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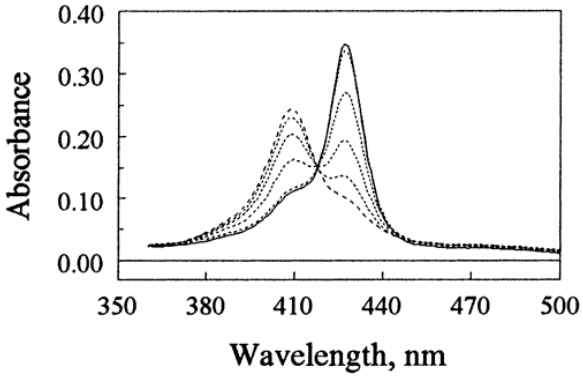

Abstract

The reaction of hydroxylamine with a series of metal porphyrins was examined in methanol/chloroform media. The reductive nitrosylation reaction was observed for the manganese and iron porphyrins, leading to a nitrosyl complex that precipitated out of the solution in good isolatable yield (80−90%). This reaction could be used synthetically for the generation of iron and manganese porphyrin nitrosyl complexes and was particularly useful for making isotopically labeled nitrosyl complexes. On the other hand, Co^{II}(TPP) and Cr(TPP)(Cl) did not react with hydroxylamine under anaerobic conditions. With trace amounts of oxygen, the reaction of Co^{II}(TPP) with hydroxylamine led to the formation of a stable cobalt(III)−bis(hydroxylamine) complex. The infrared, resonance Raman, and proton NMR spectra were consistent with a cobalt(III)−bis(hydroxylamine) complex. The cyclic voltammetry and visible spectroelectrochemistry of this complex were examined. The one-electron reduction of $Co^{III}(TPP)(NH_2OH)_2^+$ formed Co^{II}(TPP), for which there was no evidence for the coordination of hydroxylamine. Further reduction led to $Co^{I}(TPP)^-$, which reacted with the halogenated solvent to form a cobalt−alkyl complex. The difference in the reactivity of these four metal porphyrins with hydroxylamine correlated well with their $E_{1/2}$ values. Iron(III) and manganese(III) porphyrins were relatively easy to reduce and readily underwent the reductive nitrosylation reaction, while cobalt(II) and chromium(III) porphyrins are unreactive. The one-electron oxidation of the hydroxylamine complex with a M(III) porphyrin would be expected to oxidize the N-atom in the coordinated hydroxylamine. The oxidation of $M^{III}(NH_2OH)$ with the loss of a proton would form $M^{II}(N^{I}H_2O)^+$ by an internal electron transfer, which will eventually lead to M(NO). The relationship between the reductive nitrosyl reaction and the enzymatic interconversion of NO and hydroxylamine was discussed.

Synopsis

The reaction of hydroxylamine with a series of metal porphyrins was examined. Iron and manganese porphyrins were reductively nitrosylated to their respective nitrosyl complexes, while no reaction was observed for cobalt and chromium porphyrins. In the presence of trace amounts of oxygen, Co^{II}(TPP) was oxidized to the bis(hydroxylamine)cobalt(III) complex. The reactivity of hydroxylamine with these metal porphyrins can be explained on the basis of their redox potentials, and the similarity with the reduction of the nitrosyl complexes was examined.

Introduction

Electrochemical reduction of metal complexes can result in electron transfer to either a metal or a ligand site. For mixed ligand complexes (e.g., metal + porphyrin + axial ligand), there can be three sites for the redox chemistry (as well as orbitals that have extensive M−L bonding or antibonding characteristics). We have examined such systems where the coordinated ligand, as well as the iron or porphyrin, may undergo redox changes. Of particular interest has been the reduction of iron−nitrosyl and iron−hydroxylamine complexes. Both ligands have been either observed (nitrosyl) or postulated (hydroxylamine) intermediates in assimilatory nitrite reductase.[1]

The reaction of hydroxylamine with iron porphyrins has been previously reported,[2] and it has been shown to form a bis(hydroxylamine) complex with iron(II) at reduced temperatures. When hydroxylamine was mixed with a ferric porphyrin, a ferrous complex was rapidly formed, which, at room temperature, decomposed further to form Fe(TPP)(NO), probably by way of the disproportionation of hydroxylamine.[2,3] This is a well-known reaction of hydroxylamine, called reductive nitrosylation, where a coordinated hydroxylamine is oxidized to nitric oxide (nitrosyl ligand) and an additional molecule of hydroxylamine is reduced to ammonia. The use of alkylated hydroxylamines prevents the reductive nitrosylation reaction, and bis(alkyl) hydroxylamine complexes with iron porphyrins have been reported.[3] The reduction of hydroxylamine with cob(I)alamins was reported by Balasubramanian and Gould.[4]

