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The Effect of Substituents on the Oxidation Potentials of Substituted Tetraphenylporphinatosilver(II) Complexes

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The oxidation potentials of several substituted tetraphenylporphyrin (p-OCH$_3$, p-CH$_3$, m-CH$_3$, -H, p-F, p-Cl, and p-Br(TPP)) complexes of silver(II) have been measured in CH$_2$Cl$_2$ using the cyclic voltammetry method. The $E_{1/2}$ values obtained for the first ring oxidation and the Ag(II) ⇌ Ag(III) + e redox reaction have been correlated using the Hammett LFER equation and the respective ρ values are 0.21 and 0.10 v. It was found that electron donating substituents make ring oxidation easier while electron withdrawing substituents have the opposite effect. The non-coplanar nature between the phenyl rings and the porphyrin plane permits the correlation of the electron-chemical data with σ° values for insulated reaction centers.

Introduction

In recent years a number of electrochemical studies on porphyrins and metalloporphyrins have been made [1–18]. In nonaqueous solvent the coordinated and the free porphyrin tetrapyrrolic macrocycles can be either oxidized or reduced in two successive, reversible one electron transfer steps forming Π cation radicals and dications, and Π anion radicals and dianions, respectively according to the following reactions.

Oxidation:

$$MP \rightleftharpoons MP^{+\cdot} + e^- \qquad \text{cation radical} \qquad (1)$$

$$MP^{+\cdot} \rightleftharpoons MP^{+2} + e^- \qquad \text{dication} \qquad (2)$$

Reduction:

$$MP + e^- \rightleftharpoons MP^{-\cdot} \qquad \text{anion radical} \qquad (3)$$

$$MP^{-\cdot} + e^- \rightleftharpoons MP^{-2} \qquad \text{dianion} \qquad (4)$$

MP in the above reactions represents H$_2$P for the free porphyrin or the metalloporphyrins.

Several studies have already been performed on ms-tetraphenylporphyrin (TPP) containing the central metals V [12c], Mn [13], Fe [15], Co [15], Ni [12b], Cu [13], Zn [13], and Au [16] as well as the free base H$_2$TPP and the ms-tetraarylporphyrins H$_2$(m,p-X)TPP [12a]. In general, it was found that as the porphyrin ring basicity increases reductions become more difficult and oxidations more facile. To quantify this electrochemical reactivity, that is, the effect of electron-donating and electron-withdrawing substituents attached to the porphyrin ring, a Hammet linear free energy relationship is used [19].

$$\Delta E_{1/2} = 4\sigma\rho \qquad (5)$$

$\Delta E_{1/2}$ is the difference in half-wave potential between the substituted and unsubstituted porphyrin system related to benzene, ρ is a constant characteristic of the reaction involved and σ is a constant characteristic of the substituent. In the present study, a factor of four is incorporated in equation (5) to account for the additive effects of the four phenyl rings in TPP.

By using equation (5) the change in electrochemical reactivity induced by either electron-donating or electon-withdrawing substituents attached to the porphyrin ring can be found for the four reactions, equations (1) to (4). In addition, the central silver(II) ion can undergo a reversible one-electron oxidation process, equation (6).

$$Ag^{II}(\text{p or m-X})TPP \rightleftharpoons Ag^{III}(\text{p or m-X})TPP^+ + e^- \qquad (6)$$

Cyclic voltammetry experiments have been carried out in CH$_2$Cl$_2$ with 0.1 *M* tetrabutylammonium perchlorate (TBAP) to observe the substituent effect on the redox potentials of reactions (1), (2) and (6). No results on the reduction steps $E_{1/2}$ values will be reported because of experimental difficulty in obtaining reproducibility.

