

Solvent and Substituent Effects on the Redox Reactions of Para-Substituted Tetraphenylporphyrin

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Abstract: The redox reactions of a series of para-substituted tetraphenylporphyrins, $H_2(p-X)TPP$, have been investigated in nonaqueous media by cyclic voltammetry. The potentials of the four reversible electrode reactions were found to be a function of electron-donating or -withdrawing substituent and solvent dielectric constant. Plots of $E_{1/2}$ vs. Hammett σ gave a linear relationship from which reaction constants were calculated. Reaction constants for reduction or oxidation of compounds containing substituents on the four phenyl rings are about one-sixth as large as that for direct substitution on the porphyrin ring.

Introduction

The effect of electron-withdrawing or -donating groups on the para or meta position of tetraphenylporphyrins has recently been quantitated in regard to ligand addition to nickel and vanadyl complexes of tetraphenylporphyrin¹ (I). In nonaqueous media these porphyrins, as well as other metalloporphyrins may be oxidized in single electron-transfer steps to yield π cation radicals and dication or reduced in single steps to yield π anion radicals and dianions.²⁻⁴ In several metalloporphyrins the central metal may also be oxidized or reduced.²⁻⁷ For all metal oxidation states of +2, +3, and +4, the thermodynamic redox potentials for anion and cation radical formation are a function of the type and electronegativity of the central metal as well as the basicity of the porphyrin ring.⁸ A recent study has elucidated the influence of central metal on porphyrin ring redox potentials of 25 different metalloctaethylporphyrins.² However, to date no detailed study has been reported which quantitates the effect of electron-donating or electron-withdrawing substituents on free base porphyrins in terms of ring basicity and its relationship to redox potentials.

One of the best means of quantifying the effects of electron-withdrawing and electron-donating groups on the reactions and physical properties of metalloporphyrins is the Hammett linear free energy relationship⁹

$$\log (K^X/K^H) = \sigma\rho' \quad (1)$$

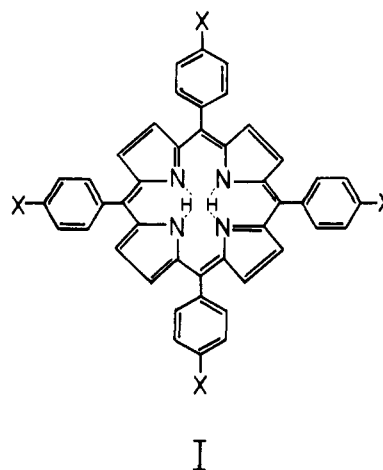
This relationship has been used to quantitate substituent effects on shifts of electronic absorption spectra,¹⁰ relative spectral intensities,¹¹ and equilibrium constants for the addition of one or two axial ligands to the central metal of metalloporphyrins.^{12,13} It is valid for both equilibrium and rate constants and, suitably modified, can be applied to measure changes in half-wave potentials of electrochemical redox reactions¹⁴

$$\Delta E_{1/2} = \sigma\rho \quad (2)$$

In each case, σ , a substituent constant, measures the electron-donating or electron-withdrawing characteristics of X, and ρ , the "reaction constant", measures the sensitivity of the reaction to the electron-donating or -withdrawing characteristics of substituents. Since the para-substituted tetraphenylporphyrins (I) have substituents on each of the four phenyl rings, 4σ is used as the total substituent constant, and the relevant equation becomes

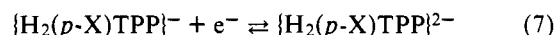
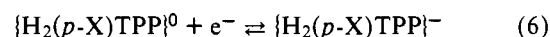
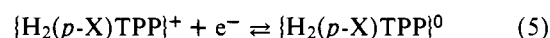
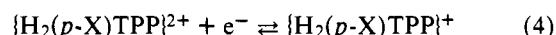
$$\Delta E_{1/2} = 4\sigma\rho \quad (3)$$

