chelate ring size may therefore be expected in substitution reactions of boron. Finally, as opposed to Ni^{2+} substitution reactions, complexes in aqueous solution in which only one end of the dicarboxylate coordinates are not known. Hydrolysis of such a species would presumably occur rapidly. These results strongly support the conclusion that low rates of complex formation are primarily responsible for the very low stability of larger ring systems in boron complexes of this type.

This study presents additional evidence for two previous conclusions: ligand donor atom protonation is required for reaction and the rate of substitution increases with increasing ligand acidity. In addition, these results indicate that chelate ring closure is a significant rate-limiting step in boron substitution processes involving chelate rings of six atoms or larger. This last conclusion also supports the suggestion[1,3] that there is a close formal similarity between these boron substitution reactions and other labile substitution processes.

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Substituent Effects on the Oxidation–Reduction Reactions of Nickel Para-Substituted Tetraphenylporphyrin in Nonaqueous Media

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In nonaqueous media, porphyrins and metalloporphyrins may be oxidized in two single-electron-transfer steps to yield π-cation radicals or dications or reduced in two single-electron-transfer steps to yield π-anion radicals or dianions.[1-3] In several metalloporphyrins, such as those containing Cr, Mn,
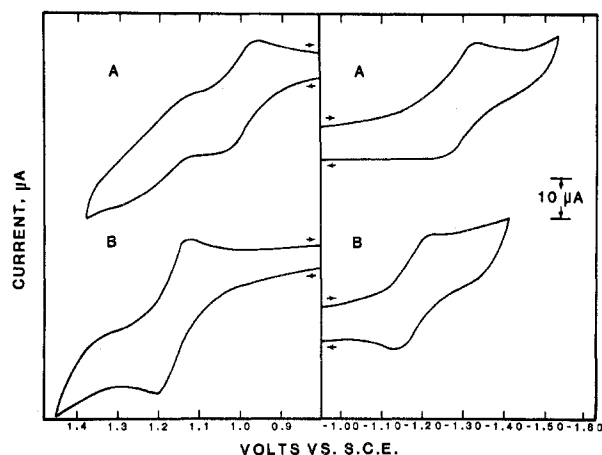

Figure 1. Cyclic voltammograms of (A) 0.2 mM Ni(p-CH₃)TPP and (B) 0.2 mM Ni(p-COOCH₃)TPP in 0.1 M TBAP, CH₂Cl₂; scan rate 0.050 V/s.

Fe, Co, Ni, and Ag, the central metal may also be oxidized or reduced[4-7] to yield complexes of metal oxidation states +1, +2, +3, or +4. Differentiation of metal from ring oxidation is often accomplished by optical and ESR spectra or electrochemical techniques.[1-7] During a comprehensive electrochemical study of solvent and substituent effects on a number of different transition metal para-substituted tetraphenylporphyrins, certain trends were noted which could be used as a basis for deciding whether a given electrode reaction is that of the porphyrin ring or the central metal.[8]

We have observed that, by attachment of an electron-donating or -withdrawing group at the para position of the four phenyl groups of several metallotetraphenylporphyrins, the half-wave potentials for both ring and metal redox reactions would shift in a manner predicted by the Hammett linear free energy relationship[9]

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

where σ is the total polar substituent constant which is dependent on the kind and position of the four substituents, and ρ is the reaction constant which is given in volts and expresses the susceptibility of the electrode reaction to the total polar effect of the substituents. Its value depends on the kind of electroactive group and the composition of the solvent and supporting electrolyte, as well as the temperature.

In this note we present a new electrochemical criterion for differentiating between metal and ring reactions based on the magnitude of the Hammett reaction constants.

Experimental Section

Nickel *meso*-tetraphenylporphyrin and its para-substituted derivatives were synthesized by the method of Adler.[10] Tetrabutylammonium perchlorate, TBAP (Southwestern Analytical, Inc.), was recrystallized from methanol and dried at reduced pressure at room temperature over P₄O₁₀. Methylene chloride, "Distilled-in-Glass", Burdick and Jackson Laboratories, Inc., was used as received.

Cyclic voltammograms were obtained with a three-electrode system using a PAR Model 174 polarographic analyzer, in conjunction with a Houston Instruments Model 2000 X-Y recorder. The working electrode was platinum, and a platinum wire served as the auxiliary electrode. A commercial saturated KCl calomel electrode (SCE) was the reference electrode. This was separated from the bulk of the solution by a fritted-glass compartment. Deaeration was accomplished by bubbling solvent-saturated high-purity nitrogen through the solutions for 10 min prior to analysis. N₂ blanketed the solution during analysis.

