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REDOX POTENTIAL – HAMMETT'S σ OR TAFT'S σ* CONSTANT RELATIONSHIPS AT FERROCENE DERIVATIVES

M. EMÍLIA N.P. RODRIGUES, ARMANDO J.L. POMBEIRO[*]

Centro de Química Estrutural, Complexo I
Instituto Superior Técnico, Av. Rovisco Pais,
1096 Lisboa Codex, Portugal

RUDOLF HERRMANN

Organisch-Chemisches Institut, Technische
Universitat München, Federal Republic of Germany

Abstract

The redox potential of a variety of ferrocene derivatives has been measured by cyclic voltammetry and correlated linearly with the Hammett's σ_p or the Taft polar σ^* constant of the substituent; the latter correlation has been recognized for the sp^3-C ligating substituents.

Results and discussion

The redox bahaviour of ferrocene derivatives and the

substituent effects on their redox potential have been widely investigated [1]. However, such studies have commonly been performed on complexes with substituents presenting already known electron donor/acceptor properties.

In this study, we extend our preliminary investigation [2] of the redox properties of such compounds to a variety of substituents which may be of organic or bioorganic significance and, often, whose electron withdrawing/releasing character has not yet been clearly established.

The complexes can be represented by [FcX] where Fc denotes the ferrocenyl group $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)$ and X the ring substituent.

The substituents can be grouped in the following main classes:

- CHYZ (Y = H, alkyl, aryl, Fc or CN; Z = NR_2, OR, OCOR, unsaturated di- or tri-nitrogenated moiety, NR_3^+ or phosphinyl group);

- C(Y)=Z (Y = H or alkyl, Z = CR_2 or an isolobal organometallic group) or -COY.

These complexes, in tetrahydrofuran, CH_2Cl_2 or NCMe/0.2 M [Bu_4N][BF_4], at a Pt electrode, undergo, by cyclic voltammetry, a quasi-reversible one-electron anodic process centred at the iron centre.

For ferrocene derivatives with substituents presenting known values of the Hammett's σ_p constant and without any anomalous influence on the redox potential, a linear relationship was observed between $E^{ox}_{1/2}$ and σ_p [Figure 1 and equation 1, where δ_x is the half-wave oxidation potential (in V) relative to that of ferrocene].

An enhancement of the electron-acceptor character of the substituent (X), by resonance or inductive effects, leads to an increase of the oxidation potential of the complex, therefore to a stabilization of the HOMO.

$$\delta_x = 0.037 + 0.473\ \sigma_p \qquad (1)$$

Moreover, within substituents with a sp^3 hybridized ligating C atom (typically alkyls and α-aminoalkyls), $E^{ox}_{1/2}$ (or δ_x) varies linearly with the Taft's polar σ^* constant for aliphatic series
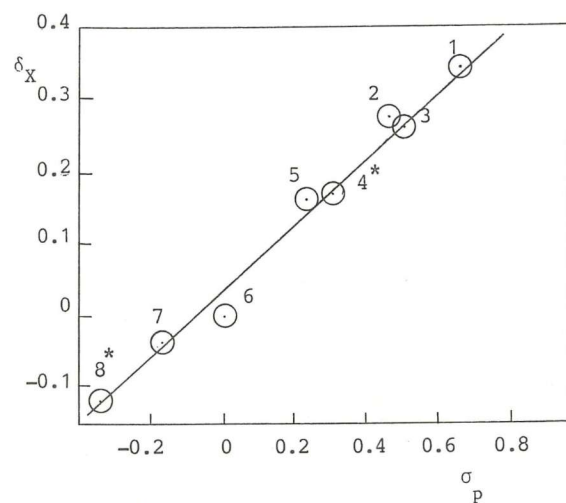
Fig. 1 - Plot of δ_X versus Hammett's σ_p constant for substituted ferrocenes [FcX]

$$\delta_X = E^{OX}_{1/2}\,[FcX] - E^{OX}_{1/2}\,[FcH]$$

Point	1	2	3	4*	5	6	7	8*
-X	-CN	-COPh	-COMe	1,1'-di(SH)	-Br	H	-Me	1,1'-di(Me)

* Disubstituted ferrocene; σ_p is considered to be additive.