The chemistry of hydroxylamine, which has been reviewed by Wieghardt,[5] shows a wide variety of behaviors. For example, the oxidation of electrochemically generated Ti(III) by hydroxylamine has been investigated by a variety of electrochemical techniques.[6-8]Alternatively, manganese(III) or cobalt(III) can oxidize hydroxylamine to nitrate, dinitrogen or nitrous oxide, depending upon the pH.[9-11]Similar reactions have been observed with heme-containing proteins. Hydroxylamine is a substrate for hydroxylamine oxidoreductases,[12-14]which oxidize hydroxylamine to nitrite. Conversely, hydroxylamine is presumed to be an intermediate in the assimilatory reduction of nitrosyl to ammonia. Bagchi and Kleiner[15] have recently reported on a hydroxylamine dismutase which catalyzes the disproportionation of hydroxylamine to nitrite and ammonia. Hemoglobin has been reported to decompose hydroxylamine to form ammonia and dinitrogen, as well as some nitrous oxide.[16] In this work, we examined the chemistry of hydroxylamine with metal porphyrins in order to determine the scope and generality of the reductive nitrosylation reaction in metal porphyrins.

Experimental Section

Equipment.

Cyclic voltammograms were obtained with an IBM Instrument EC/225 voltammetric analyzer with a Hewlett Packard 7045A X-Y recorder. The reference electrode was a 0.1 M $Ag/AgNO_3$ (in acetonitrile) electrode, and the working and auxiliary electrodes were platinum. The UV−visible spectra were recorded on a HP 8452A diode array or a Perkin-Elmer 320 UV−visible spectrophotometer. An optically transparent thin-layer electrochemical (OTTLE) cell was used for the spectroelectrochemical experiments.[17] The NMR spectra were obtained on a 60-MHz (proton) JEOL JNM-FX60Q Fourier transform NMR spectrometer.

Chemicals.

The porphyrin complexes (Fe(TPP)(Cl) (TPP = tetraphenylporphyrin), Fe(OEP)(Cl) (OEP = octaethylporphyrin), Co(TPP), and Mn(TPP)(Cl)), hydroxylamine hydrochloride, methylene chloride, and sodium methoxide were obtained from Aldrich Chemical Co, while Fe(PPDME)(Cl) (PPDME = protoporphyrin dimethyl ester) was obtained from Porphyrin Products. Tetraphenylchlorin (H_2TPC)[18] and Fe(TPC)(Cl)[19] were synthesized by literature procedures. Tetrabutylammonium perchlorate (TBAP) was obtained from GFS Chemical Co. ^{15}N-Hydroxylamine hydrochloride was obtained from MSD Isotopes.

$Co(TPP)(NH_2OH)_2ClO_4$.

Co(TPP) (0.30 g) was dissolved in 100 mL of chloroform. To that solution was added 100 mL of 2% hydroxylamine in methanol, which contained 0.20 g of TBAP. After mixing, the solvent was evaporated. The solid was then dissolved in a minimum amount of chloroform and filtered to remove the excess TBAP and hydroxylamine. The solvent was removed and mixed with methanol. After filtration and drying, the solid was redissolved in chloroform, the solution was filtered, and the solvent was removed. The solid obtained was vacuum dried. The visible spectrum was identical to that obtained from mixing Co(TPP) with hydroxylamine. Yield: 82%. Anal. Calcd for $C_{44}H_{34}ClCoN_6O_6$; C, 63.12; H, 4.10; N, 10.04; Co, 7.04. Found: C, 63.14, H, 4.07, N, 9.58; Co, 6.86. Spectral

characterization of the product is given in the Results and Discussion section. *As a precaution with all perchlorate salts, quantities of the material were kept to a minimum for safety reasons.*

Fe(TPP)(NO) and Mn(TPP)(NO).

A 50 mg amount of Fe(TPP)(Cl) or Mn(TPP)(Cl) was dissolved in chloroform or methanol. To this solution was added at least a 2-fold excess of hydroxylamine, prepared as described below. The product nitrosyl complex precipitated out of solution in a period of 30 min and was isolated by filtration. Isolatable yields of 85−90% were obtained.

2% Hydroxylamine Solution.

One equivalent of sodium methoxide was added to a solution obtained by addition 200 mg of hydroxylamine hydrochloride to 10 mL of methanol. Sodium chloride precipitated and was removed by filtration. Fresh solutions were used for all reactions. Solid hydroxylamine is unstable above 0°C. As a precaution, the volume of hydroxylamine solution was kept to a minimum. For ^{15}N-labeled hydroxylamine and nitrosyl complexes, $^{15}NH_3OHCl$ was used in the preparation of this solution.

Procedures.

All the voltammetric solutions were deoxygenated by deaerating the solution for 15 min with prepurified dinitrogen. The dinitrogen was presaturated with the solvent in order to prevent evaporation. The spectroelectrochemical data were obtained after the current had decayed to the background. All the reactions between the metal porphyrins and hydroxylamine were carried out under anaerobic conditions in a glovebox, except as noted.

Analysis of Ammonia.