TABLE I. Electrochemical Data for Substituted Tetraphenylporphinatosilver(II) Complexes.[a]

Complex	Porphyrin[b] $E_{1/2}(1)$	Metal $E_{1/2}(6)$	σ	σ°
$Ag^{II}(p\text{-}OCH_3)TPP$		+0.46	−0.268[c]	−0.12[d]
$Ag^{II}(p\text{-}CH_3)TPP$	+1.15	+0.46	−0.170	−0.14
$Ag^{II}(m\text{-}CH_3)TPP$	+1.24	+0.51	−0.069	−0.06
$Ag^{II}TPP$	+1.34	+0.54	0	0
$Ag^{II}TPP$	+1.64 [14]	+0.55 [14]		
$Ag^{II}(p\text{-}F)TPP$		+0.57	+0.062	+0.15
$Ag^{II}(p\text{-}Cl)TPP$		+0.63	+0.277	+0.24
$Ag^{II}(p\text{-}Br)TPP$	+1.49	+0.64	+0.232	+0.26
ρ value	0.21v	0.10v		

[a] Units are in V *vs.* SCE. [b] 0.10 *M* TBAP in CH_2Cl_2. [c] σ values from ref. 21. [d] σ° values from ref. 25.

Experimental Section

Chemicals

The following porphyrins were obtained from Man-Win Chemical Company and used without further purification: $p\text{-}OCH_3TPP$, $p\text{-}CH_3TPP$, $m\text{-}CH_3TPP$ and H_2TPP. Purification from benzene was found necessary for the following: p-FTPP, p-BrTPP, p-ClTPP, and p-CNTPP. Eastman Kodak Company's tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) were recrystallized once from ethanol water solution and stored for at least 48 hours in the dark under vacuum at 60 °C prior to use. Silver acetate was obtained from Mallinckrodt Chemical Company. Other chemicals used in the study were of reagent grade. Solvents such as benzene, chloroform, methylene chloride, acetonitrile and N,N-dimethylformamide were of reagent or spectral grade quality and are purified according to procedures described elsewhere [20].

Preparation of Silver–Porphyrin Complexes

ms-Tetraphenylporphinatosilver(II), Ag(II)TPP, was prepared and purified according to described procedure of Rothemund and Menotti [21]. Synthesis of the ms-tetraarylporphinatosilver(II) complexes with the electron-donating substituents such as $p\text{-}OCH_3$, $p\text{-}CH_3$, and $m\text{-}CH_3(TPP)$ were done in the same manner as the Ag(II)TPP. However, metallation occurred more rapidly with more electron-donating substituents. In the case of $Ag(II)p\text{-}OCH_3TPP$, it took less than 15 minutes to form the complex in greater than 95% yield. For the electron-withdrawing substituents a slightly different procedure was necessary. This essentially involved the purification of the free porphyrins in benzene. These ms-tetraarylporphyrins are p-FTPP, p-ClTPP, p-BrTPP and p-CNTPP. Synthesis procedure as described before was followed except that reflux time required for the preparation of Ag(II)p-FTPP was over 4 hours and for the Ag(II)p-ClTPP and Ag(II)p-BrTPP over 8 hours was required to get 70% conversion. Greater than 50% conversion to Ag(II)p-CNTPP was not obtained even after two days of refluxing in the dark. Usual electronic spectra of Ag(II)p–CNTPP solutions were not observed and no useful cyclic voltammetry information was obtained. All the syntheses and subsequent electrochemical studies have to be performed in the dark, preferably in the evenings, with little or no room light. Purities of all the silver(II) complexes were determined by spectrophotometry method.

Instrumentation

Ultraviolet–visible spectral analyses were performed on a Beckman Model 25 uv–vis spectrophotometer. Cyclic voltammetry measurements on the ms-tetraarylporphinatosilver(II) solutions were conducted using a three-electrode potentiostatic circuit and a MPI Model MP-1042 Voltammetry Controller in conjunction with a PAR Houston Model 2000 X-Y recorder with a 0.5 second response time.

The working electrode consisted of a platinum bead electrode while the counter electrode was either a platinum bead or platinum gauze electrode. Either the Beckman saturated calomel reference electrode (SCE) or the silver/silver chloride reference electrode was used as the reference electrode. Solutions were degassed with pre-purified and solvent saturated nitrogen gas to purge oxygen from the solutions. A blanket of N_2 atmosphere was kept above the solution during quiescent potential scans. All experiments were performed at ambient room temperature of 24.0° ± 1.5 °C.