In eq 2 and 3, ρ is given in volts. Its value depends on the kind of electroactive group, the composition of the supporting electrolyte, and temperature.¹⁴ Since $E_{1/2}$ is approximately equal to E^0 when measured by cyclic voltammetry¹⁸ and $E^0 = 0.059 \log K_{eq}$ at 25 °C, it can be shown that ρ' from eq 1 is



related to ρ from eq 2 and at 25 °C, $\rho \approx (0.059 \text{ V})\rho'$. Thus a chemical reaction constant of 1.00, defined for hydrolysis of meta- and para-substituted benzoic acid,¹⁵ would correspond to an electrochemical reaction constant of 0.059 V at 25 °C.

In this paper we present results which quantitate substituent effects on the oxidation and reduction of para-substituted tetraphenylporphyrin ($H_2(p-X)TPP$, I) in nonaqueous media. The four electrode reactions which occur are written as follows:



Reactions 5 to 7 will be discussed in detail in terms of solvent and substituent effects on the electrode reactions.

Experimental Section

Reagents. Reagent grade *N,N*-dimethylformamide (DMF) was dried over activated Linde 4A molecular sieves 24 h before distillation over activated alumina at room temperature and reduced pressure, just prior to analysis. Other solvents were spectral or reagent grade and were used as received. Tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) (Southwestern Analytical, Inc.), used as supporting electrolytes, were recrystallized from absolute methanol and dried over P_4O_{10} at room temperature. Para-substituted free base tetraphenylporphyrins ($H_2(p-X)TPP$) were the generous gift of Dr. F. Ann Walker and were synthesized from the para-substituted free base tetraphenylporphyrins by the method of Adler et al.¹⁶ Meso-substituted octaethylporphyrin, $H_2OEP(ms-X)$, was generously provided by J. H. Fuhrhop.

Instrumentation and Data Analysis. Cyclic voltammograms were obtained on a PAR 174 polarographic analyzer, in conjunction with

Table I. Hammett Reaction Constants (ρ) Calculated from Eq 3 for Redox Reactions of $H_2(p-X)TPP$ and Half-Wave Potentials ($E_{1/2}^H$) for $H_2(p-H)TPP$ in Several Solvents^a

Solvent	Dielectric ^d constant	Reaction 7		Reaction 6		Reaction 5	
		ρ , V	$E_{1/2}^H$, V	ρ , V	$E_{1/2}^H$, V	ρ , V	$E_{1/2}^H$, V
Methylene chloride ^b	9	0.073	-1.20	0.064	-1.55	0.065	1.02
Pyridine ^b	12	0.068	-1.13	0.061	-1.49		
<i>n</i> -Butyronitrile ^b	20	0.063	-1.13			0.054	1.06
Benzonitrile ^c	25	0.056	-1.13				
Dimethylformamide ^c	37	0.055	-1.05	0.051	-1.43		
Dimethyl sulfoxide ^c	46	0.053	-1.03				

^a See text for explanation of reactions. ^b 0.1 M TBAP. ^c 0.1 M TEAP. ^d Reference 25.

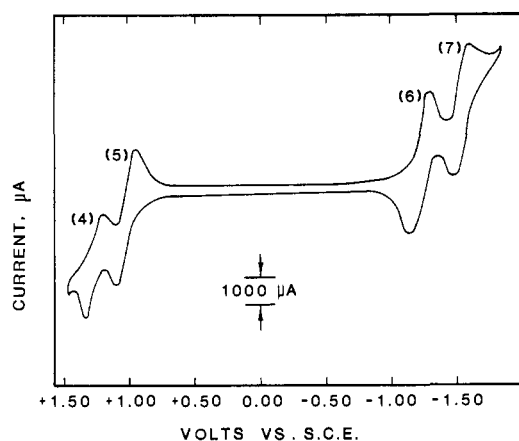


Figure 1. Cyclic voltammogram of 2.6×10^{-3} M H_2TPP in CH_2Cl_2 , 0.1 M TBAP; scan rate, 0.05 v/s.

