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A Study of Solvent and Substituent Effects on the Redox Potentials and Electron-Transfer Rate Constants of Substituted Iron *meso*-Tetraphenylporphyrins

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Abstract: The effect of substituents on the electrode reactions of para- and meta-substituted iron tetraphenylporphyrins was investigated by the technique of cyclic voltammetry. In all cases electron-donating substituents produce a more difficult reduction, as evidenced by a cathodic shift of the reversible polarographic half-wave potentials. For each reaction, a Hammett linear free-energy relationship was observed between the half-wave potentials, $E_{1/2}$, and the σ constants of the substituents on the four phenyl rings of Fe(p-X)TPP and Fe(m-X)TPP. Results in five nonaqueous solvent systems indicate a decrease in substituent effects on half-wave potentials with increase in solvent dielectric constant, and that an increase in the solvent complexing ability gives rise to an increased stability of the Fe(II) species relative to Fe(III). For almost all compounds investigated, the electron-transfer rate constants were larger for reactions at the porphyrin ring than those at the central metal. Electron-donating substituent were observed to increase the rate of electron transfer, suggesting that high electron density on the ring or metal is important in fast electron-transfer reactions of metalloporphyrins.

Studies of electron-transfer reactions involving iron porphyrins are of evident interest because of their importance as biological electron-transfer agents, especially in cytochromes.[2] In nonaqueous media, iron(III) porphyrins may be oxidized in two single electron-transfer steps[3-5] or reduced in three one-electron transfer steps.[6-8] The potentials and reversibility of the electrode reactions are dependent on solvent medium and axially coordinated ligands,[8,9] dimer formation,[10] and overall porphyrin basicity.[11-13] Recently, several studies have examined the effect of substituents on the chemical and physical properties of metalloporphyrins. These have included substituent effects on electronic absorption spectra,[14] equilibrium constants for addition of one or two axial ligands to the central metal of the metalloporphyrin,[15-19] and half-wave potentials of porphyrin redox reactions.[18,20-22]

In earlier papers we have quantitated the effect of substituents on the thermodynamic half-wave potentials for oxidation or reduction of +3 and +2 transition metal complexes of para-substituted tetraphenylporphyrins.[18,20] This paper concentrates on the electrode reactions of Fe(p-X)TPPCl to yield complexes of Fe(I), Fe(II), Fe(III), and Fe(IV), and includes a comparison of kinetic and thermodynamic substituent effects.

The electrode reactions described in this paper can be summarized as follows:

$$[Fe^{IV}P]^{2+} \rightleftarrows [Fe^{IV}P]^{3+} + e \tag{1}$$

$$[Fe^{III}P]^{+} \rightleftarrows [Fe^{IV}P]^{2+} + e \tag{2}$$

$$[Fe^{III}P]^{+} + e \rightleftarrows [Fe^{II}P]^{0} \tag{3}$$

$$[Fe^{II}P]^{0} + e \rightleftarrows [Fe^{I}P]^{-} \tag{4}$$

$$[Fe^{I}P]^{-} + e \rightleftarrows [Fe^{I}P]^{2-} \tag{5}$$

P is (p-X)TPP^{2-} or (m-X)TPP^{2-}, TPP^{2-} represents tetraphenylporphyrin, and X is an electron donating or withdrawing substituent placed at the para or meta position of the four phenyl rings, as listed in Table I. The species in eq 1-5 may be expected to be coordinated with solvent and/or an anion. The existence of these complexes is assumed when the notation $[Fe^{III}P]^+$ is used in this paper.

The Hammett linear free-energy equation[23]

$$\Delta E_{1/2} = 4\sigma\rho \tag{6}$$

describes shifts in half-wave potentials as a result of changing substituents. The value 4σ is the total of substituent constants, representing the sum of inductive and resonance effects of all substituents, and is dependent on the kind and position of the four substituents, one on each of the phenyl rings of substituted tetraphenylporphyrin complexes. The reaction constant, ρ, given in volts, measures the susceptibility of the electrode reaction to the polar effect of the substituents. Applicability of this equation in describing redox potentials of porphyrins has been discussed in previous publications.[18,20,21]

Experimental Section

The porphyrins listed in Table I were obtained from several sources.

