

Figure 3. Plot of $-\Delta H_{12}$ (squares) for reaction of R_3P with $HgCl_2$ in C_6H_6 and $-\Delta H_{13}$ (crosses) for reaction of R_3P with $(R_3P)HgCl_2$ in C_6H_6 vs. $-\Delta H_{HP}$ for R_3P . Numbers refer to Table I; points not numbered are for $(n-Bu)_3P$.

0.977) for the five phosphines (ΔH_{HP} for $(n-Bu)_3P$ estimated from eq 8), but $(c-C_6H_{11})_3P$ (point number 10) is obviously out of line. The correlation with the point for $(c-C_6H_{11})_3P$ removed is practically perfect ($r = 1.000$). The deviation of $(c-C_6H_{11})_3P$ can be attributed to specific steric hindrance ($\theta = 170^\circ$ for this phosphine)^{1d} to adduct formation. (There may also be some contribution from a repulsive π -interaction between $(c-C_6H_{11})_3P$, which can act as a π -donor,³ and the filled d orbitals of $HgCl_2$). The values of ΔH_{13} are not correlated well with ΔH_{HP} 's ($r = 0.910$). For this reaction, steric effects would be expected to be more

important; this, coupled with the now variable electronic properties of the acceptor, $(R_3P)HgCl_2$, eliminates any expectation of a linear correlation with ΔH_{HP} .

Conclusion

The present study demonstrates that protonation enthalpies (ΔH_{HP} 's, determined by calorimetric titration with CF_3SO_3H in DCE) are valid and consistent measures of phosphine basicity and are directly related to the electron-donating ability of phosphines in other solution media. The protonation reactions are highly exothermic ($-\Delta H_{HP} \geq 18 \text{ kcal mol}^{-1}$) for the phosphines studied; thus, errors due to secondary reactions (such as acid dimerization or ion-pair dissociation) are not significant. The method described also offers the ability to measure basicity for a wide range of base strengths under the same conditions. The ΔH_{HP} values should prove to be extremely useful tools for investigations of reactivity in transition-metal chemistry; such studies aimed at determining the relationship between phosphine and metal-phosphine complex basicity are in progress in our laboratories.

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Registry No. $(p-ClC_6H_4)_3P$, 1159-54-2; $(p-FC_6H_4)_3P$, 18437-78-0; Ph_3P , 603-35-0; $(o-MeC_6H_4)_3P$, 6163-58-2; $(p-MeC_6H_4)_3P$, 1038-95-5; $(p-MeOC_6H_4)_3P$, 855-38-9; $MePh_2P$, 1486-28-8; Me_2PhP , 672-66-2; Me_3P , 594-09-2; $(c-C_6H_{11})_3P$, 2622-14-2; Et_3P , 554-70-1; $(t-Bu)_3P$, 13716-12-6.

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Electrochemical and Spectral Characterization of the Monomer-Dimer Equilibrium Involving (*meso*-Tetrakis(1-methylpyridinium-4-yl)porphinato)nickel(II) in Dimethylformamide

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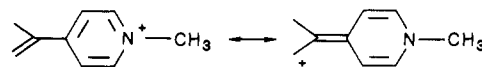
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The electrochemistry of $(TMPyP)Ni(ClO_4)_4$ (where $TMPyP$ is the dianion of *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin) was characterized in DMF by polarography, cyclic voltammetry, spectroelectrochemistry, and ESR spectroscopy. The neutral and reduced $(TMPyP)Ni(ClO_4)_4$ exist in a monomer-dimer equilibrium in DMF, and this equilibrium results in the presence of four two-electron reductions. The dimerization was also characterized by electronic absorption and NMR spectroscopy. At concentrations of porphyrin close to 10^{-6} M the monomeric and dimeric forms of the complex exist in essentially equal amounts, but at polarographic concentrations the dimeric form prevails in solution. A dimerization constant was calculated from cyclic voltammetric measurements and was of the same order of magnitude as observed for dimerization of other $TMPyP$ complexes in aqueous media.