The spectrophotometric analysis of ammonia was carried out using Russell's procedure with the phenolate−hypochlorite reagent.[20,21] A 50 mg amount of MnTPPCl (FeTPPCl) was dissolved in 10 mL of methanol (chloroform) and then was added to 10 mL of 0.2 M hydroxylamine/methanol. The solution was purged with argon for 30 min, and the ammonia was trapped with 4.0 mL of 0.01 M HCl. After the purging was complete, 5 drops of 0.003 M manganese sulfate, 3.0 mL of cold alkaline phenol, and 1.5 mL of chlorine solution were added. The mixture was shaken well and placed in a boiling water bath for 5 min. The concentration of ammonia was then determined from the visible absorbance at 624 nm.

Results

Iron Porphyrins.

It has been previously shown that hydroxylamine reacts with Fe(TPP)(Cl) at room temperature by the following net reaction:[2]

$$\mathrm{Fe(TPP)(NH_2OH)_2^+ \rightarrow Fe(TPP)(NO) + NH_4^+ + H_2O}$$

This reaction is quite rapid, and it is not clear if it is initiated by uncoordinated hydroxylamine or by intramolecular electron transfer. The reaction above can be used as a general synthetic procedure with a mixed methanol/chloroform (1/1) solvent system. For most porphyrin macrocycles, the Fe(P)(NO) complex that was formed by the reductive nitrosylation reaction was insoluble in this solvent system, and the nitrosyl complex could be isolated in over 80% yield using small quantities of iron porphyrin. Nearly quantitative yields were obtained for Fe(P)(NO) complexes, where P = tetraphenylporphyrin (TPP), octaethylporphyrin (OEP), and tetraphenylchlorin (TPC). In order to precipitate Fe(PPDME)(NO) (PPDME = protoporphyrin dimethyl ester) complex, an 80/20 methanol/chloroform solution was used. This synthetic method is particularly advantageous

in the generation of ^{15}N-labeled nitrosyl complexes, starting with ^{15}N-hydroxylamine. The UV/visible and infrared spectra, as well as the voltammetric behavior, were identical to authentic material synthesized from the reaction of Fe(TPP)(Cl) with NO.[22,23] In addition to Fe(TPP)(NO), ammonia was also detected as a product of the reductive nitrosylation reaction. The yield of ammonia was well in excess of the stoichiometric amount (≈10 times the expected amount), indicating that the nitrosyl complex itself may also be catalyzing the disproportionation of hydroxylamine.

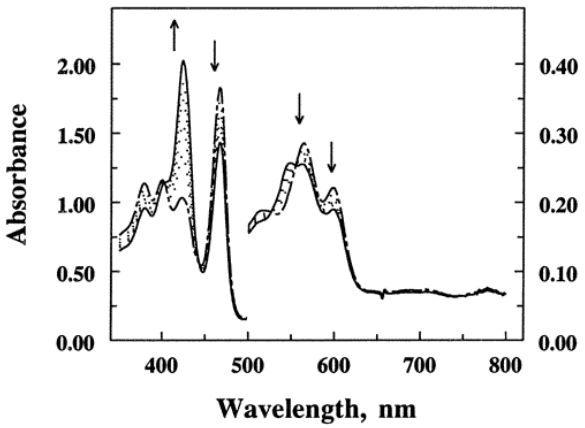

Figure 1 Visible spectra of Mn(TPP)Cl obtained after adddition of hydroxylamine. The concentration of Mn(TPP)Cl = 0.10 mM, concentration of hydroxylamine = 0.10 M, and the solvent is methanol. Interval between spectra: 60 s. Spectrum just after mixing: dashed. Spectrum after 360 s: solid. Intermediate spectra: dotted.

Manganese and Chromium Porphyrins.

In the absence of hydroxylamine, Mn(TPP)(Cl) in methanol has an intense Soret band at 466 nm, with additional bands at 378, 400, 418, 516, 562, and 598 nm. Upon addition of hydroxylamine, the original bands between 350 and 470 nm decreased, and a new, single Soret band appeared at 424 nm (Figure 1). In the longer wavelength region, bands at 542, 572, and 602 nm appeared. Several isosbestic points were observed in the spectrum during the reduction (Figure 1), indicating that no intermediates could be observed under these conditions in the conversion of Mn(TPP)Cl to Mn(TPP)(NO). Later in the reaction, the isosbestic points disappeared and the 424 nm band decreased due to precipitation of the product. When the reaction was complete (not shown in Figure 1), the original 350 and 470 nm bands completely disappeared, and the bands in the final product were identical to independently synthesized Mn(TPP)(NO) (Table 1). The product of the reaction was isolated, and an infrared spectrum of the product in KBr had a strong band at 1747 cm^{-1}, which was characteristic of a nitrosyl complex. Therefore, like the iron porphyrins, Mn(TPP)(Cl) underwent a reductive nitrosylation reaction.