Table I. Substituents and Values of 4σ for Para and Meta Iron-Substituted Tetraphenylporphyrins

Compd	Substituent	$4\sigma^{26}$
1	p-NO_2	3.12
2	m-CN	2.72
3	p-CN	2.64
4	p-$COOCH_3$	1.80
5	p-COOH	1.64
6	m-Br	1.56
7	m-Cl	1.48
8	m-F	1.36
9	m-OCH_2Ph	1.20
10	p-Cl	0.92
11	p-F	0.24
12	p-Ph	0.04
13	H	0.00
14	m-CH_3	−0.28
15	p-CH_3	−0.68
16	p-$C(CH_3)_3$	−0.80
17	p-OCH_3	−1.08
18	p-OH	−1.48
19	p-OCH_2Ph	−1.64

Table II. Reversible Half Wave Potentials of Fe(p-H)TPPCl Electrode Reactions in Various Solvents

	Potential, V vs. SCE				
Reaction[c]	CH_2Cl_2[a]	n-PrCn[a]	DMF[b]	Me_2SO[b]	DMA[b]
1	1.40	1.35			
2	1.14	1.17			
3	−0.29	−0.32	−0.15	−0.11	−0.11
4	−1.06	−1.06	−1.04	−1.14	−1.08
5	−1.63	−1.72	−1.61	−1.61	−1.66

[a] 0.1 M TBAP. [b] 0.1 M TEAP. [c] See text.

Tetraphenylporphyrin was purchased from Strem Chemical Inc. and was used without further purification. Initial samples of para-substituted tetraphenylporphyrins, where the substituent was p-OCH_3, p-CH_3, p-NO_2, p-F, p-Cl, and p-CN, were the generous gift of Dr. F. Ann Walker. The same compounds were also synthesized in these laboratories by the method of Adler et al.[24] Samples requiring further purification were chromatographed on alumina in chloroform or dichloromethane. Iron insertion was accomplished by refluxing the appropriate free base porphyrin with ferrous chloride in DMF for 45 min.[25] The solution was then allowed to cool to room temperature, poured onto ice, and filtered. The filtrate was washed with water, dried under vacuum at 90 °C, and then chromatographed on alumina in chloroform or dichloromethane. HCl gas was bubbled through the Fe(p-X)TPP fraction to destroy any μ-oxo dimers that may have formed. The fraction was then taken to dryness under vacuum. The starting compound for all electrochemical work was Fe(p-X)-TPPCl or Fe (m-X)TPPCl.

Methylene chloride ("Distilled in Glass", Burdick and Jackson Labs, Inc.) and dimethyl sulfoxide (Me_2SO) ("Spectro-quality", MCB) were used without further purification. Butyronitrile (MCB) was vacuum distilled, the middle 69% collected and stored over activated alumina under nitrogen. Dimethylformamide (DMF) was similarly treated immediately before use. Tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) (Southwestern Analytical Lab., Inc.) were recrystallized from methanol and vacuum dried over P_4O_{10} at room temperature. Deaeration was accomplished by passing high-purity nitrogen or argon through the solution for 10 min and blanketing the solution during analysis.

Cyclic voltammetric measurements were obtained with a three-electrode system with a PAR Model 174 polarographic analyzer and Houston Instruments Model 2000 recorder or a PAR Model 173 potentiostat, using a PAR Model 175 universal programmer and a storage oscilloscope. The working electrode was a platinum button and a platinum wire served as the auxiliary electrode. A commercial saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass disk. For rate measurements, a Luggin capillary was employed to reduce IR losses.

Values of 4σ used in this study are given in Table I, and were taken from Jaffe.[26] Reaction constants were evaluated by the least-squares best-fit method.

Results and Discussion

Figure 1 illustrates a typical cyclic voltammogram of $[Fe(p\text{-}H)TPP]^+Cl^-$ in CH_2Cl_2, 0.1 M TBAP. The four reversible diffusion-controlled peaks correspond to reactions 1-4. In the absence of strong axial coordination of ligands, $[Fe^{III}TPP]^+$ is known to undergo two diffusion-controlled oxidations to yield $[Fe^{IV}TPP]^{2+}$ (reaction 2) and the cation radical $[Fe^{IV}TPP]^{3+}$ (reaction 1).[3,4] The formal potentials of these reactions have been reported as occurring at 1.13 and 1.40 V in methylene chloride[4] and 1.17 and 1.38 V in butyronitrile.[5] The potential of $[Fe^{I}TPP]^-$ reduction to yield the anion radical varies only slightly with solvent and has been reported to occur at −1.61 V in DMF,[8,10] −1.68 V in Me_2SO,[9] −1.72 V in butyronitrile or pyridine,[9] and −1.61 V in DMF containing 10^{-3} M imidazole.[8]