Introduction

The free base porphyrin $[(TMPyP)H_2]^{4+}$ (where $TMPyP$ is the dianion of *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin) and its metal derivatives have potential therapeutic use because of their ability to react with DNA.²⁻⁷ These "water soluble"

meso-tetrakis(1-methylpyridinium-4-yl)porphyrins play an important role as photosensitizers and as labels for DNA and other biological cells. The diamagnetic $[(TMPyP)H_2]^{4+}$ complex has a positive charge on the pyridinium nitrogen atoms, which is delocalized over the porphyrin ring via resonance structures of the type⁸



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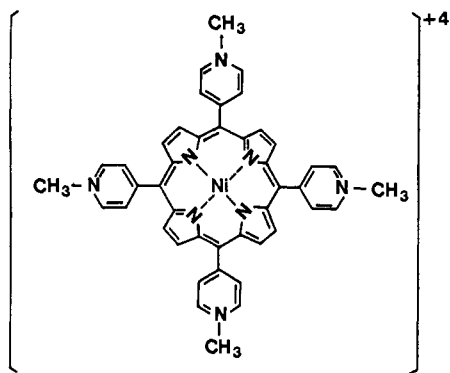


Figure 1. Structure of (TMPyP)Ni(ClO₄)₄ in the dissociated [(TMPyP)Ni]⁴⁺ form.

The free base porphyrin and its metalated zinc derivative [(TMPyP)Zn]⁴⁺ are proposed to dimerize in aqueous solutions when at low concentrations.^{9,10} Aggregation is one of the fundamental properties of metalloporphyrins in aqueous media, and it is believed that the positive charge on [(TMPyP)H₂]⁴⁺ is responsible for its dimerization in water.

The [(TMPyP)H₂]⁴⁺ complex exists in one of three isomeric forms.¹¹ A recent assignment for dimerization was based on fluorescence experiments⁸ and contradicts earlier suggestions that two of the isomeric [(TMPyP)H₂]⁴⁺ complexes are monomeric in aqueous solutions.¹²⁻¹⁵ More recently, Brookfield et al.⁸ confirmed dimerization of the 4-isomer of [(TMPyP)H₂]⁴⁺, but no mention of aggregation was made for the 2- and 3-isomers. [(TMPyP)Fe^{III}]⁵⁺,¹⁶⁻¹⁹ and [(TMPyP)Mo^VO]²⁺²⁰ have also been extensively investigated in aqueous solutions, and these monomeric compounds may also exist in equilibrium with their dimeric forms, depending upon the experimental conditions.

Free base *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin, [(TMPyP)H₂]⁴⁺, is reduced via three two-electron-transfer steps in both DMF²¹ and water.²² Similar two-electron-transfer processes occur for reduction of the corresponding Mn(III) and Zn(II) derivatives^{21,23} as well as for the Sb(V), Sn(IV), Ga(III), Al(III), and Pb(II) complexes of TMPyP.²³ These two-electron reductions may be due to the presence of the positively charged 1-methylpyridinium-4-yl groups,^{24,25} and for the Mn(III) derivative these reductions have been rationalized as due to the very basic substituents on the porphyrin ring.²⁵

This present work concentrates on the electrochemical and spectroelectrochemical behavior of (*meso*-tetrakis(1-methylpyridinium-4-yl)porphyrinato)nickel(II)perchlorate, (TMPyP)Ni(ClO₄)₄, in DMF containing 0.1 M TBAP as supporting electrolyte. This compound is totally dissociated in aqueous media

and exists as the monomeric [(TMPyP)Ni]⁴⁺ species, which is in an equilibrium mixture between diamagnetic four-coordinate nickel and paramagnetic six-coordinate nickel complexed by water molecules at the axial positions.²⁶ However, in DMF only limited dissociation of the complex occurs.