Controlled-potential coulometry was accomplished on a large platinum gauze electrode using a PAR Model 173 potentiostat, Model 179 digital coulometer, and time base X-Y recorder. The coulometric cell was similar to that used for cyclic voltammetry and has been

described in a previous publication.[5]

Results and Discussion

Typical cyclic voltammograms of Ni(p-CH3)TPP and Ni(p-COOCH3)TPP are given in Figure 1. All compounds yielded similar voltammograms, and from the calculated reversible half-wave potentials, plots of $E_{1/2}$ vs. 4σ were constructed in order to obtain the reaction constant, ρ, according to eq 1. All reaction series yielded linear plots of $E_{1/2}$ vs. σ indicating an identical reaction mechanism throughout the series. Generally, the reaction constant increased in magnitude on going from a solvent of high dielectric constant (DMSO) to a solvent of low dielectric constant (CH_2Cl_2). A discussion of solvent and substituent effects on free base para-substituted tetraphenylporphyrin,[11] $H_2(p-X)TPP$, and cobalt para-substituted tetraphenylporphyrin,[12] Co(p-X)TPP, is presented elsewhere. For a constant solvent and supporting electrolyte, we have observed that the calculated reaction constants for ring oxidations or ring reductions to yield π cations and anions fall into well-defined patterns.

Reaction constants for the first porphyrin ring reduction in CH_2Cl_2 fell within the range 0.061 ± 0.007 V, while ρ for the first ring oxidation in the same solvent was within the range 0.068 ± 0.021 V regardless of the charge of the reacting species or the nature of the central metal ion.[8] This was true for porphyrins containing the metal ions V^{4+}, Mn^{3+}, Fe^+, Fe^{4+}, Co^+, Co^{3+}, and Ni^{2+}. Changes in the metal oxidation state appeared to have little effect on the observed ρ. The only exception was Mn^{2+}, for which ρ is significantly larger and appears to be unusually solvent dependent.

Constancy of these ρ values over a wide range of central metal ions is a good indication that the electron transfers involve the porphyrin ring and not the metal. Conversely, apparent deviations can be regarded as an indication that the reaction possibly involves a change in metal oxidation state. Optical and ESR spectroscopy can then be used to elucidate fully the electrode reaction. For example the ρ for the reduction of $Co^{III}(p-X)TPP$ was calculated as 0.034 V in DMF.[12] This reaction has been well characterized as involving a transition of cobalt(III) to cobalt(II).[3a] In a similar manner, the ρ values of 0.064 and 0.073 V obtained for the respective oxidation and reduction of the free base para-substituted tetraphenylporphyrin, $H_2(p-X)TPP$, in CH_2Cl_2 fit nicely the analysis of two-ring reactions.[2,3a] The reaction constant, ρ, from eq 1 expresses the susceptibility of the electrode reaction to the total polar effect of the substituents. For constant-solvent conditions, if an identical mechanism is followed throughout a reaction series, one might expect similar reaction constants for reactions involving the same electroactive group in different compounds. With the apparent exception of Mn(p-X)TPP, reduction of all para-substituted metalloporphyrins to yield anion radicals gave a ρ of 0.061 ± 0.007 V independent of the central metal for complexes containing metals varying from d^1 (VO) to d^7 (Co) as well as the free base porphyrins, $H_2(p-X)TPP$. For these same compounds, oxidation reaction constants (to yield π-cation radicals) were relatively insensitive to the central metals. ρ varied from 0.064 V in the free base porphyrin to 0.085 V in Co(p-X)TPP. In marked contrast, however, the reaction constant of each metal reaction was apparently dependent on the number of d electrons of the metal and was in all cases smaller in magnitude than the ρ for either ring oxidation or ring reduction of the same compound. As the number of d electrons increases from d^4 [Mn(II)] to d^5 [Fe(II)] to d^8 [Ni(II)], ρ decreases from 0.054 to 0.038 to 0.018 V in CH_2Cl_2. This is in agreement with similar results reported by Baker et al.,[13] which showed that Hammett plots for addition of pyridine to substituted deuteroporphyrins containing Ni(d^8), Cu(d^9), and Zn(d^{10}) gave a ρ of 1.66, 0.66, and 0.24 V, respectively. Similar plots

