

PRELIMINARY STUDIES ON THE REDOX PROPERTIES OF
SUBSTITUTED FERROCENE COMPLEXES

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Summary

The electron donor/acceptor character of a variety of organic groups (X), $-\text{CH}(\text{R})(\text{NR}'_2)$, $-\text{CH}(\text{R})(\text{OR}')$, $-\text{CH}(\text{R})(\text{OCOR}')$, $-\text{CH}(\text{R})\text{N}_\text{X}$ and $>\text{C}=\text{Y}$, was investigated by studying the redox properties (by cyclic voltammetry), the electronic absorption and the ^1H n.m.r. spectra of substituted ferrocene complexes (FcX) with those groups as substituents. An ordering of these groups(X) according to their electron acceptor character was proposed on the basis of the electrochemical data, and the results were discussed in terms of the energy dependence of the involved molecular orbitals of FcX on the electronic properties of the substituent group(X).

I - INTRODUCTION

The oxidation potential of a complex reflects the energy difference between the oxidized and the reduced forms, although other effects should also be taken into account such as the differences in the solvation energies and in the heats of formation of those species.

If one considers the oxidation as resulting from the removal of an HOMO electron, a correlation between the energy of this orbital and $E_{1/2}^{OX}$ of the complex would be expected, within a series of closely related compounds. It also would be possible to relate $E_{1/2}^{OX}$ with other parameters which depend on (or affect) the HOMO energy, namely the ionizing energy of the central metal, the energy of the metal to ligand charge transfer band and parameters which may express the electronic effects of the ligands.

Such correlations have been observed for a variety of complexes and ligands with different substituents, and the subject has been reviewed⁽¹⁾.

However, the ligand substituents which have been reported present generally well defined electronic effects, and the purpose of the present work was to study the electron donor/acceptor properties of a variety of organic groups whose electronic features are not yet well understood.

Substituted ferrocenes (FcX where Fc denotes the ferrocenyl group and X stands for the ferrocene substituent at the cyclopentadienyl ring) are particularly promising for the purpose since a wide variety of substituents(X) are known with a considerable complexity and electronic effects remain yet to be fully studied.

II - EXPERIMENTAL RESULTS AND DISCUSSION

II.A - CYCLIC VOLTAMMETRIC STUDIES

The redox properties of the substituted ferrocene complexes (FcX) were studied by cyclic voltammetry at a Pt electrode in $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{thf}$. They usually present a one-electron quasi-reversible oxidation step ($E_{1/2}^{OX}$) followed, at a higher potential, by an irreversible oxidation wave.

They appear susceptible to be grouped in four different classes (Table 1), the X organic substituent ligating the cyclopentadienyl ring

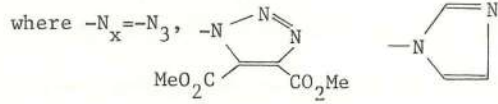
X	Class	Symbol	$E_{1/2}^{OX}$
-CH(R)(NR' ₂) -CH(R)(OR')	<u>A</u>	⊙	0.51-0.52
-CH(R)(O-C(=O)-R')	<u>B</u>	△	ca. 0.57
-CH(R)N _x where -N _x =-N ₃ , 	<u>C</u>	◇	0.57-0.63
-C=Y where Y=C<, W(CO) ₅	<u>D</u>	□	0.51-0.95

Table 1 - Types of ferrocene substituents (X) studied in the present work and half-wave oxidation potentials ($E_{1/2}^{OX}$) of the FcX complexes, $E_{1/2}^{OX}$ values in volt vs. s.c.e., measured at a Pt electrode in $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{thf}$.

through a carbon atom (denoted by C_α) which presents a sp³ (in classes A, B and C) or a sp² (in class D) hybridization.

In class A, the C_{α} also ligates an amine or an alkoxy group, whereas in class B it binds an ester group; in class C, an unsaturated poli-nitrogenated species (azide, triazene derivative or imidazolyl group) is present and in class D the C_{α} is unsaturated ($-C=Y$), Y being an organic or anorganometallic moiety (in the latter case the ferrocene substituent constitutes a ligand carbene at a transition metal centre).