The structure of monomeric (TMPyP)Ni(ClO₄)₄ in its dissociated cationic form is shown in Figure 1. In this present investigation different electrochemical techniques are combined with ESR, NMR, and electronic absorption spectroscopy to investigate the prevailing monomer-dimer equilibrium of (TMPyP)Ni(ClO₄)₄ in DMF and to explain the multielectron-transfer reduction of the complex.

Experimental Section

Instrumentation and Methods. UV-visible spectra were recorded on an IBM-9430 spectrophotometer or a Tracor Northern 1710 holographic optical spectrometer/multichannel analyzer. ¹H NMR spectra at 300 MHz were recorded on a Nicolet NT-300 spectrometer controlled by a Model 293C programmer. Spectra were measured on 3-mg solutions of complex in DMF-*d*₇ with tetramethylsilane as internal reference. Samples for ESR measurements were electrolyzed under an inert atmosphere by Schlenk techniques. The samples were transferred to ESR cells that were modified for use on a Schlenk line and immediately frozen in liquid nitrogen. ESR spectra were recorded on an IBM Model ED-100 electron spin resonance system. Cyclic voltammetric and polarographic measurements as well as bulk controlled-potential coulometry were carried out by using either BAS-100 analyzer or a Princeton Applied Research Model 174A/175 polarographic analyzer/potentiostat coupled with an Omnigraphic Houston 9002A X-Y recorder for potential scan rates less than 0.5 V/s.

The working and counter electrodes were platinum. A platinum-mirrored electrode was used for the thin-layer spectroelectrochemical cell. Potentials were measured vs a saturated calomel electrode (SCE), which was separated from the bulk solution by means of a fritted-glass-disk junction. Thin-layer spectrophotochemical measurements were made with an IBM EC 225 voltammetric analyzer coupled with a Tracor Northern 1710 spectrometer multichannel analyzer.

Materials. Free base [(TMPyP)H₂]⁴⁺ and (TMPyP)Ni(ClO₄)₄ were synthesized according to procedures reported by Pasternack et al.¹⁴ Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Eastman Kodak Co., recrystallized from ethyl alcohol, and stored in a vacuum oven at 40 °C. A 0.2 M solution of TBAP was used as a supporting electrolyte for bulk electrolysis and spectroelectrochemical measurements, and 0.1 M TBAP was used for polarographic and voltammetric measurements. The solvent used was DMF (*N,N*-dimethylformamide), which was vacuum distilled twice over molecular sieves prior to use.

Results and Discussion

Spectral Characterization of (TMPyP)Ni(ClO₄)₄. The electronic absorption spectra of (TMPyP)Ni(ClO₄)₄ at different concentrations in DMF are shown in Figure 2. The complex has two sets of peaks in the Soret and visible regions. The Soret peaks are located at 422 and 440 nm while the two visible bands are at 524 and 565 nm. Beer's law is obeyed at both very low and very high concentrations, but at intermediate concentrations of the porphyrin a deviation from Beer's law is observed. This is shown in Figure 2b, which illustrates Beer's law plots for the bands at 422 and 524 nm.

The spectral data in Figure 2 indicate both a monomeric and an aggregated form of (TMPyP)Ni(ClO₄)₄ in DMF. The concentration dependence of the two Soret band absorbances suggests that monomeric (TMPyP)Ni(ClO₄)₄ absorbs at 440 nm and that the aggregate form of the complex absorbs at 422 nm. This assignment of the Soret band for monomeric and aggregated (TMPyP)Ni(ClO₄)₄ is in good agreement with assignments for iron tetrakis(1-methylpyridinium-4-yl)- and tetrakis(*p*-sulfonatophenyl)porphyrins, which exist in a monomer-dimer equilibrium.^{17,18}

[(TMPyP)Ni]⁴⁺ has been proposed to exist in two forms in aqueous media.²⁶ One form is a diamagnetic, four-coordinate nickel(II) species, while the other is a paramagnetic six-coordinate nickel(II) complex that contains bound water molecules at each