Table 1. Visible Spectra of Metal Porphyrin Complexes

compd	solvent	λ, nm (ε, cm^{-1} mM^{-1})	ref
Co(TPP)	CH_2Cl_2	410 (295), 528 (16)	24
Co(TPP)(pyridine)	CH_2Cl_2	435, 549, 585sh	25
Co(TPP)(NO)	$CHCl_3$	416, 540	this work
$Co^{III}(TPP)^+$	CH_2Cl_2	427 (193), 540 (19.2)	24
$Co^{III}(TPP)(H_2O)^+$	CH_2Cl_2	426 (95), 536 (6.9)	26
	CH_3OH	425 (95), 539 (7.6)	26
$Co^{III}(TPP)(pyridine)(Cl)$	CH_2Cl_2	437 (100), 552 (9.1), 588 (4.0)	26
$Co^{III}(TPP)(pyridine)_2^+$	CH_2Cl_2	434 (132), 550 (9.8), 580 (4.5)	26
$Co^{III}(TPP)(NH_2OH)_2^+$	$CHCl_3$	427 (93), 542 (9.2)	this work
	CH_3CN	312, 427, 544, 578s	this work
	DMF	416s, 432, 544, 582	this work

	pyridine	436, 552, 590	this work
$Mn^{III}(TPP)(Cl)$	$CHCl_3$	376 (43.5), 476 (76.5), 581 (7.5), 617 (8.5), 690 (0.6), 769 (0.50)	27
$Mn^{III}(TPP)(CH_3OH)_2^+$	CH_3OH/CH_2Cl_2	377, 399, 419, 465, 563, 596	this work, 28
$Mn^{III}(TPP)(pyridine)_2^+$	pyridine	380 (38.5), 476 (63.0), 578 (7.6), 613 (76), 690 (1), 826 (0.67)	27
$Mn^{II}(TPP)(CH_3OH)$	CH_3OH/CH_2Cl_2	434[a]	28
$Mn^{II}(TPP)$	toluene/77 K	431, 537, 580, 617	29
$Mn^{II}(TPP)(NO)$	toluene/77 K	434, 540, 568, 609	29
	THF	430, 540, 568, 606	this work

[a] Only Soret band given in reference.

The ultimate product of the oxidizing agent (hydroxylamine) was not established. The initial product of the one-electron reduction of hydroxylamine is the $NH_2^{\bullet}$ radical (and hydroxide).[8,30]No detectable amounts of ammonia were generated in the reaction, using the same procedure as was used with the iron reaction, indicating an alternate fate for this radical. Because the primary focus of this work was on the metalloporphyrin, the ultimate fate of the oxidizing agent was not investigated. The order of the reaction with respect to hydroxylamine and Mn(TPP)Cl was investigated, using the initial rates of the reaction, measured spectrophotometrically (the precipitation of Mn(TPP)(NO) made it difficult to investigate the entire kinetic curve). From the variation in the observed rate constants as a function of hydroxylamine concentration and Mn(TPP)Cl concentration, the reaction was found to be first order with respect to both reactants with a rate constant of $(6.2 \pm 0.9) \times 10^{-2}$ M^{-1} s^{-1}. The first order nature of the reaction is consistent with the reaction of Mn(TPP)Cl with hydroxyalmine being the rate-limiting step. This rate-limiting step may be the electron transfer from hydroxylamine to Mn(TPP)Cl to form Mn(TPP) and NH_2 radical or the initial formation of the complex followed by an internal electron transfer. Unlike manganese and iron, no reaction was observed when Cr(TPP)(Cl) was mixed with hydroxylamine.

Cobalt Porphyrins.

As was observed with Cr(TPP)(Cl), no reaction was detected when Co(TPP) was mixed with hydroxylamine in a chloroform/methanol solution under strictly anaerobic conditions. Outside the glovebox, small quantities of dioxygen slowly leaked into the UV−visible cell, oxidizing Co(TPP). This caused the Co(TPP) bands at 410 and 528 nm to shifted to 427 and 542 nm (Figure 2), indicative of a cobalt(III) complex (Table 1). There was no evidence for the formation of Co(TPP)(NO) nor was there any ammonia generated.

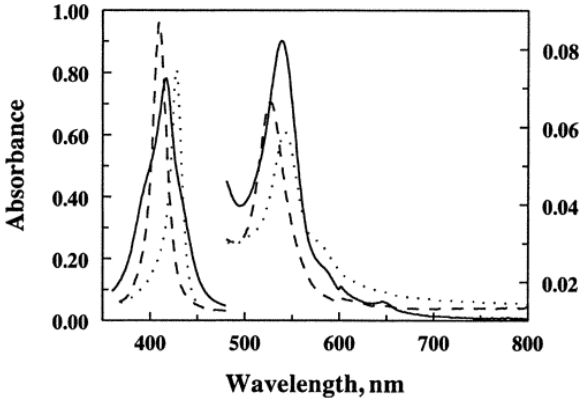

Figure 2 Visible spectrum of $Co^{II}(TPP)$ (dashed line) in methanol/methylene chloride prior to the addition of hydroxylamine. After addition of hydroxylamine, $Co^{III}(TPP)(NH_2OH)_2^+$ was formed (dotted line). Also shown is the visible spectrum of authentic Co(TPP)NO (solid).