either an MFE Model 1015 or a Houston Instruments 2000 X-Y recorder, with a 1-s pen response. A three-electrode system was used, consisting of platinum working and counter electrodes and a commercial saturated calomel electrode (SCE), separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SCE. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min just before running cyclic voltammograms. For volatile solutions, the nitrogen was presaturated with the solvent. After degassing, a blanket of nitrogen was kept over the solution. The auxiliary instrumentation and cell design have been described in a previous publication.¹⁷ All experiments were carried out in a controlled-temperature room of 20 ± 1 °C. Potentials are reported with respect to the saturated calomel electrode.

The $E_{1/2}$ values were measured as the potential halfway between the oxidation and reduction peak for a given couple. For diffusion-controlled reactions, the reduction peak potential is 0.029 mV more cathodic than $E_{1/2}$. This latter potential is the potential where the current is equal to 85.17% of the diffusion peak current and is virtually interchangeable with the thermodynamically significant formal potential, E^0 .¹⁸ Slopes of $E_{1/2}$ vs. 4σ plots were analyzed by a least-squares best fit to calculate the reaction constant, ρ . Since all four phenyl rings of tetraphenylporphyrin are substituted, 4σ was used as the substituent constant. McDaniel and Brown¹⁹ substituent constants, 4σ , used in this paper are: (H) = 0.000; (*p*-OCH₃) = -1.072; (*p*-CH₃) = 0.68; (*p*-F) = -0.248; (*p*-Cl) = 0.908; (*p*-COOCH₃) = 1.240; (*p*-CN) = 2.640; (*p*-NO₂) = 3.112.

Results and Discussion

Figure 1 shows a typical cyclic voltammogram of H_2TPP in methylene chloride, 0.1 M TBAP. All cyclic voltammograms were similar in shape and yielded three or four peaks depending on the specific phenyl ring substituents. The electron transfers were in all cases diffusion controlled and yielded well-defined current-voltage curves with the theoretical peak separation for a one-electron transfer.¹⁸ Reactions at the electrode surface

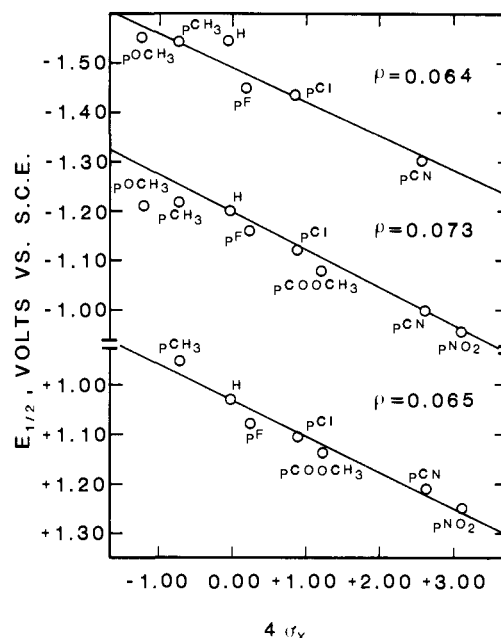


Figure 2. Plot of $E_{1/2}$ vs. 4σ for the oxidation of $[H_2(p-X)TPP]^+$ and the two single-electron reductions to yield successively $[H_2(p-X)TPP]^-$ and $[H_2(p-X)TPP]^{2-}$; solvent, CH_2Cl_2 -0.1 M TBAP. Values of σ are from ref 19.

corresponded to either the oxidation or the reduction of the neutral porphyrin ring, or the oxidation or reduction of the cation or anion radical according to reactions 4 to 7.