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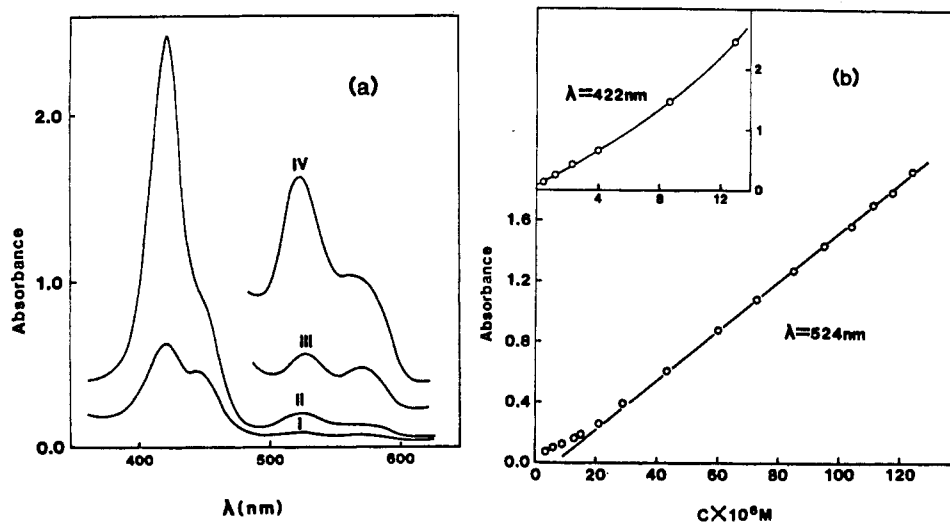


Figure 2. (a) Electronic absorption spectra of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$ in a 1-cm cell in DMF at the following concentrations: (i) 3.76×10^{-6} M; (ii) 1.30×10^{-5} M; (iii) 2.94×10^{-5} M; (iv) 7.34×10^{-5} M. (b) Concentration dependence of absorption peaks at 524 and 422 nm.

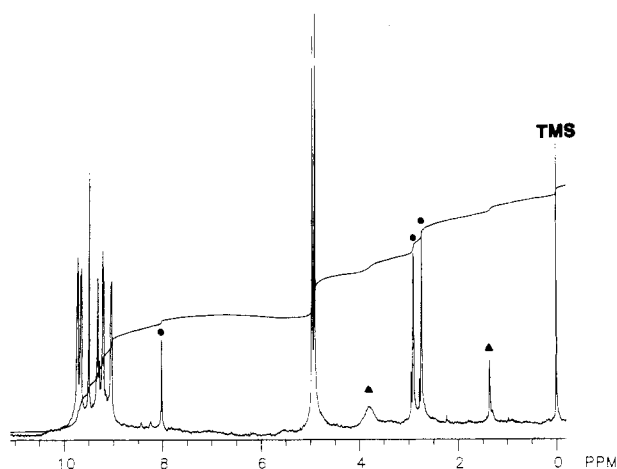


Figure 3. ^1H NMR spectrum of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$ in $\text{DMF}-d_7$ at 17°C . The extra peaks are due to DMF (●) and background (▲).

of the two axial positions. The four-coordinate species is proposed to absorb at 420 nm, while the six-coordinate species absorbs at 440 nm. The UV-visible spectral characteristics of $[(\text{TMPyP})\text{Ni}]^{4+}$ are similar both in water and in DMF, but an NMR characterization of the complex indicates a dimerization in the latter solvent. This is illustrated by Figure 3, which shows the NMR spectrum of $[(\text{TMPyP})\text{Ni}]^{4+}$ in $\text{DMF}-d_7$ with Me_4Si as internal standard.