The X substituents in classes A and B exhibit an inductive acceptor (-I) and a resonance donor (+R) effect, the latter predominating in the former class (with $E_{1/2}^{OX}$ at ca. 0.51-0.52 V, which is below the value found for unsubstituted ferrocene, FcH, at 0.55 V), whereas the inductive acceptor character of X dominates in class B with $E_{1/2}^{OX}$ above the ferrocene value in spite of the presence of the (+I,+R) electron donor R alkyl group.

Within each of these families of substituents, only a weak sensitivity of $E_{1/2}^{OX}$ on the R' group is observed, conceivably due to its considerable distance to the aromatic ring.

Complexes with C type substituents have $E_{1/2}^{OX}$ values which are higher than those observed for the previous classes, which suggests a stronger electron acceptor character of the unsaturated polinitrogenated group relative to the amine, alkoxy and ester groups.

Within class C, the trinitrogenated groups exhibit stronger electron acceptor character than the dinitrogenated imidoazolyl species.

The complexes with class D substituents (which are unsaturated at the α -carbon with a sp^2 hybridization) have $E_{1/2}^{OX}$ values spread over a much wider range (0.51-0.95 V) than those of the previous types; this behaviour may be rationalized on the basis of the stronger substituent effect on the ferrocenyl redox centre as a result of the interaction of the p_z orbital of the $sp^2 C_{\alpha}$ atom with the ferrocenyl π -system.

On the basis of the observed $E_{1/2}^{OX}$ values, the X substituents which were studied in this work may be ordered according to their electron acceptor character as shown in figure 1.

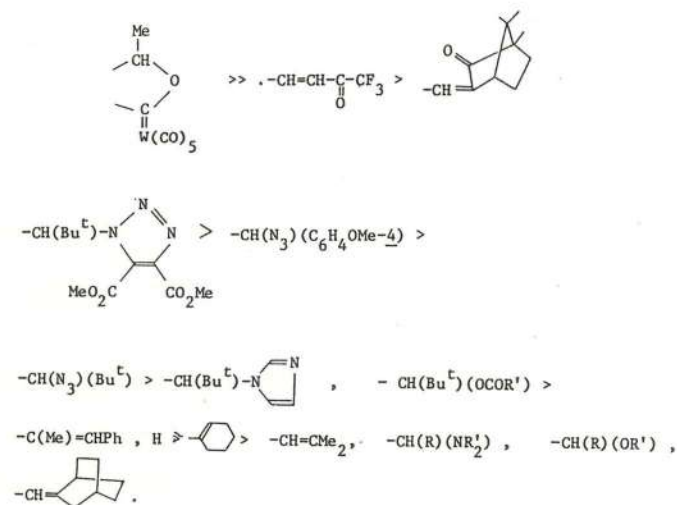
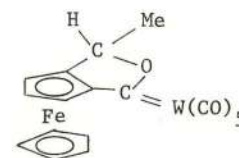


Figure 1 - Ordering of X substituents according to their electron acceptor character.

Within all the studied substituents, the strongest electron acceptor character is displayed by the carbene group of class D in the complex



which exhibits $E_{1/2}^{OX}$ at +0.95 V. The observed anodic shift (ca. 400 mV) relative to the ferrocene/ferricinium pair is even higher than that quoted by other authors⁽²⁾ in related ferrocenylcarbene complexes.

II.B - Electronic absorption spectroscopic studies. $E_{1/2}^{OX}$ versus energy of a metal to ligand charge transfer band

The electronic absorption spectra in thf were recorded for complexes of both the D and the A series, the former corresponding to a wide range of $E_{1/2}^{OX}$ and the latter with a high number of elements although with close $E_{1/2}^{OX}$ values.

Two bands were observed, one at $\lambda_1=423-518\text{nm}$ in the visible region, and the other, with higher intensity, at $\lambda_2=268-402\text{ nm}$ in the ultra-violet region. By analogy with studies reported by other authors,⁽³⁾ the former is ascribed to a metal d-d transition ($e_{2g} \rightarrow a_{1g}^*$) whereas the latter is believed to correspond to a metal to ligand ($e_{2g} \rightarrow a_{2u}^*$) charge transfer band.

The energy of this charge transfer band and $E_{1/2}^{OX}$ follow an inverse linear relationship as shown in figure 2. The point with the highest $E_{1/2}^{OX}$ value corresponds to the carbene substituent of class D, whereas the points with the lowest $E_{1/2}^{OX}$ values belong to class A substituents.