The potentials of all reactions were a function of supporting electrolyte and solvent and, for a given solvent medium, shifted along the potential axis depending on the electron-donating or -withdrawing ability of the four substituents (X). The magnitude of the shift is expressed by the Hammett linear free-energy relationship given by eq 3 and is shown in Figure 2, where linear free-energy plots of $E_{1/2}$ vs. 4σ for reactions 5 to 7 are illustrated. A summary of the reaction constants and half-wave potentials are given in Table I for several solvents. Reaction 4 is not included since for most substituents the reaction was shifted beyond the range of the solvent. All four reactions were diffusion controlled and, in agreement with previous electrochemical results, the potential difference between anion and cation radical formation was 2.25 ± 0.15 V.^{2,5} In all solvents, shifts in half-wave potentials, as a result of changing the substituent X, were found to obey the Hammett relationship given by eq 3. The validity of this equation is dependent on a similarity of electrode mechanism throughout the series of substituted compounds.¹⁴ The number of electrons transferred was the same throughout the series. The degree of reversibility of electron transfer, measured by peak shape for cyclic voltammetry, was also similar.

There is a marked change on going from a solvent of rela-

tively low dielectric constant, such as methylene chloride ($\epsilon = 9$), to a solvent of high dielectric constant, such as dimethyl sulfoxide ($\epsilon = 46$), in a constant supporting electrolyte concentration of 0.1 M TEAP or TBAP. An increase in dielectric constant decreases the reaction constant and shifts $E_{1/2}$. It is interesting to note that ring oxidations to yield π cations are not significantly more sensitive to substituents than ring reductions to yield π anions. This is in marked contrast to similar reactions of cobalt para-substituted tetraphenylporphyrin, Co(*p*-X)TPP, to yield anion and cation radicals where, in all solvents, the reaction constants are invariably 1.5 to 2.5 times as large for the oxidations as for the reductions.^{13b,c} These latter data agree well with the results of spectroscopic studies which show that the presence of an extra positive charge on the ring increases the sensitivity to substituent effects and that the largest effects are observed with the acid dications.^{10a}

The calculated reaction constants of 0.051 to 0.073 are six to seven times as small as the value of 0.38 reported by Callot, Giraudeau, and Gross²⁰ for the reduction in DMF of tetraphenylporphyrin, where zero to four cyano groups are substituted directly onto the pyrrole carbons of the porphyrin ring. This effect of decreasing sensitivity to ring substituents on going from direct attachment on the porphyrin ring to attachment at the distal phenyl group of tetraphenylporphyrins would be expected, since the phenyl rings are not coplanar with the porphyrin ring,²¹ and hence would exhibit reduced interaction.

In order to further investigate the decrease of reaction constant for phenyl ring vs. direct porphyrin substitution, we performed the oxidation of a series of meso-substituted octaethylporphyrins, H₂OEP(*ms*-X), in *n*-butyronitrile 0.1 M TBAP. All oxidations were diffusion controlled and plots of half-wave potentials vs. σ gave a Hammett plot of slope 0.50 V. A survey of the literature indicates that the reaction constant of 0.50 V for the oxidation of H₂OEP(*ms*-X) is one of the highest observed for any electrooxidation.

While extreme care must be used in comparing results of this study with other reaction series, the ρ calculated from plots of $E_{1/2}$ vs. σ is of the same magnitude as the reaction constants for the reduction of a series of substituted phenyl rings attached to an electroactive heterocyclic ring, including substituted phenyl- and diphenylsydnones,²² triphenyltetrazolium salts,²³ and *N*-phenylpyridines.²⁴

In conclusion, electrochemical studies of substituent and solvent effects on the redox properties of free base para-substituted tetraphenylporphyrin are an essential first step in understanding substituent effects and metal-porphyrin interactions in the biologically important cobalt and iron metalloporphyrins. Since Hammett reaction constants have been shown to be solvent dependent, extreme care must be taken in directly comparing physical measurements obtained under

different experimental conditions in different solvents. Work is presently in progress which quantitates solvent and substituent effects on redox properties, chemical reactions, and oxygen binding characteristics of various para-substituted cobalt and iron tetraphenylporphyrins, Co(*p*-X)TPP and Fe(*p*-X)TPP, as well as reactions of other first-row transition metalloporphyrins.

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