A splitting of the pyridyl H signals of the complex results in the appearance of four doublet peaks between 9 and 10 ppm, and the spectrum is similar to NMR spectra observed for dimers of other metalloporphyrins.²⁷ A downfield shift of the pyrrolic protons is also observed upon dilution. When the concentration of $[(\text{TMPyP})\text{Ni}]^{4+}$ is decreased over the range 3.5–0.15 mM, the signal of the pyrrole protons shifts from 9.45 to 9.77 ppm. An analogous concentration dependence of the NMR spectrum is observed for coproporphyrins and was explained in terms of an association of the porphyrin, where the dimer consisted of two porphyrin molecules stacked one above the other with the planes of the porphyrin rings parallel.²⁷ All of these data indicate that a dimerization of $[(\text{TMPyP})\text{Ni}]^{4+}$ also occurs in DMF.

Electrochemistry of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$. Figure 4 shows dc polarograms of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$ at two different concentrations in DMF. The complex is reduced in four steps ($E_{1/2} = -0.50$, -0.62 , -0.82 , and -1.01 V) and does not undergo any oxidations within the potential range of the solvent. The reduction potentials

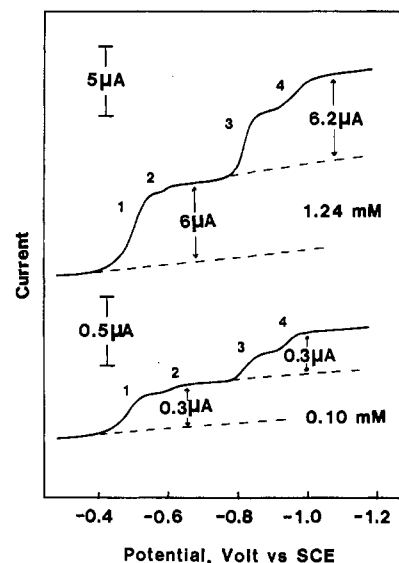


Figure 4. Dc polarograms of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$ at two concentrations in DMF, 0.1 M TBAP.

are shifted positively in comparison with reduction potentials of other previously studied nickel porphyrins,^{28–30} and this can be attributed to the positive charge of the porphyrin ring substituents.^{24,25} Generally, as the porphyrin ring basicity decreases, the reductions become more facile and the oxidations become more difficult.²⁸

The limiting currents for the reductions of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$ are not directly proportional to the bulk concentration, but the sum of currents for processes 1 and 2 is approximately equal to that for processes 3 and 4 at all concentrations (see Figure 4). The half-wave potentials are independent of the bulk concentration, and the limiting currents of each wave increase linearly with the square root of the mercury height. Polarographic wave analysis of the first and third reduction gives a slope of 32 ± 2 mV, thus implying the addition of two electrons in these processes. The second and fourth reduction waves are ill-defined, and wave analysis could not be carried out.

Cyclic voltammograms of $(\text{TMPyP})\text{Ni}(\text{ClO}_4)_4$ at three different concentrations are shown in Figure 5. There are four reduction waves located at $E_{1/2} = -0.51$, -0.61 , -0.84 , and -0.97 V. At scan

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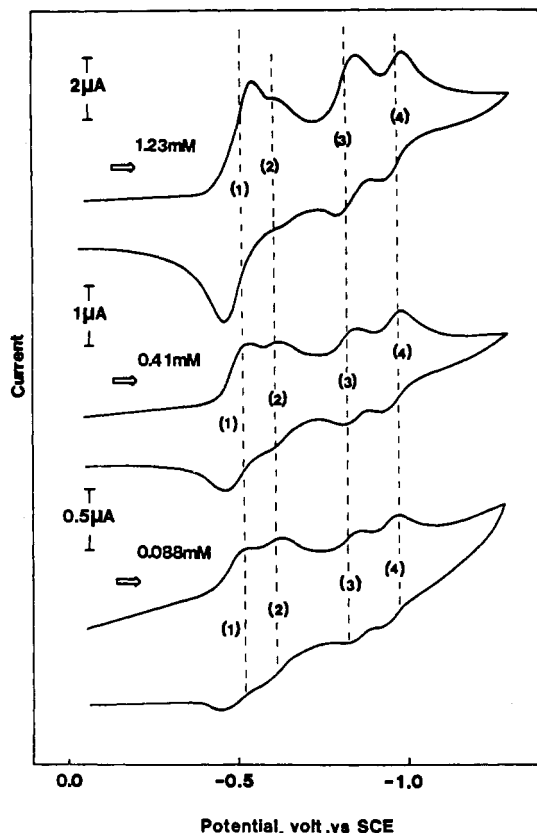