In contrast to the small solvent dependence on electrode reactions involving reduction of Fe(I), the Fe(III) → Fe(II) transition is highly dependent on the coordinating ability of the solvent. This is illustrated in Table II, where half-wave potentials of reactions 1-5 are listed for several solvents. In strongly coordinating solvents[27] such as Me_2SO, DMA, and DMF the reduction occurs at −0.11, −0.11, and −0.15 V, respectively, while in poorly coordinating solvents such as methylene chloride and butyronitrile the half-wave potentials have shifted to −0.29 and −0.32 V, respectively. The cathodic shift of $E_{1/2}$ can be accounted for by an increased stability of $[Fe^{II}TPP]^0$ with coordinating solvents.[28]

A solvent dependence has also been observed for the $[Co^{III}TPP]^+/[Co^{II}TPP]^0$ reactions,[18] but in this case the potential shifts are in the opposite direction. The most difficult reduction occurs in Me_2SO and the most facile in butyronitrile and CH_2Cl_2. This is compatible with an increased stability of the oxidized form relative to the reduced; that is, $[Co^{III}TPP]^+$ increases in stability relative to $[Co^{II}TPP]^0$ with an increased solvent coordination ability.

Effect of Substituents on Thermodynamic Half-Wave Potentials. A plot of $E_{1/2}$ vs. 4σ for the compounds of Table I is shown in Figure 2. Nonlinear plots of $E_{1/2}$ vs. σ imply either a change in reaction mechanism or species involved in the electron transfer.[23] The nonlinearity of the Hammett plot for the iron(III) to iron(II) reduction (reaction 3) appears to be real, and of the solvents investigated, is unique to butyronitrile. One possible explanation is that electron-donating groups change the coordination number of the central iron ion by gain or loss of a butyronitrile molecule. A break in the plot of $E_{1/2}$ vs. 4σ does not occur for the Fe(III) → Fe(II) reaction in CH_2Cl_2, DMF, or Me_2SO, and a value of ρ can be calculated in each solvent.

Reaction constants, ρ, calculated using eq 6 are given in Table III for all five iron reactions in several complexing and noncomplexing solvents. The sign of ρ is defined as positive when electron-donating substituents shift a redox reaction to a more cathodic potential.

It has been reported that the sensitivity of redox reactions involving the central metal of metalloporphyrins is a function of the number of metal d electrons, and ρ for M(III) porphyrin reductions will decrease on going from d^4 to d^8 transition metals.[20] No such trend exists on going from Fe(IV) to Fe(I) by successive electron addition. An explanation for this de-

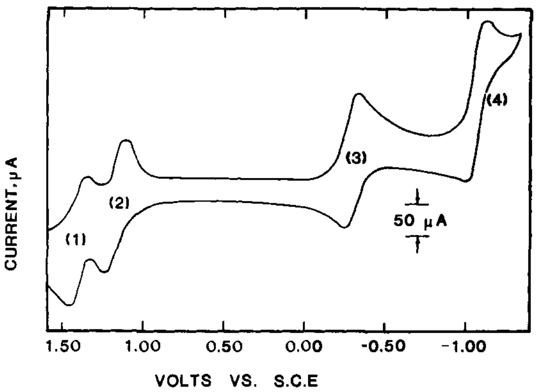

Figure 1. Cyclic voltammogram of FeTPPCl in CH_2Cl_2, 0.1 M TBAP.

Table III. Summary of Hammett Reaction Constants for the Electrode Reactions of Para- and Meta-Substituted Iron Tetraphenylporphyrins in Several Solvents

	Reaction constant ρ, V				
Reaction[d]	CH_2Cl_2[a]	*n*-PrCN[a]	DMF[b]	Me_2SO[b]	DMA[b]
1	0.048	0.053			
2	0.098	0.056			
3	0.038	*c*	0.030	0.025	0.020
4	0.068	0.024	0.037	0.035	0.020
5	0.067	0.054	0.068	0.063	

[a] 0.1 M TBAP. [b] 0.1 M TEAP. [c] See text and Figure 2. [d] See text.

viation of the previously reported order of substituent effects vs. number of metal d electrons might be related to the charge of the central metal and/or the overall charge on the complex as well as an increased interaction of iron(I) with the porphyrin ring. The charge on the oxidized or reduced complex of $[Fe(p\text{-}X)TPP]^+Cl^-$ varies from -2 on the radical $[Fe^ITPP]^{2-}$ to $+3$ on the species $[Fe^{IV}TPP]^{3+}$. The spin state is not constant, being high, low, or mixed spin for Fe(II),[29] high spin for Fe(III)[30] and Fe(IV),[3-4] and either high or low spin for Fe(I), depending on temperature.[7] In addition, the number of axially coordinated solvent molecules may change on going from Fe(III) complexes to Fe(I) complexes.

