A Study of Substituent Effect on the Redox Potential of *meso*-Substituted Octaethylporphyrins and their Zinc Complexes

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The first and second oxidation potentials of *meso*-substituted octaethylporphyrins are observed to follow a Hammett linear free energy relationship, with the ρ values an order of magnitude higher than those obtained for *meso*-substituted tetraphenylporphyrins.

The degree and mode of transmission of electronic effects from various points on the ring to the extended conjugated system of porphyrin rings has been a subject of intense investigation.[1] Kadish *et al.*[2—4] have reported on the electronic effect on the redox potential of a series of $H_2(p\text{-X})TPP$ (TPP = tetraphenylporphyrin; X = OMe, Me, H, F, Cl, CO_2Me, CN, NO_2). A linear relationship is observed between $E_{1/2}$ and Hammett σ values, with ρ values of the order of 6×10^{-2}.[2] In the $Co(p\text{-X})TPP$ series, the ρ value increases up to 1×10^{-1},[3] while in the $Fe(p\text{-X})TPP$ series the ρ value remains of the same order as that of the free base.[4] In this communication, we report our recent findings on the electronic effect of substituents directly attached to the porphyrin ring.

The electrode reaction we studied can be summarized by equations (1) and (2). The first and second oxidation potentials of ZnOEP (OEP = octaethylporphyrin) and free base OEPs are measured by cyclic voltammetry {with a 3-electrode system: reference, saturated Ag–AgCl; working electrode, glassy carbon; auxiliary electrode, Pt wire; solvent, CH_2Cl_2; [OEP], [ZnOEP] = 3×10^{-3} M; [TBAP] = 0.1 M (TBAP = tetrabutylammonium perchlorate)}. Good reversible waves were observed for the first oxidation potential, while less well-defined reduction waves were obtained for the second oxidation potential.

$$\text{MOEP} \rightleftharpoons \text{MOEP}^+ + e \qquad 1^{st} \text{ oxidation potential} \qquad (1)$$

$$\text{MOEP}^+ \rightleftharpoons \text{MOEP}^{2+} + e \qquad 2^{nd} \text{ oxidation potential} \qquad (2)$$

Plotting $E_{1/2}$ of the first and second oxidation potentials of the substituted porphyrins against the substituent constants,

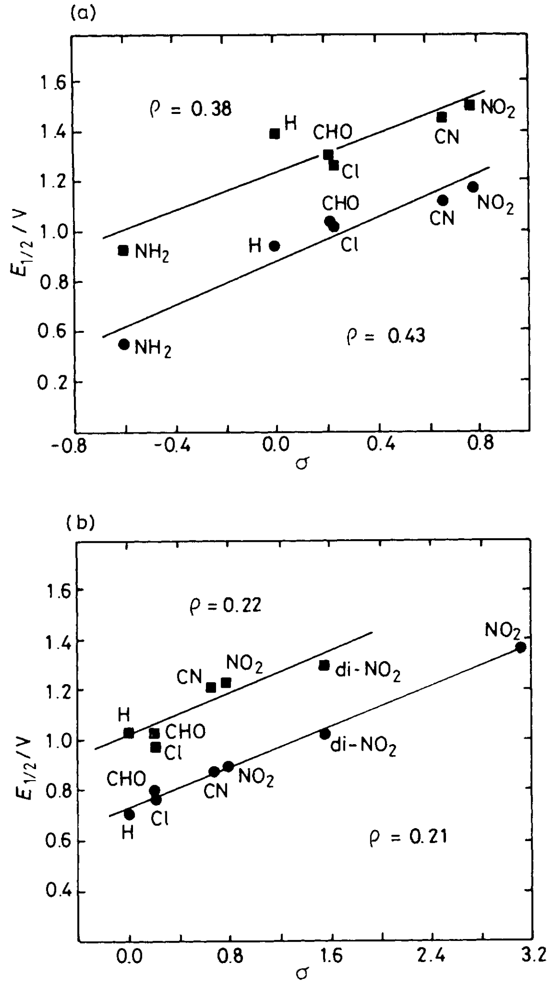

Figure 1. Hammett plots of $E^{ox}_{1/2}$ (1st) (●) and $E^{ox}_{1/2}$ (2nd (■) *vs.* σ values for (a) free base OEPs and (b) ZnOEPs.

i.e. σ values[5] yields four very good straight lines (Figure 1), agreeing well with the Hammett linear free energy relationship,[6] $E_{1/2} = \sigma\rho$. For the free base OEP, the reaction constants, which are a measure of the susceptibility of the electrode reaction to polar effects of the substituents, were $\rho = 0.43$ for the first oxidation potential (coefficient of correlation = 0.96), and $\rho = 0.38$ (coefficient of correlation = 0.91) for the second oxidation potential. For the ZnOEP series, we obtained values of $\rho = 0.21$ (coefficient of correlation = 0.99) and $\rho = 0.22$ (coefficient of correlation = 0.90) for the first and second oxidation potentials, respectively.

We note that the ρ values we obtained for the free base OEP are by far the highest ever observed in any porphyrin system. They are an order of magnitude higher than those of the TPP series. The low ρ values in the TPP series are probably due to the electron cloud of the phenyl ring being orthogonal to that of the porphyrin ring, thus diminishing to a large extent the resonance effect of the substituents on the porphyrin ring. By merely introducing substituents at the *meso*-position of the porphyrin ring, we have increased the first oxidation potential of the porphyrin by more than 1 V, thus greatly changing the redox properties of the compounds in their ground state, as well as in their excited state.

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