Figure 5. Cyclic voltammograms illustrating the concentration dependence of the four (TMPyP)Ni(ClO₄)₄ reduction processes in DMF, 0.1 M TBAP at a scan rate of 0.1 V/s.

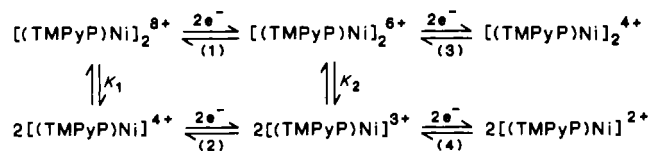
rates >0.2 V/s the peak current intensity of each reduction increases linearly with the square root of scan rate while the peak potentials are independent of scan rate. This indicates diffusion-controlled processes under these conditions. At scan rates <0.2 V/s the currents were not proportional to $v^{1/2}$. This is discussed in later sections of the paper.

Analysis of the current-voltage curves in Figure 5 gives peak potential separations $|E_p - E_{p/2}|$ and $|E_{pc} - E_{pa}|$ that range between 40 and 45 mV for the first and third reductions of (TMPyP)Ni(ClO₄)₄ at low scan rates. Analysis of the second and fourth processes was difficult due to the small currents and the closeness of these waves to processes 1 and 3. Values of i_{pc}/i_{pa} for waves 1 and 3 are close to unity and are invariant with increasing concentrations of (TMPyP)Ni(ClO₄)₄. The values of E_p are also invariant with increasing concentrations of the metalloporphyrin. However, an increase of the current ratio for the first two reductions, $(i_{pc})_1/(i_{pc})_2$, is observed at larger concentrations. This ratio also increases when the temperature is decreased and at -2 °C is about twice the ratio at room temperature. This variation of $(i_{pc})_1/(i_{pc})_2$ with concentration and temperature suggests an equilibrium between two electrochemically reducible forms of the complex.

Controlled-potential coulometry of (TMPyP)Ni(ClO₄)₄ also supports the existence of two electroreducible forms of the complex in equilibrium. Bulk electrolysis carried out at potentials of -0.58, -0.74, -0.92, and -1.2 V gave 1.1, 0.16, 1.0, and 0.23 electrons, respectively. This result is consistent with the overall global addition of two electrons per monomeric unit of (TMPyP)Ni(ClO₄)₄.

A simple reduction mechanism involving monomeric and dimeric forms of (TMPyP)Ni(ClO₄)₄ seems to prevail. Other reduction mechanisms such as disproportionation or dimerization at the surface of the electrode can be eliminated by an evaluation of diagnostic criteria involving variation of E_p or i_p with scan rate (v) and concentration (C). The experimental results are as follows: (i) scan rate variation, $\Delta E_p/\Delta \log v = \text{constant}$, $\Delta(i_p/v^{1/2})/\Delta v = \text{constant}$, $\Delta(i_{pc}/i_{pa})/\Delta v = \text{constant}$; (ii) concentration variation,

Scheme I



$\Delta E_p/\Delta C = \text{constant}$, $\Delta(i_{pc}/i_{pa})/\Delta C = \text{constant}$.

All of the above data suggest that monomeric (TMPyP)Ni(ClO₄)₄ exists in equilibrium with its dimeric form in DMF and that the electroreduction of (TMPyP)Ni(ClO₄)₄ can be described by the mechanism shown in Scheme I. In Scheme I, (TMPyP)Ni(ClO₄)₄ is shown as being totally dissociated and as existing in the cationic [(TMPyP)Ni]⁴⁺ form. This dissociation only partially occurs in DMF. In addition, two dimerization constants are shown in Scheme I. These involve the neutral and the singly reduced species and are represented by K_1 and K_2 .