of Mg(d^0) substituted deuteroporphyrins gave a ρ of about zero.[14] Spectral studies by Walker et al.[15] have shown that equilibrium constants for ligand binding of para-substituted nickel and vanadyl tetraphenylporphyrins appear to vary with the number of metal electrons, although in this case a reverse trend is noted; i.e., vanadyl (d^1) complexes interact with substitutents less favorably than nickel (d^8) complexes.
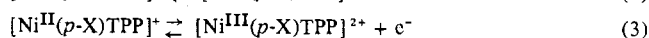
The case of para-substituted nickel tetraphenylporphyrin, Ni(p-X)TPP, is of special interest. Wolberg and Manassen[16] have observed two overlapping oxidation peaks of NiTPP and a single reverse reduction peak which could not be resolved by cyclic voltammetry. On the basis of ESR spectra they postulated the initial oxidation product $Ni^{III}TPP^+$ which was then further oxidized to the cation radical $Ni^{III}TPP^{2+}$. Neither product could be isolated. These findings are apparently in opposition to results of spectroscopic studies which show that chemical oxidation of NiTPP yields a stable product identified as $Ni^{II}TPP^+$.[17]

Of interest in settling this controversy is a comparison of the Hammett reaction constants for the oxidation of Ni(p-X)TPP with several similar para-substituted metallotetraphenylporphyrins.

Figure 1 illustrates cyclic voltammograms of Ni(p-CH3) and Ni(p-COOCH3)TPP obtained at a platinum electrode in CH_2Cl_2. The former compound (Figure 1A) undergoes two oxidations at 1.00 and 1.20 V, while the latter, Ni(p-COOCH3) (Figure 1B), undergoes a single oxidation process at 1.17 V. The peak current for this single oxidation was double that observed for reduction of the same compound at −1.20 V to yield the anion radical and give further evidence of a two-electron transfer.

As the substituent was varied from the electron-donating p-OCH3 to the electron-withdrawing p-NO2, all peaks shifted anodically along the potential axis. The magnitude of the shift was greater for the first oxidation than for the second oxidation. Consequently, for compounds containing electron-donating or weakly electron-withdrawing substituents, two separate oxidations were obtained, while for compounds containing strongly electron-withdrawing groups only a single oxidation was observed.

Plots of $E_{1/2}$ vs. 4σ for the series of Ni(p-X)TPP gave the linear relationships shown in Figure 2, and from eq 1, a value of $\rho = 0.089$ V was obtained for the first oxidation and $\rho = 0.018$ V for the second. This latter value is uncertain due to the small number of data points but is significant in its magnitude when compared to the first reaction. Also included in this figure are the values of $E_{1/2}$ vs. 4σ for reduction of $Ni^{II}(p-X)TPP$ to yield a π-anion radical.[2a] The calculated value of $\rho = 0.054$ V is somewhat less sensitive to the effect of substituents than the reduction of the free base tetraphenylporphyrin, where $\rho = 0.073$ V in the same solvent system.[11] Controlled-potential oxidation at $E = +1.32$ V vs. SCE for Ni(p-CH3)TPP or at $E = +1.40$ V for Ni(p-COOCH3)TPP yielded an identical value of 2.0 ± 0.2 electrons. Controlled-potential oxidation of Ni(p-CH3)TPP required 0.9 electron at $E = +1.05$ V while further oxidation at +1.32 V required 1.1 electrons for an overall two-electron transfer. After removal of an electron from Ni(p-CH3)TPP, the original red solution changed to brown. After a second electron was removed, the brown solution turned green. The visible spectrum of the first oxidation product was similar to that previously assigned as $Ni^{II}TPP^+$ in methylene chloride.[17] Based on these data the mechanism of eq 2 and 3 is proposed

$$[Ni^{II}(p-X)TPP]^0 \rightleftarrows [Ni^{II}(p-X)TPP]^+ + e^- \qquad (2)$$

$$[Ni^{II}(p-X)TPP]^+ \rightleftarrows [Ni^{III}(p-X)TPP]^{2+} + e^- \qquad (3)$$