A cobalt(III) complex was isolated from the reaction solution, as outlined in the Experimental Section. The elemental analysis was consistent with a bis(hydroxylamine) complex. The visible spectra of the isolated product in methylene chloride, acetonitrile, and methanol were identical to the spectrum obtained by the in situ reaction. Small shifts in the Soret band were observed in THF, DMF, and DMSO (Table 1). Significant spectral changes, though, occurred in pyridine, and the visible spectrum was the same as that for $Co^{III}(TPP)(pyridine)_2^+$.

The proton NMR chemical shifts for the cobalt−hydroxylamine and other cobalt complexes are summarized in Table 2. Four-coordinate $Co^{II}(TPP)$ has broad resonances at 15.7, 13.1, 9.8, and 8.9 ppm, due to the paramagnetic nature of the d^7 complex. Upon addition of hydroxylamine, the resonances shifted to their diamagnetic positions at 7.7, 8.2, and 9.1 ppm, and a resonance for hydroxylamine was observed at −1.4 ppm. This spectrum was typical of a diamagnetic Co(III)−TPP complex (Table 2) and was almost identical to the $Co^{III}(TPP)(pyridine)_2^+$ complex.

Table 2. Proton NMR Spectra of Various Cobalt Porphyrins

resonances, ppm				
compd	solvent	pyrrole	phenyl	ref
$Co^{II}(TPP)$	$CDCl_3$	15.7	13.1, 9.8, 8.95	this work
$Co^{II}(TPP)(pyridine)$	$CDCl_3$	12.5	8.5, 8.33, 7.82	25
$Co^{II}(TPP)(NO)$	$CDCl_3$	8.90	8.15, 7.76	31
$Co^{III}(TPP)(NH_2OH)_2^+$	$CDCl_3$	9.1	8.2, 7.7	this work
$Co^{III}(TPP)(pyridine)^+$	$CDCl_3$	8.99	7.81, 7.71	32
$Co^{III}(TPP)(pyridine)_2^+$	$CDCl_3$	9.09	8.10, 7.71	32
$Co^{III}(TPP)(H_2O)_2^+$	$CDCl_3$		8[a,b]	26
$Co^{III}(TPP)(H_2O)(Cl)$	$CDCl_3$	9.0[a]	8.8,[a] 7.7[a]	26
$Co^{II}(p\text{-}CH_3TPP)$	$CDCl_3$	15.40	12.9, 9.6[c]	33

[a] Resonance is broad. [b] Water resonance at −2.2 ppm. [c] Methyl at 4.0 ppm.

The infrared spectra of the cobalt−hydroxylamine complex were obtained using ^{14}N- and ^{15}N-hydroxylamine. Two isotope-sensitive bands were observed at 1678 (ν_3) and 1261 cm^{-1} (ν_5) for the ^{14}N-hydroxylamine complex which shifted to 1648 and 1250 cm^{-1} for the ^{15}N-hydroxylamine complex.[35] The resonance Raman spectra were also consistent with a cobalt(III) porphyrin complex. In acetonitrile, the ν_2 band for the hydroxylamine complex ($Co^{II}(TPP)$ bands in parentheses[36] occurred at 1569 cm^{-1} (1563 cm^{-1}) and the ν_4 band at 1373 cm^{-1} (1363 cm^{-1}). Overall, the spectroscopic evidence was consistent with the formation of a $Co^{III}(TPP)(NH_2OH)_2^+$ complex.

The formation of cobalt(III) porphyrins from cobalt(II) has been observed in the presence of other bases, even under anaerobic conditions. For example, Co^{II}(PPDME) (PPDME = protoporphyrin dimethyl ester) reacted with methoxide in an alcoholic solution to form $Co^{III}(PPDME)(OCH_3)_2^-$.[37] This reaction was repeated in this work with $Co^{II}(TPP)$ and methoxide in a mixed methanol/chloroform solution. A cobalt(III) spectrum was generated, with a Soret band at 427 nm, indicative of a $Co^{III}(TPP)(OCH_3)_2^-$ complex. It was possible to form Co(TPP)(NO) from the hydroxylamine product by heating the solution or letting it stand for several days.

The cyclic voltammetry of $Co(TPP)(NH_2OH)_2^+$ was carried out in methylene chloride between −40 °C and room temperature (Figure 3). Three reduction waves were observed. The first wave was an ill-defined and irreversible wave with an E_{pc} of −0.78 V vs SCE. This wave was about 500 mV positive of the $Co(TPP)^+$/Co(TPP) in the same solvent[24] and very close to the first reduction of $Co(TPP)(pyridine)_2^+$ (−0.77 V), $Co(TPP)(4\text{-picoline})_2^+$ (−0.83 V), or

$Co(TPP)(piperidine)_2^+$ (−0.81 V).[38] Spectroelectrochemical reduction of $Co(TPP)(NH_2OH)_2^+$ at the first wave in an OTTLE cell (Figure 4) led to a final spectrum that was identical to $Co^{II}(TPP)$. Reversal of the potential did not regenerate the cobalt hydroxylamine complex, confirming the irreversibility observed in the cyclic voltammograms. These results are consistent with the loss of hydroxylamine upon reduction (eq 1).