Since $E_{1/2}^{OX}$ of FcX increases with the electron acceptor character of the X substituent, these results may be rationalized in the following way: an increase of the electron acceptor character of X leads to a stabilization of the HOMO orbital (increase of $E_{1/2}^{OX}$) with a concomitant more pronounced lowering in the energy of the a_{2u}^* orbital (which has a strong ligand character) as suggested by the decrease of the energy difference between these two orbitals.

The higher sensitivity of the a_{2u}^* orbital (relative to e_{2g}) energy to a change in the X substituent agrees with the expected more intense electronic effect of X on the ligand rather than on the metal centre.

Similar correlations were previously reported for the isocyanide

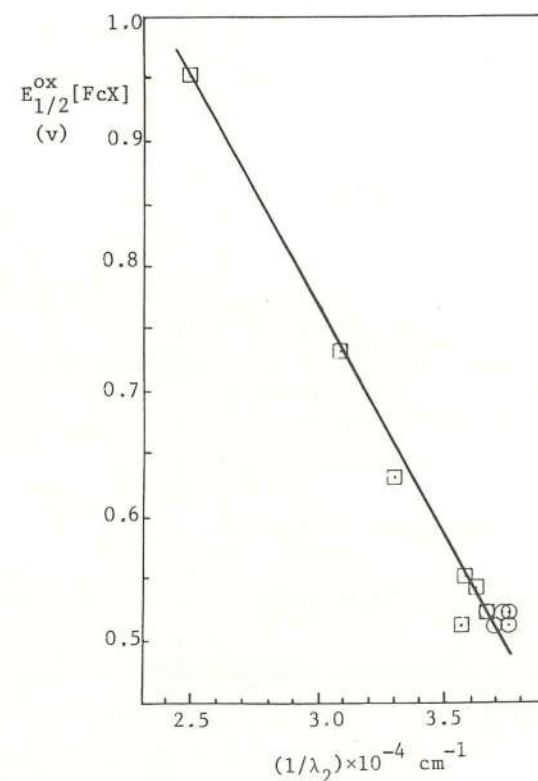


Figure 2 - $E_{1/2}^{OX}$ versus $1/\lambda_2$ in substituted ferrocene complexes (FcX).

complexes $\text{trans-}[\text{ReCl}(\text{CNR})(\text{dppe})_2]$ ⁽⁴⁾ and $\text{trans-}[\text{M}(\text{CNR})_2(\text{dppe})_2]$ (M=Mo or W).⁽⁵⁾

II.C - $E_{1/2}^{OX}$ versus $\delta(\text{C}_5\text{H}_5)$ in the ^1H n.m.r. spectra

A comparison between the variation of $E_{1/2}^{OX}$ and of the proton chemical shift (in the ^1H n.m.r. spectra) of the unsubstituted

cyclopentadienyl ring of FcX complexes was also undertaken in the present study.

In the complexes of each of the A, B or C series, in spite of the weak sensitivity of the $E_{1/2}^{OX}$ value to a change of substituent, a wide dependence of the abovementioned proton chemical shift on the substituent is observed (see figure 3).

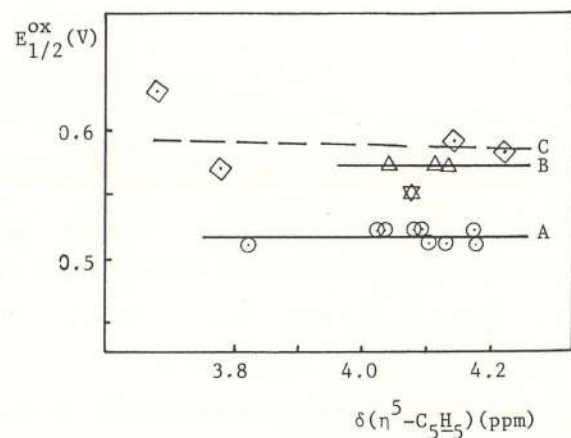


Figure 3 - $E_{1/2}^{OX}$ versus $\delta(C_5H_5)$ (1H n.m.r.) in FcX complexes (classes A, B and C).