Cyclic voltammetry scans were all run with 0.10 to 0.50 *M* TBAP as the supporting electrolyte and methylene chloride as the solvent except where solvent effects were being determined. The scans were performed in quiescent solutions between 0.00

TABLE II. Summary of Hammett Reaction Constants, ρ, for Ring Oxidation of Substituted TPP–Metal Ion Complexes in CH_2Cl_2.[a]

Central Metal	Ring Oxidation[b]				Ref.
	$E_{1/2}(1)$	ρ, v	$E_{1/2}(2)$	ρ, v	
H_2	+1.02	0.065	+1.27	0.07	(12a), e
VO^{+2}	+1.13	0.05	+1.35	0.09	12c
Mn	+1.13	0.07	(c)	(c)	12c
Fe	+1.40	0.045	(c)	(c)	12c
Co	+1.00	0.09	+1.20	0.09	11
Ni	+1.05	0.054	+1.15	0.018	12b
Cu	+1.00	0.08	+1.25	0.03	(12c), e
Zn	+0.78	0.06	+1.09	0.05	12c
Au(III)	+1.68(BN)		–	–	16, f
Ag	+1.34	0.21	(c)	(c)	e

[a] Units are in V *vs.* SCE; 0.10 *M* TBAP. [b] $E_{1/2}$ s for M(TPP) are listed. [c] All or almost all substituted TPP complexes reacted beyond potential range of solvent. [d] Irreversible reactions. [e] Electrochemical data repeated or performed in this study. [f] Only $Au(TPP)^+$ was reported.

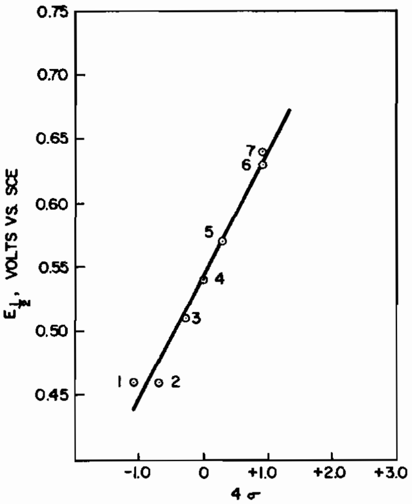

Fig. 1. Hammett LFER correlation of Ag(II)P ⇌ Ag(III)P + e redox potential; p-OCH_3 (1); p-CH_3 (2); m-CH_3 (3); H (4); p-F (5); p-Cl (6); p-Br (7).

and +1.80 v (*vs.* SCE). In all cases scan rates were 50, 100, 200 and 500 mv/sec. The silver(II)-porphyrins concentrations varied from 5 X 10^{-4} *M* to 5 X 10^{-3} *M* and never exceeded 0.01 of the supporting electrolyte concentration. All electrochemical data were converted to values *vs.* SCE.

Results and Discussions

The cyclic voltammograms of the Ag^{II}(p or m-X)-TPP complexes were similar in shape and reversibility and were shifted along the potential axis by the electron-donating or electron-withdrawing character of the substituent. When the substituents are electron-donating in nature, the electrode potentials of the porphyrin ring are shifted negatively; that is, oxidations become easier. This observation confirms the findings of earlier workers [11–13, 15]. On the other hand, when the substituents are electron-withdrawing in nature, the half-wave potentials are shifted positively and the oxidations become more difficult. By using the Hammett linear free energy relationship, equation (5), it can be determined whether the same mechanism exists throughout the series of substituent reactions and the degree of the electron-donating and electron-withdrawing effects of the substituents on the reactions.

McDaniel and Brown [22] σ values were used for Hammett plots in this study. Table I summarizes the electrochemical data obtained in this study. The Hammett plot for the cation radicals was linear and the ρ value obtained from the slope of the plot is 0.21 v. The effects of substituents on the redox potentials of Ag(II) ⇌ Ag(III) + e^- obtained from the slope of the Hammett plot is shown in Fig. 1 and has a ρ value of 0.10 v.

The ring oxidation of Ag^{II} (p- or m-X)TPP appears to be more sensitive to the electron-donating or electron-withdrawing ability of the substituents. The ρ value of 0.21 v for the first oxidation step of the silver(II)–porphyrin series is much larger than the ρ values found for the H_2TPP series and other metal ions containing TPP whose average ρ value is 0.07 ± 0.02 v. A summary of the ρ values for the ring oxidation of all the metalloporphyrins studied is listed in Table II. We have exhaustively repeated the H_2 (p-or m-X)TPP and the Cu^{II}(p or m-X)TPP series in the same solvent and electrolytes to check for any possible experimental error in our present study. In both instances we were able to reproduce the results and ρ values in complete agreement with the literature values [12]. This suggests that the high ρ value for the ring oxidation of the silver(II)–porphyrin series is not due to any experimental error. The reason for the high ρ value is not known except for the fact that Ag(II) is $4d^9$ and that Ag(II) is more covalently bonded to the porphyrin ring than the $3d^9$ Cu(II)–TPP system [23]. This could possibly make the ring oxidation more sensitive to change in electron density.