The ratio of currents for the initial 2e reduction of the dimer (process 1) to those for the initial 2e reduction of two monomers (process 2) increases with increasing sweep rates up to 0.2 V/s. This change in current ratio (given by $(i_{pc})_1/(i_{pc})_2$) can be attributed to the fact that when the dimer is first reduced via process 1, its concentration in the vicinity of the electrode is less than that in the bulk of the solution. Because of this, the neutral monomer then associates in order to reestablish equilibrium. However, at scan rates greater than 0.2 V/s, the ratio of currents for processes 1 and 2 remains almost constant, indicating that the equilibrium is then frozen on the electrochemical time scale. Under these conditions the true solution concentrations of the monomer and dimer are electrochemically detected.

Spectroelectrochemistry and ESR Spectra of Electroreduced (TMPyP)Ni(ClO₄)₄. In order to confirm the validity of the mechanism shown in Scheme I, controlled-potential electrolysis was carried out for each reduction and the products were investigated by electronic absorption and ESR spectroscopy. Electronic absorption spectra were taken before and during the controlled-potential reduction of (TMPyP)Ni(ClO₄)₄. Typical time-resolved thin-layer spectra at potentials negative of processes 1 and 3 are shown in Figure 6.

The spectrum obtained during controlled-potential reduction of (TMPyP)Ni(ClO₄)₄ at -0.57 V shows a decrease of the Soret band intensity at 422 nm and the appearance of a new band at 474 nm (see Figure 6a). At the same time another new band appears at 842 nm. This is at a characteristic absorbance for a porphyrin π anion radical.

After this reduction an equilibrium is established between two different reduced forms of the complex in solution. This is evident by cyclic voltammograms obtained after electrolysis at -0.57 V. Under these conditions there is a decrease but not a disappearance of the first wave.

UV-visible spectra obtained after bulk electrolysis at -0.9 V (Figure 6b) and -1.2 V have the same features, i.e., a progressive decrease of the peak intensity at 842 nm. The spectrum of the species in solution initially has one broad band in the Soret region, but this band splits into two separate bands with progressive time of electrolysis. Thus, it is clear from spectral data in the Soret region that the singly and doubly reduced forms of (TMPyP)Ni(ClO₄)₄ also exist in a monomer-dimer equilibrium at the end of electrolysis.

The ESR spectrum of the solution after bulk electrolysis at -0.60 V at liquid-nitrogen temperature exhibits a signal at $g_{\parallel} = 1.99$ and at $g_{\perp} = 2.02$. After bulk electrolysis at -1.20 V there is no longer an ESR signal. These data are consistent with the global addition of one electron to each of the porphyrin π ring systems in processes 1 and 2 and two electrons to each of the π ring systems in processes 3 and 4.

Calculation of Dimerization Constant. Cyclic voltammetric data have been used in the past for calculation of dimerization constants.^{17,31} In this present study the peak current ratios for the first and second reduction processes and for the third and fourth reduction processes at fast sweep rates represent the relative

