 1 and 2, the latter two compounds oxidizing at about the same potential. A small inductive effect of about 20 mV is expected for the first oxidation due to the ferrocenylamino group or the diferrocenylamino group, based upon the behavior of methylferrocene and diferrocenylmethane (-0.06⁴ and -0.04 V,⁶ respectively). This includes a statistical factor of 18 mV for the diferrocenylmethyl and diferrocenylamino systems. A larger statistical factor of 28 mV should work in favor of oxidation of triferoenylamine (3) and reduce the oxidation potential by 10 mV (28 - 18 mV). However, triferoenylamine (3) is significantly harder to oxidize than its two homologues, 1 and 2, and this is likely due to the unusual structure of the triferoenylamine.

A possible explanation is that there is a strong electronic interaction between the amine nitrogen and the ferrocenyl substituents, accompanied by some molecular distortion. This would require the ascent of a steric energy barrier for the sterically hindered triferoenylamine (3) but would not be important in the diferrocenylamine (2) or monoferrocenylamine (1) which could adopt unhindered conformations. Thus, both the facile reduction of ferrocenylamine and the anomalous behavior of triferoenylamine (3) are consistent with resonance interaction being an important factor in the stabilization of the ferrocenium ions by nitrogen.

The importance of the nitrogen lone pair interaction with the ferrocene is supported by other results shown in Table II. When a hydrogen or a methyl group on nitrogen is replaced with a phenyl ring, a competition between phenyl and ferrocene for the nitrogen lone pair is established, which is manifested in the positive shift in the ferrocene oxidation potential. Also compared in Table II are diferrocenylphenylphosphine and diferrocenylphenylamine. The data show that the substituted phosphorus acts as an electron withdrawing group. Electron donation by ferrocene to vacant 3d orbitals on phosphorus has been suggested on the basis of kinetic and X-ray crystallographic data²⁸ and is consistent with our observations here.

Acknowledgment. This work was aided by Grant AT-748 from the Robert A. Welch Foundation.

Registry No. 1, 1273-82-1; 2, 12770-46-6; 3, 80376-11-0; Fc-(CH₃)₁₀, 12126-50-0; FcOEt, 32627-00-2; FcOPh, 1294-11-7; FcI, 1273-76-3; FcCl, 1273-74-1; FcBr, 1273-73-0; FcCO₂H, 1271-42-7; Fc, 102-54-5; FcCOPh, 1272-44-2; FcCOCH₃, 1271-55-2; FcCN, 1273-84-3; FcPH, 1287-25-8; Fc-1,1'-Ph₂, 12098-13-4; FcCHO, 12093-10-6; FcOCH₃, 1273-87-6; FcNMe₂, 67251-69-8; FcNPh₂, 51156-30-0; Fc-1,1'-(NMe₂)₂, 75830-49-8; Fc-1,1'-(NPh₂)₂, 84976-01-2; Fc₂NPh, 84976-00-1; Fc₂PPh, 12278-69-2.

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