It is of some interest to draw parallels between the first two reductions of $[Fe^{III}TPP]^+$ and $[Co^{III}TPP]^+$ in the same solvent. Both complexes undergo a metal(III) → metal(II) and a metal(II) → metal(I) electrode reaction. Comparisons of ρ for oxidation of negatively charged d^8, $[Co^I(p\text{-}X)TPP]^-$ and neutral d^7, $[Co^{II}(p\text{-}X)TPP]^0$, show that the negatively charged complex is more sensitive to substituents in solvents of both high and low dielectric constant.[18] This parallels the results in Table III and points toward the influence of not only the number of d electrons, but also metal charge state on ρ for electron transfers involving the central metal.

Table III indicates there is also a solvent effect on the ρ values of the different iron couples. It has been shown that for free-base porphyrins there is a linear relationship between dielectric constant and ρ,[21] and larger ρ's are obtained for low dielectric constant solvents. A similar solvent effect was seen for the redox reactions of $Co(p\text{-}X)TPP$, where ρ for all reactions increases by 30% on going from Me_2SO to CH_2Cl_2.[18] This solvent dependence is also evident for the reactions of $[Fe(p\text{-}X)TPP]^+Cl^-$. As seen in Table III, ρ decreases for both reaction 3 and 4 on going from CH_2Cl_2 as solvent (ϵ 9) to DMA, DMF, or Me_2SO (ϵ 39, 37, and 46, respectively). For reactions 1, 2, and 5 the relationship between ρ and solvent is less evident. However, for all reactions superimposed on the dielectric effect is the ability of the solvent to coordinate with the central iron, which may alter the value of ρ.

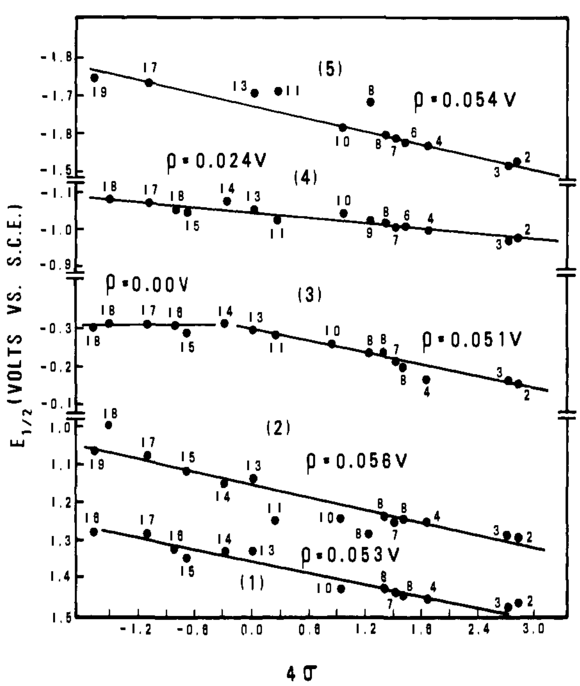

Figure 2. Plot of $E_{1/2}$ vs. 4σ for the five electrode reactions of $Fe(p\text{-}X)TPPCl$ and $Fe(m\text{-}X)TPPCl$ in butyronitrile, 0.1 M TBAP. Numbers correspond to reactions 1–5 in text.

Effect of Substituents on Electron-Transfer Rate Constants. Electron-transfer rate constants have been measured electrochemically for a variety of iron and cobalt porphyrins.[31-34] These studies have shown that larger rate constants are obtained when both Fe(III) and Fe(II) have the same spin state and that low-spin complexes give faster rates than high-spin complexes.[31,32] Also, faster rates are obtained if the axial ligand on the metal does not change on reduction.[31-34] Axial ligands, which are not conjugated and thus presumably cannot conduct electrons, markedly slow down the rate.[33] Likewise, there are important solvent effects. For noncoordinating solvents in which $[Fe^{III}TPP]^+Cl^-$ exists as a five-coordinate complex, electron-transfer rates are slower.[31]

Iron porphyrin concentrations for electron-transfer rate measurements are usually on the order of 1 mM. Thus, the perchlorate ion of the supporting electrolyte (0.1 M) may replace the chloride. The effect of variation of the anion on the oxidation rate of $Co^{II}TPP$ indicates a marked reduction in rate for bromide.[33] Also, rate constants increase as the concentration of water increases in mixed solvents.[32,33]

Table IV lists the experimental heterogeneous electron exchange rate data for the para-substituted complexes and Table V lists the data for the meta-substituted complexes of iron tetraphenylporphyrin in butyronitrile. The potentials for the electrode reactions of $Fe(p\text{-}X)TPPCl$ in butyronitrile indicate minimal interaction between the solvent and metalloporphyrins. The fact that solvent effects are minimized and that butyronitrile can be used over a wide potential range dictated its choice for electron-transfer rate measurements.