(Figure 2), indicating the importance of the inductive effects for such a type of substituents; as expected, their resonance effects are not effectively transmitted to the aromatic ring through the sp³-C atom.
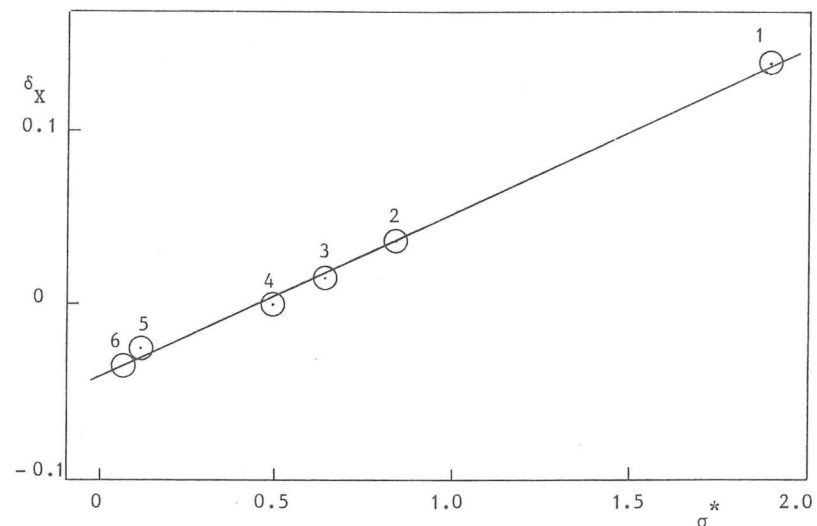
Fig. 2 - Plot of δ_X versus Taft σ^* constant for substituted ferrocenes [FcX] with sp³ ligating C substituents (X = = CHYZ).

Point	1	2	3
X	$-CH_2NMe_3^+$	$-CH(Bu^t)OCOMe$	$-CH(Pr^i)NHCO_2CMe_2CCl_3$
Point	4	5	6
X	H	$-CH(Bu^t)NH_2$	$-CH(Pr^i)NMe_2$

From the plots of figures 1 or 2, the Hammett's σ_p or the Taft σ^* constant was estimated for a number of substituents whose corresponding substituted ferrocenes were studied by cyclic voltammetry.

Related correlations have been reported by others, involving, e.g., the chronopotentiometric quarter-wave potential ($E_{1/4}$)[3].

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Spectroelectrochemistry characterization of the Trinuclear [Ru₃O(O₂CCH₃)₆(Pyrazine)₃]⁰,⁺ clusters

$$[Ru_3O(O_2CCH_3)_6(Pyrazine)_3]^{0,+}$$ clusters

Henrique E. Toma* and Cecilia Cipriano**

The chemistry of the trinuclear clusters $[Ru_3O(CH_3CO_2)_6L_3]$ where L = imidazole, pyridine or pyrazine type of ligands, was investigated based on spectroscopic and electrochemical techniques[1,2]. These complexes are of great interest[3] from the point of view of their electronic and redox properties, providing multisite species for electron transfer processes. They were isolated in solid state, and characterized by means of elementary analyses and infrared spectra.

The electrochemical behavior in acetonitrile solution was typically reversible; the cyclic voltammograms exhibited a series of four or five monoelectronic waves in the range of potentials from -1.8 to 2.0 V (fig. 1) ascribed to the sucessive $Ru^{IV}Ru^{III}Ru^{III}$ / $Ru^{III}Ru^{III}Ru^{III}$ / ... $Ru^{II}Ru^{II}Ru^{II}$ redox couples. The ratios of the anodic and cathodic peak currents are very close to unity. The separation between the anodic and cathodic peak potentials was approximately 60 mV at low potential scan rates (e.g. 20 mV s⁻¹), increasing up to 70 mV at 200 mV s⁻¹. A fifth wave was detected near the limiting potentials (2.4 V) in acetonitrile but the electrochemical response was much less reversible. The differences between the successive redox potentials were about 1 V, indicating strong metal-metal interaction in the trinuclear Ru_3O centre. A difference decreases from 1.0 to 0,45 V in the case of the redox couple involving the $Ru^{II}Ru^{II}Ru^{II}$ complex, which has no empty $d\pi$ orbital contributing to the electron delocalization in the trinuclear cluster. The E° values were strong sensitive to the nature of the N-heterocyclic ligand, increasing with the pi-acceptor properties of the pyridine and pyrazine derivatives, but in a much less pronounced way in the case of the imidazole derivatives. The redox potentials decrease linearly with the pka of the N-heterocyclic ligands. The variation is relatively small at high oxidation states, but increases rapidly as the oxidation states decrease, reflecting the role of π-backbonding in the complexes[4].

In order to characterize the chemical species involved in the electrochemical processes, spectroelectrochemical measurements were carried out for the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster in acetonitrile solutions. The electronic spectra exhibited three characteristic

*Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, SP (Brazil)
**Instituto de Química, Universidade Federal do Rio de Janeiro, 21910, Rio de Janeiro, RJ (Brazil)

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