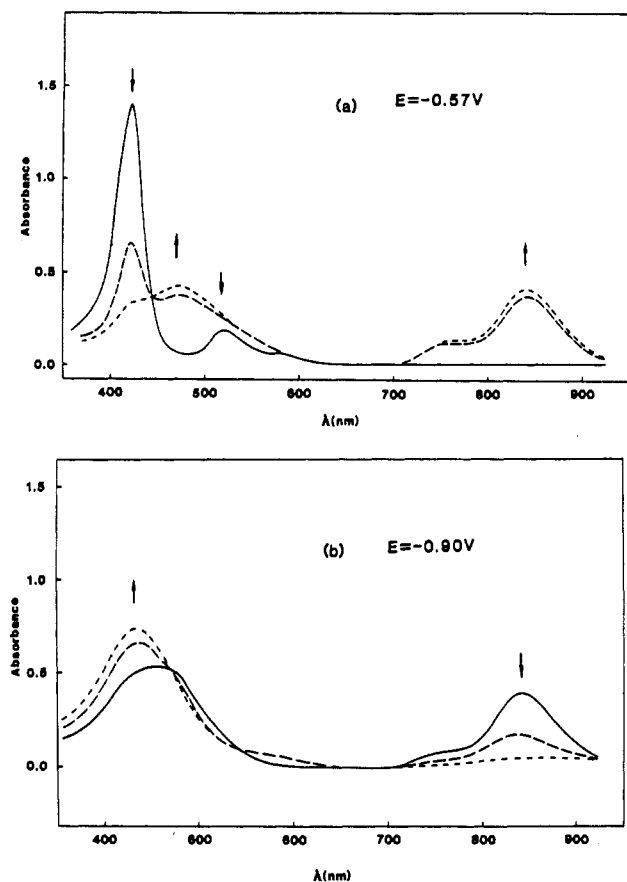


Figure 6. Time-resolved electronic absorption spectra during controlled-potential electrolysis of 1.66×10^{-4} M (TMPyP)Ni(ClO₄)₄ in DMF, 0.2 M TBAP at (a) -0.57 V and (b) -0.9 V.

concentrations of the dimeric and monomeric forms of (TMPyP)Ni(ClO₄)₄ in solution. Thus, these values can be used to calculate the dimerization constants K_1 and K_2 in Scheme I.

If the diffusion coefficients of the dimer, D_D , and monomer, D_M , are equivalent,^{17,31} then the Randles-Sevcik equation can be arranged to give the ratio of reduction peak currents as shown

in eq 1, where $(i_p)_D$ and $(i_p)_M$ represent peak currents for the first

$$\frac{(i_p)_D}{(i_p)_M} = \frac{C_D n_D^{3/2}}{C_M n_M^{3/2}} \quad (1)$$

reduction of the dimer and monomer, respectively. The numbers of electrons transferred, n_D and n_M , are 2 for the dimer and 1 for the monomer, and eq 1 can thus be written as

$$\frac{(i_p)_D}{(i_p)_M} = 2.83 \frac{C_D}{C_M} \quad (2)$$

The total porphyrin concentration is given by

$$C_T = C_M + 2C_D \quad (3)$$

and the dimerization constant K_D (where K_D is either K_1 or K_2 in Scheme I) is given by

$$K_D = \frac{C_D}{(C_T - 2C_D)^2} \quad (4)$$

Combining eq 2 with eq 3 and 4 enables calculation of the dimerization constants. The calculated values of K_1 and K_2 are 7×10^3 and 2×10^3 M⁻¹, which compare with an electrochemically calculated dimerization constant of 2×10^3 M⁻¹ for [(TMPyP)Fe(OH)₂]³⁺ in basic aqueous media.¹⁷ The value of 7×10^3 M⁻¹ for [(TMPyP)Ni]⁴⁺ can also be compared with a larger K_D value of 9×10^5 M⁻¹ which was calculated for dimerization of [(TMPyP)Fe(OH)₂]³⁺ by using spectral data.¹⁶ However, it should be noted that the calculation for [(TMPyP)Ni]⁴⁺ is based solely on electrochemical data and may be influenced by a dynamic equilibrium between monomeric and dimeric forms of the complex. For this reason, the calculated value is probably good only to $\pm 50\%$.

In conclusion, (TMPyP)Ni(ClO₄)₄ is reduced in four electron-transfer processes that involve the overall global addition of two electrons per (TMPyP)Ni(ClO₄)₄ unit. The electrochemical and spectroelectrochemical data agree with the existence of an equilibrium between the neutral and singly reduced monomeric and dimeric forms of the complex. Similar equilibria may exist for other [(TMPyP)M]⁴⁺ complexes in DMF. This is presently under investigation.

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