for the electrooxidation of $Ni^{II}(p-X)TPP$, where X = OCH3, CH3, H, F. $[Ni^{II}(p-X)TPP]^0$ represents the neutral com-
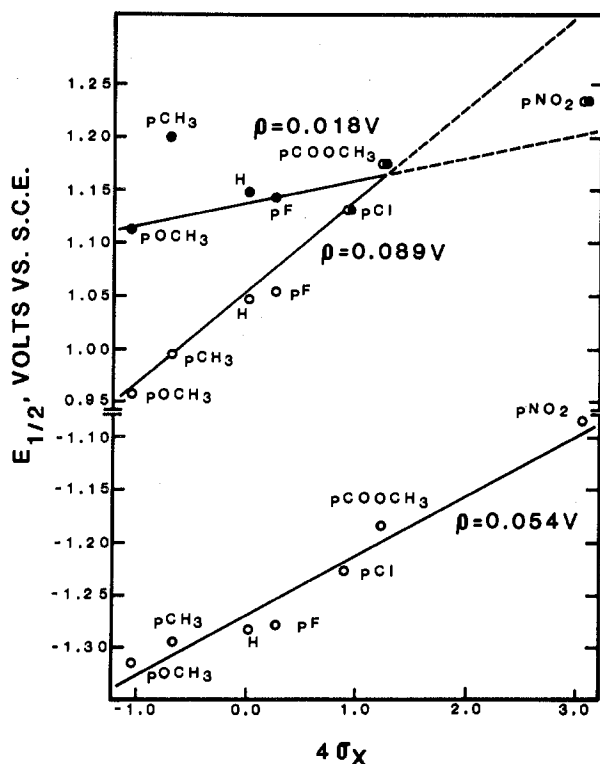
Figure 2. Plot of $E_{1/2}$ vs. 4σ for the redox reactions of Ni(p-X)TPP in 0.1 M TBAP, CH_2Cl_2: ○, first oxidation peak or first reduction peak to yield anion or cation radical; ●, second oxidation peak to yield nickel(III) cation radical.

pound, $[Ni^{II}(p\text{-}X)TPP]^+$ the cation radical of nickel(II), and $[Ni^{III}(p\text{-}X)TPP]^{2+}$ the cation radical of nickel(III). This agrees with the data of Dolphin et al.[17] which show the initial single-electron oxidation of NiTPP in CH_2Cl_2 yields a stable species whose optical spectrum resembles those of $MgTPP^+$ and $ZnTPP^+$. Oxidation of nickel octaethylporphyrin, NiOEP, by ferric perchlorate also yields optical and ESR spectra characteristic of ring oxidation.[18]

The electrochemical ρ of 0.018 V obtained for reaction 3 is consistent with a reduced interaction of the central nickel d_π electrons and the π electrons of the porphyrin ring. It has been shown that transmission of electronic effects from the periphery of the porphyrin ring is along the plane of the porphyrin to the central nitrogens where a cis and trans effect may be observed.[19] A "normal" pattern of substituent effects is noted for ligand addition to nickel(II) for a series of neutral metalloporphyrins containing substituents at either the porphyrin ring[20] or the four phenyl groups of tetraphenylporphyrin.[15] The ρ of 0.089 V for reaction 2 is close to the ρ of 0.085 V for the ring oxidation of $Co^{III}(p\text{-}X)TPP$[12] and fits into the range observed for other transition metal tetraphenylporphyrins, 0.068 ± 0.021 V. Of special note is the fact that the metal reaction apparently occurs after the formation of the cation radical for the compounds containing electron-donating substituents. This role may be reversed for electron-withdrawing substituents (as indicated by slope of Hammett plot for reaction 2). Studies are now in progress which show that, through the judicious placement of electron-donating or -withdrawing substituents on a porphyrin ring, the reactivities of metalloporphyrins can be drastically altered, and in certain cases, reversals may be observed in the order of ring vs. metal reaction.

for stimulating discussions.

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Preparation and Some Reactions of Diethylenetriaminepalladium(II)–Solvento Complexes

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Complexes in which solvents are present as ligands are of interest for several reasons. They are potential intermediates in reactions carried out in solution. Many solvents form relatively weak bonds to metal ions so that solvento complexes are highly reactive starting materials. Solvento complexes may show unusual and interesting reactions such as that of [Pt-(dien)H₂O](ClO₄)₂[3] with sodium tetraphenylboron to yield [Pt(dien)Ph]BPh₄.[4] Here we describe the preparation of aquo, hydroxide, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile complexes of palladium(II), together with the reaction of the aquo complex with sodium tetraphenylboron and the hydroxy complex with carbon monoxide.

Experimental Section

[Pd(dien)I]I,[5] [Pd(dien)H₂O](ClO₄)₂,[5] and [Pd(dien)Cl]Cl[6] were prepared as described previously. Methanol, acetone, and acetonitrile were dried as in the literature.[7] Tetrahydrofuran was stored over sodium wire (48 h) and then fractionally distilled under oxygen-free