All rate constants were measured by the cyclic voltammetric technique of Nicholson.[35] The separation of the peak potentials for each redox couple was measured as a function of scan rate. Shifts of the peak potentials from the reversible value of 60 mV are considered quasireversible and under these conditions the rate of electron transfer can be calculated from the following equation[35]

Table IV. Rate Constants for Various Para-Substituted Iron Tetraphenylporphyrin Complexes, Fe(p-X)TPP, in butyronitrile, 0.1 M TBAP

	Log heterogeneous rate constant k^0, cm/s				
Ring substituent	Ring oxidation[a] (1)	Metal reactions[a] (2)	(3)	(4)	Ring reduction[a] (5)
p-CN	−2.77	−2.09	−2.89	−3.19	−2.52
p-COOCH$_3$	−1.67	−2.09	−3.00	−2.48	−2.24
p-Cl	−1.74	−1.49	−2.69	−2.41	−1.95
p-Br	−1.18	−1.93	−2.11	−2.14	−2.32
p-F	−1.99	−2.00	−2.46	−2.11	−1.98
p-H	−1.68	−1.82	−2.51	−2.13	−1.98
p-CH$_3$	−1.17		−3.10	−2.40	
p-C(CH$_3$)$_3$	−1.83	−2.07	−2.04	−2.25	
p-OCH-$_3$01−1.44	−1.43	−2.89	−2.08		
p-OH		−1.79	−2.18	−2.01	−1.87
p-OCH$_2$Ph	−1.59	−1.45	−2.10	−1.48	−1.77

[a] Number corresponds to reaction given in text.

Table V. Rate Constants for Various Meta-Substituted Iron Tetraphenylporphyrin Complexes, Fe(m-X)TPP, in butyronitrile, 0.1 M TBAP

	Log heterogeneous rate constant k^0, cm/s				
Ring substituent	Ring oxidation[a] (1)	Metal reaction[a] (2)	(3)	(4)	Ring reduction[a] (5)
m-CN	−1.83	−2.12	−2.72	−3.16	−2.54
m-Br	−1.69	−1.71	−2.62	−2.62	−2.12
m-Cl	−1.57	−1.63	−2.09	−2.55	−1.87
m-F	−1.90	−1.88	−2.08	−2.27	−1.98
m-OCH$_2$Ph	−1.81	−1.83	−2.34	−2.14	−1.97
m-CH$_3$	−1.68	−1.79	−2.07	−1.75	−1.89

[a] Number corresponds to reaction given in text.

$$k^0 = \Psi/\gamma^\alpha \sqrt{\frac{nFv}{RT}D} \tag{7}$$

where k^0 is the heterogeneous electron-transfer rate constant (cm/s), n is the number of electrons transfered in each step, v is the potential sweep rate (V/s), D is the diffusion coefficient of the reacting species, $\gamma = (D_o/D_r)^{1/2}$ (where D_o is the diffusion coefficient of the oxidized form of the reactant and D_r is the diffusion coefficient of the reduced form of the reactant), α is the electron-transfer coefficient; π, F, and RT have their usual significance. Ψ is related to ΔE_p, the potential difference between the cathodic and anodic peak potentials. Values of Ψ, as defined by eq 7 for various values of ΔE_p, have been tabulated after the solution of the appropriate equations by numerical analysis.[35]

The general trend observed from Tables IV and V is that electron-withdrawing groups on the porphyrin ring decrease the electron-transfer rate constants for all reactions. This has not been reported previously and would indicate that a high electron density on the porphyrin ring or central metal is important for a fast reaction.

It might also be noted that usually reaction 1 has a higher rate than the others, although reaction 5 shows larger rates in a number of instances. Thus, it may be that reactions which involve removing or donating an electron to the conjugated π ring system proceed more rapidly than those in which the electron is added directly to or removed from the central metal. Studies of electron-transfer kinetics involving other para- and meta-substituted metalloporphyrins are now in progress and should indicate whether this is a general phenomenon or is particular to the iron metalloporphyrin system.

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