When comparing the metal redox couple (reaction 6), a ρ value of 0.10 v is found. The metal atom itself is situated in a position more distant from the substituent than the porphyrin ring and one would predict reaction (6) to be less sensitive to substituent effect. Nevertheless, a trend can be developed to support the above finding, that is, the ρ value for $Fe(II)P \rightleftharpoons Fe(III)P^+ + e^-$ is 0.038 v (in CH_2Cl_2) but the ρ value is 0.053 v with respect to the first ring oxidation [13]. The ρ value for $Co(II)P \rightleftharpoons Co(III)P^+ + e^-$ is 0.034 v while the porphyrin ring reaction is 0.09 v [11]. In all three cases, the metal oxidation potentials have the lowest ρ values indicating they are less sensitive toward substituent electron-donating or withdrawing effect.

The silver atom being at the center of the porphyrin ring which is situated at a distance seven atoms away from the substituent and that the four phenyl rings being tilted at an angle less than 90° to the porphyrin plane [24] lead us to apply σ° in this study. The σ° values are for non-conjugating reaction centers insulated by a CH_2 group such as those of substituted phenylacetic acids [25]. An improvement in the $E_{1/2}$ *vs.* $4\sigma^\circ$ LFER is obtained and the ρ value is slightly increased to 0.11 v.

Giraudeau and coworkers [17] in studying the effects of β-substitution on the redox potentials of ms-tetraphenylporphyrins have reported the existence of two sites for electron transfer, the pyrrolic nitrogens in oxidations and the π electron system in reductions. In addition to the above result, calculations by Wolberg [26] suggested that in solution H_2-TPP assumes a structure with the two π rings systems closer to coplanarity by 17° than the solid state metallo-TPP which is reported to be at about 40°. If strong π resonance interaction between the phenyl π system and porphyrin π system exists as have been suggested through spectral and pK_a studies on a series of substituted TPP [27], then the application of redox potentials $E_{1/2}$ *vs.* $4\sigma^\circ$ LFER plots for the ring redox reactions should fail as in σ^I and σ^R which were attempted. On the contrary, when H_2(p-X)TPP $E_{1/2}$ data of Kadish and Morrison [12a] for the first ring oxidation and the two ring reduction reactions were replotted against $4\sigma^\circ$, remarkable fit of LFER were obtained [28]. The points normally that fall off the plots are now shifted along the $4\sigma^\circ$ to fall on or lie closer to the lines. The points which are significantly affected are p-OCH_3, p-CH_3 and p-F. However, the ρ values are not significantly altered by using the $4\sigma^\circ$ parameter. We have extended the $4\sigma^\circ$ plots *versus* metallo-TPP [11, 12b, 12c, 13] redox potentials variation, substitution reactions equilibrium constants variation [11, 15, 29] and the rate constants of the kinetics of formation of p- and m-tetraarylporphyrins [30] and in many instances improvement in linear plots can be obtained. Plotting the $pK_{obs'd}$ [27] for the para substituted TPP *versus* $4\sigma^\circ$, a linear correlation can be obtained for all the points except for (p-OH)TPP which is above the line. This can be explained by the fact that the hydroxyl group in protic-aprotic solvents mixture would exhibit hydrogen bonding as well as strong solvation effect and would give a poor fit if the σ° does not take account of these effects. The good correlation between published data and the Hammett σ° values indicate perhaps only some small π resonance effect between the two rings system exists and not the strong non-coplanar resonance-type substituent effect as suggested [27]. Nevertheless, it must be borne in mind that the utilization of any σ values or LFER fitting method that seems to work best can be a way of hiding experimental errors or precision. It seems that further rigorous theoretical considerations and experimental data are needed to clarify the LFER interpretation of the π resonance contribution from the four phenyl rings in TPP and the para-substituted TPP.

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