(1)

$$Co(TPP)(NH_2OH)_2^+ + e^- \rightarrow Co(TPP) + 2NH_2OH$$

Previous studies using NMR[25] and cyclic voltammetry[38] have shown that pyridine complexes weakly with Co(TPP), and it is unlikely that stoichiometric amounts of hydroxylamine would lead to a stable cobalt(II) complex.

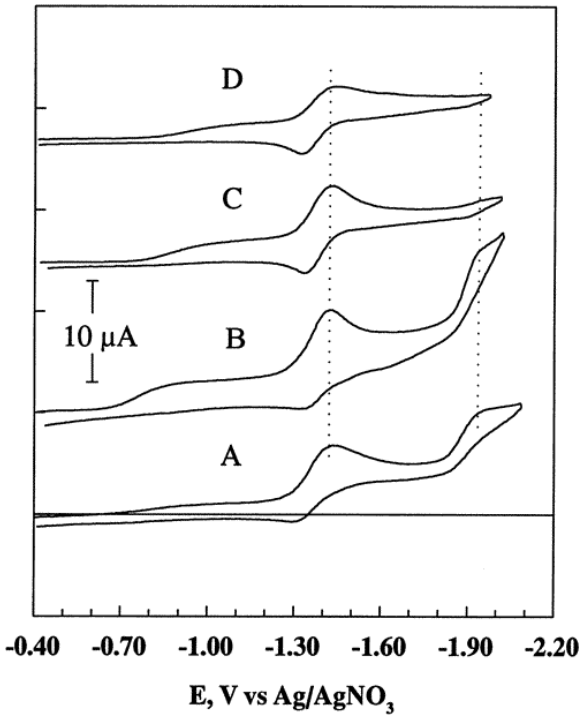

Figure 3 Cyclic voltammetry of $Co^{II}(TPP)$ (A, 21 °C) and $Co^{III}(TPP)(NH_2OH)_2^+$ (B, 21 °C; C, −25 °C; D, −40 °C) in methylene chloride. Working electrode: platinum; 0.1 M TBAP. Scan rate: 100 mV/s.

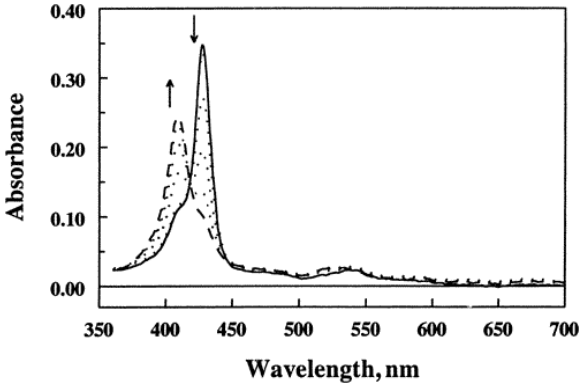

Figure 4 Visible thin-layer spectroelectrochemistry of $Co^{III}(TPP)(NH_2OH)_2^+$ in methylene chloride. Solid line: +0.11 V vs SCE. Dashed line: −0.22 V vs SCE. Other lines: intermediate spectra.

The second reduction wave was irreversible at room temperature and was located close to the $Co(TPP)/Co(TPP)^-$ reduction wave (Figure 3). This wave became more reversible as the temperature was reduced. Previous

studies[24] have shown that $Co(TPP)^-$, the reduction product, was not stable in methylene chloride and reacted with the solvent to form $Co(TPP)(CH_2Cl)$ (eqs 2 and 3).

(2)

$$Co(TPP) + e^- \rightarrow Co(TPP)^-$$

(3)

$$Co(TPP)^- + CH_2Cl_2 \rightarrow Co(TPP)(CH_2Cl) + Cl^-$$

The third wave, which could not be seen at −40 °C, was due to the reduction of the cobalt−alkyl complex.[24] At low temperatures, reaction 3 did not occur fast enough, and the reduction wave for the cobalt−alkyl complex is not observed.

The cyclic voltammetry of $Co(TPP)(NH_2OH)_2^+$ in acetonitrile was similar to the methylene chloride results. Unlike in methylene chloride, though, the second reduction wave (formation of Co^I) was reversible. The thin-layer spectroelectrochemistry of the hydroxylamine complex led to the formation of $Co^{II}(TPP)$. Unfortunately, the product appeared to be insoluble under the conditions studied and slowly precipitated out of solution during the OTTLE scan. This precipitation was too slow to be observed in cyclic voltammetry.