However, in class D complexes, the approximate dependence between $E_{1/2}^{OX}$ and $\delta(C_5H_5)$ is apparent (figure 4): an increase of $\delta(C_5H_5)$ corresponds to an increase of $E_{1/2}^{OX}$, in agreement with the decrease of the electron richness of the ferrocenyl group (of both the cyclopentadienyl ligand and the metal centre) with the increase of the electron acceptor character of the substituent.

A relationship of a similar type between $E_{1/2}^{OX}$ and the proton chemical shift of the cyclopentadienyl ring has been reported⁽⁶⁾ for a series of bisocyanide complexes, $[Fe(\eta^5-C_5H_5)(CNC_6H_4X-4)_2]Br$.

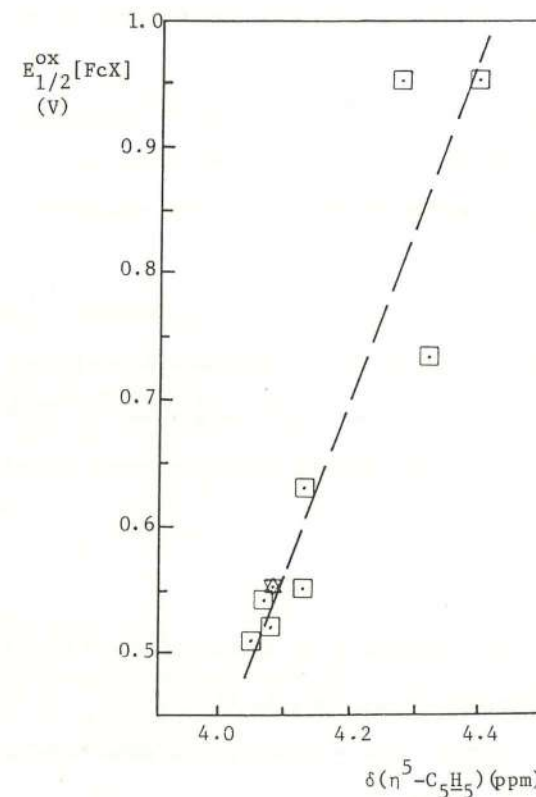


Figure 4 - $E_{1/2}^{OX}$ versus $\delta(C_5H_5)$ (1H n.m.r.) in FcX complexes (class D).

III - Final comments

From the abovementioned results a few preliminary conclusions may be derived, such as the following:

- In substituted ferrocene complexes with substituents bonded to the ring through a sp^3 carbon atom, a weak sensitivity of $E_{1/2}^{OX}$ to a variation of the substituent which involves β or γ atoms is observed. However, when the α carbon presents a sp^2 hybridization, being involved in an unsaturated bond with possible conjugation with the cyclopentadienyl

ring, a clear sensitivity of the redox centre to the substituent electronic effect is observed.

- On the basis of the $E_{1/2}^{ox}$ values, it is possible to order the substituents according to their electron acceptor character.

- For some types of substituents, $E_{1/2}^{ox}$ appears to be susceptible to correlation with the energy of the metal to ligand charge transfer band as well as with the proton chemical shift of the unsubstituted cyclopentadienyl ring.

These types of studies are currently being extended to other substituents on the aim to test these conclusions and to propose more general correlations, as well as to estimate values of Hammett's σ parameter for a variety of organic groups whose electronic effects are not yet well understood.

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ELECTROCHEMICAL REDUCTION OF VITAMIN B1 ON THE MERCURY ELECTRODE

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SUMMARY

The polarographic reduction of vitamin B1 was studied as a function of pH by using three different buffer solutions, namely, acetate, phosphate, and ammoniacal solutions. The results show the possibility of following electrochemically the transformations of thiamine in its yellow and thiole forms by measuring the height of the corresponding reduction waves for thiamine and its yellow form, and the height of the oxidation wave of the thiole form. A way of calculating the pK value of the transformation Th — YF is also suggested.

1 - INTRODUCTION

Vitamin B1, Aneurine or Thiamine, is a component of the B Complex of the water soluble group of vitamins. The absence of those vitamins in the human body causes serious disorders of the nervous system.

Chemically, Vitamin B1 is composed of a pyrimidine ring methylated in the C (2) position with an amine group at C (6). This ring is connected to thiazole ring through a methyl group at position C (5) on the pyrimidine ring and the nitrogen atom of the thiazole ring. The thiazole ring is methylated at the C (4) position and has a 2-hydroxyethylene group located on the C (5) position.

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