Discussion

The reductive nitrosylation reaction is particularly interesting in that it couples the reduction of the metal with the disproportionation of hydroxylamine:

$$2NH_2OH \rightarrow NO + NH_4^+ + H_2O + e^-$$

$$M^{III}(P) + e^- \rightarrow M^{II}(P)$$

The presence of a reducible metal atom allows a pathway to link 3-electron oxidation of hydroxylamine to NO with the 2-electron reduction of another hydroxylamine to ammonia. In neutral to alkaline solutions, it is known that hydroxylamine generally acts as an oxidizing agent.[39] If we assume that the initial step in the reaction is the one-electron oxidation of $M^{III}(P)(NH_2OH)^+$ by free hydroxylamine to form $M^{III}(P)(N^0H_2O)^+$ and $NH_2^\bullet$ (plus water), an internal electron transfer would lead to $M^{II}(P)(N^IH_2O^+)$. This species can readily lose two protons to form $M^{II}P(NO^-)$, which can be further oxidized to $M^{II}(P)(NO)$ by hydroxylamine or $NH_2^\bullet$.

This process would be the reverse of the reduction of $Fe^{II}(P)(NO)$ to form $Fe^I(P)^-$ and hydroxylamine in which the key kinetically observed intermediate was $Fe^{II}(P)(NH_2O^+)$.[40,41]

(4)

$$Fe^{II}(P)(NO) + e^- \rightarrow Fe^{II}(P)(NO)^-$$

(5)

$$Fe^{II}(P)(NO)^- + 2PhOH \leftrightharpoons Fe(P)(NH_2O)^+ + 2PhO^-$$

(6)

$$Fe(P)(NH_2O)^+ + PhOH + 3e^- \rightarrow Fe(P)^- + NH_2OH + PhO^-$$

Here PhOH is phenol and PhO^- is the phenolate anion. For the reductive nitrosylation reaction, the reverse of reactions 4 and 5 would occur: loss of 2 protons and a one-electron oxidation. On the basis of the voltammetry of Fe(P)(NO), this process is both thermodynamically and kinetically favored for iron.[40]

From the mechanism above, an easily reduced metal atom would favor the internal electron transfer. The $E_{1/2}$ values of a number of metalloporphyrin complexes are shown in Table 3. The easiest metals to reduce were iron(III) and manganese(III) porphyrins, which were also the metals that underwent the reductive nitrosylation reaction. In addition, their $E_{1/2}$ values were not significantly affected by coordination to N-ligands. In fact, for the reduction of iron(III), the wave was generally shifted to more positive potentials upon N-coordination (e.g., $E_{1/2}$ of $Fe(TPP)(NH_3)_2^+$ = −0.09 V). Similarly, the Mn(III)/Mn(II) potential was not shifted significantly in the presence of nitrogen ligands because of the similar affinity of both oxidation states to these ligand.[49] On the other hand, the $E_{1/2}$ of the Co(III)/Co(II) couple was shifted to much more negative potentials when cobalt(III) was coordinated to nitrogen ligands. For example, Co(TPP)(Cl) reduced irreversibly at −0.06 V,[45]while $Co(TPP)(pyridine)_2$+ reduced at −0.77 V.[38] Further reduction of cobalt(II) porphyrins occurred at more negative potentials (−0.85 V), as did Cr(TPP)(Cl) (−1.06 V).

Table 3. Half-Wave Potentials for Metal−Porphyrin Complexes

complex	solvent	$E_{1/2}$, V vs SCE	ref
Fe(TPP)(Cl)	$EtCl_2$[a]	−0.29	42
Fe(TPC)(Cl)	$EtCl_2$[a]	−0.28	42
Fe(OEP)(Cl)	CH_2Cl_2	−0.52	43
$Fe(TPP)(NH_3)_2^+$	THF	−0.09	this work
Fe(TPP)	CH_2Cl_2	−1.07	44
Co(TPP)(Cl)	CH_2Cl_2	−0.06[b]	45
$Co(TPP)(NH_2OH)_2^+$	CH_2Cl_2	−0.78[b]	this work
Co(TPP)	CH_2Cl_2	−0.85	46
Mn(TPP)(Cl)	CH_2Cl_2	−0.29	47
Cr(TPP)(Cl)	CH_2Cl_2	−1.06	48

[a] $EtCl_2$ = ethylene chloride.[b] Wave was irreversible, $E_{p,c}$ value reported.

The ability of the metal−porphyrin to coordinate with hydroxylamine was a less significant factor than the half-wave potential. But, for an internal electron transfer to occur, hydroxylamine must remain coordinated to the metal, and one would expect reasonable affinity for the metal ion to hydroxylamine. Selected formation constants for metal−porphyrins studied in this work with pyridine are given in Table 4. While the mechanism proposed requires initial coordination of hydroxylamine, all the metalloporphyrins studied were strong enough Lewis acids to form measurable amounts of the starting complex. In examining Table 4, we see that ferric and ferrous porphyrins coordinated well with pyridine and underwent reductive nitrosylation. On the other hand, cobalt(II) porphyrin formed weak complexes with pyridine and did not react with hydroxylamine. Both manganese(III) and chromium(III) porphyrins coordinated weakly with pyridine, yet the former reacted rapidly with hydroxylamine while no reaction was observed for the latter. This was in spite of the fact that the $Cr^{III}(TPP)(Cl)$ formation constant was about 100 times stronger than Mn^{III} (TPP)(Cl) (see Table 4). Finally cobalt(III) formed strong complexes with hydroxylamine, yet underwent the reductive nitrosylation reaction very slowly.

Table 4. Coordination of Pyridine with Cobalt, Iron, and Manganese Porphyrins

compd	solvent	log K_1	log β_2	ref
$Fe^{II}(TPP)$	CH_2Cl_2		7.8	50
$Fe^{III}(TPP)(ClO_4)$	CH_2Cl_2		10.2	50
$Mn^{II}(TPP)$	$EtCl_2$[a]	4.55		47

$Mn^{II}(TPP)(Cl)^-$	CH_2Cl_2	2.70		49
$Mn^{III}(TPP)(ClO_4)$	$EtCl_2$	4.08	6.99	47
$Mn^{III}(TPP)(Cl)$	CH_2Cl_2	1.10		49
$Co^{II}(TPP)$	CH_2Cl_2	2.90		51
$Co^{III}(TPP)$	CH_2Cl_2		15.6	51
$Cr^{III}(TPP)(Cl)$	20% THF/	3.15		52
	80% toluene	2.13[a]		52

[a] Ligand: 2-butylamine.

The reaction between hydroxylamine and cob(I)alamins has been previously reported.[4] In this case, there was no evidence for the coordination of Co^{I} with hydroxylamine, and the reaction involves the oxidation of Co^{I} to Co^{III} and the reduction of hydroxylamine to ammonia. The mechanism for this reaction was the nucleophilic attack of Co^{I} on hydroxylamine. None of the complexes studied in this work were sufficiently nucleophilic for this mechanism to be feasible here. However, the products of reaction 6 were $Fe(P)^-$ and hydroxylamine. Fe^{I} is known to be nucleophilic and could reduce hydroxylamine by the same mechanism used by Co^{I}. In the coulometric reduction of Fe(P)(NO), only ammonia was observed as the ultimate product of the reduction.[40]

The similarity of proposed intermediates in the oxidation of hydroxylamine and the reduction of NO may have implications for the mechanism of assimilatory nitrite reductases and hydroxylamine oxidoreductases. For both of these enzymes, the heme group (siroheme for most assimilatory nitrite reductases) carries out the transformations. While the structure of the hydroxylamine oxidoreductases is not known, a similar mechanism could occur if there is a basic amino acid side chain near the active site that can abstract a proton while the prosthetic group is oxidized. Conversely, acidic residues near the prosthetic group of nitrite reductases could add two protons concurrent with the reduction of the NO group, leading to the same intermediate, $Fe^{II}(P)(NH_2O)^+$, which can be readily reduced to $Fe^{II}(P)(NH_2OH)$. Axial coordination by sulfide may make the iron siroheme nucleophilic enough to carry out an internal 2-electron transfer combined with the loss of hydroxide, as was observed for cobalt(I).[4] This could be facilitated by an easily oxidized macrocycle (an isobacteriochlorin).[53-58]

$$\mathrm{Fe^{II}(P)(NH_2OH) \rightarrow Fe^{III}(P)(NH_2)^+ + OH^-}$$

$$\mathrm{Fe^{III}(P)(NH_2)^+ + 2e^- + H^+ \rightarrow Fe^{II}(P) + NH_3}$$

In some model complexes, in fact, the oxidation of the macrocycle has been observed before the oxidation of the ferrous atom.[53,54]

Conclusion

The reductive nitrosylation reaction of metalloporphyrins was observed for those complexes where the metal was easily reduced. Among the metals studied, iron and manganese porphyrins formed nitrosyl complexes readily. Cobalt porphyrins were rapidly oxidized by air to form a stable bis(hydroxylamine)cobalt(III) complex. No reaction was observed between chromium(III) porphyrins and hydroxylamine. These results were consistent with the trend in $E_{1/2}$ values of the metalloporphyrins.

The one-electron oxidation of a metal−hydroxylamine complex, followed by an internal electron transfer between the metal and the hydroxylamine, led to a complex which has the same structure as the one observed kinetically in the voltammetric reduction of Fe(P)(NO), $Fe^{II}(P)(NH_2O^+)$. This would indicate that the oxidation of hydroxylamine to NO or the reduction of NO to hydroxylamine by metalloporphyrins proceeds through a common intermediate.

The reductive nitrosylation reaction provides a convenient method for the preparation of isotopically labeled nitrosyl or the nitrosylation of small amounts of porphyrin. The yields are nearly quantitative, and the product is insoluble in the solvent used.

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