Ring Reduction of [*N*-Methyltetrakis(4-sulfonatophenyl)porphinato]cobalt(II), -nickel(II), and -copper(II) and Subsequent Methyl Group Migration. Reversible Reaction between Methyl Radicals and Ni^IITSPP

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[*N*-Methyltetrakis(4-sulfonatophenyl)porphinato]cobalt(II), -nickel(II), and -copper(II) [M^II(*N*-Me)TSPP] have been prepared, and their reduction in aqueous solutions has been studied by radiolytic methods. In all cases, one-electron reduction takes place on the ligand to form transient π-radical anions, [M^II(*N*-Me)TSPP]^•−. These species may undergo two competing reactions, (a) disproportionation and protonation to yield the two-electron reduced phlorin anions, M^II(*N*-Me)TSPPH−, a process that is favored at high radical concentration, or (b) migration of the methyl group from the pyrrole nitrogen to the metal center to form metal–carbon bonds, MeM^IIITSPP. Both pathways were observed with the Co and Ni derivatives whereas only disproportionation was noted for the Cu complex. The Ni derivative, moreover, produced MeNi^IIITSPP which was unstable and gave Ni^IITSPP and methyl radicals. Independent experiments on the reaction of methyl radicals with Ni^IITSPP indicated an equilibrium process.

Introduction

N-Alkyl- and *N*-arylprotoporphyrins are known to be produced in biological systems by cytochrome P-450 and the catalase enzymes from a variety of substrates and cause such deleterious effects as the inhibition of heme biosynthesis.[1] The formation of such porphyrins substituted at a pyrrole nitrogen involves a redox reaction as a key step, and therefore, the redox properties of the N-substituted metalloporphyrins are of chemical and biochemical interest. Alkylation of a pyrrole nitrogen forces the porphyrin into a nonplanar configuration, and compared with the parent compound, the N-alkylated derivatives are stronger bases toward protons and react orders of magnitude faster with metal ions.[2] Crystal structures show that the alkyl group and the metal are on opposite sides and well above and below the mean porphyrin plane. Whereas Co^II, Fe^II, and Mn^II porphyrins in aqueous solution undergo rapid oxidation by O_2 to the trivalent state, the corresponding *N*-alkylmetalloporphyrins are stable in these divalent forms under aerobic conditions.[2]

Several *N*-alkylmetalloporphyrins have been shown to undergo a reductive intramolecular migration of the alkyl group from the nitrogen to the metal center.[2] This reaction is induced by a one-electron reduction and takes place by a subsequent formation of a fourth strong metal–nitrogen bond as well as a metal–carbon bond. Intramolecular back-migration of the alkyl group takes place upon oxidation. These processes have been demonstrated for Co(II)[2,3] and Fe(II) porphyrins.[2,4]

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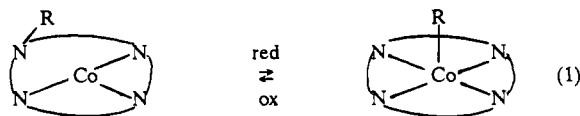
Previous studies on N-substituted porphyrins of Co[3], Fe[4], Rh,[5] and Ir[6] have been carried out mainly with octaethyl- and tetraphenyl-type porphyrins in nonaqueous systems. Since the solvent may have a profound effect on the reactivity of such porphyrins in redox reactions and on the outcome of such processes, we have prepared the water-soluble *N*-methyl derivative of tetrakis(4-sulfonatophenyl)porphyrin [(*N*-Me)TSPP] and several of its metal complexes (Co^II, Ni^II, Cu^II) and have examined their reduction by radiolysis in aqueous solutions. For Co^II(*N*-Me)TSPP we find the same methyl migration products in aqueous solutions as reported previously for Co^II(*N*-Me)TPP in organic solvents.[3] Our observation of the initial reduction product and its subsequent reactions clarifies the mechanism, and we also determine the rate constant for methyl group migration. For the Ni and Cu derivatives, however, we find different pathways; the former undergoes a reductive demethylation and the latter is reduced to a phlorin anion with no migration or loss of the methyl group.

Experimental Section

The free base (*N*-Me)TSPP was synthesized by the sulfonation of (*N*-Me)TPP[7] in concentrated H_2SO_4 overnight at 100 °C and purified following literature procedures.[8,9] This compound moved as a single band on Whatman KC-18 reversed-phase TLC plates developed with 90:10 MeOH/H_2O containing 0.01 M phosphate buffer at pH 7.4. In contrast, sulfonation of (*N*-Me)TPP for 4 days at room temperature resulted in the addition of 1–4 sulfonic acid groups to the porphyrin, as evident from multiple spots on the TLC plates. Metal complexes of the
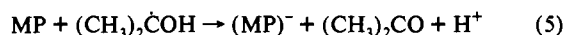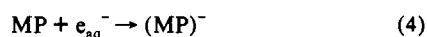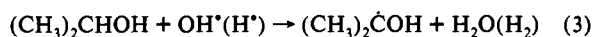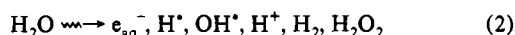
† NIST.
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(1) Ortiz de Montellano, P. R. *Ann. Rep. Med. Chem.* **1984**, *19*, 201.
(2) Lavallee, D. K. *The Chemistry and Biochemistry of N-Substituted Porphyrins*; VCH Publishers: New York, 1987.
(3) (a) Ogoshi, H.; Watanabe, E.; Koketzu, N.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* **1974**, 943. (b) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348. (c) Callot, H. J.; Metz, F. *J. Chem. Soc., Chem. Commu.* **1982**, 947. (d) Callot, H. J.; Metz, F.; Cromer, R. *Nouv. J. Chim.* **1984**, *8*, 759. (e) Callot, H. J.; Cromer, R.; Louati, A.; Gross, M. *Nouv. J. Chim.* **1984**, *8*, 765.
(4) Ortiz de Montellano, P. R.; Kunze, K. L.; Augusto, O. *J. Am. Chem. Soc.* **1982**, *104*, 3545. Mansuy, D.; Battioni, J.-P.; Dupre, D.; Sartori, E.; Chottard, G. *J. Am. Chem. Soc.* **1982**, *104*, 6159. Lancon, D.; Cocolios, P.; Guilard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472. Balch, A.; Renner, M. W. *J. Am. Chem. Soc.* **1986**, *108*, 2603. Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding* **1987**, *64*, 205.
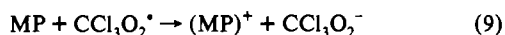
(5) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461.
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(9) Lavallee, D. K.; McDonugh, T. J., Jr.; Cioffi, L. *Appl. Spectrosc.* **1982**, *36*, 430.

tetrasulfonate were prepared by warming an aqueous solution containing 10^{-4} M porphyrin and 10^{-2} M metal sulfate or chloride until the metal-free porphyrin bands disappeared, followed by the removal of excess metal ions by passage through a cation-exchange resin. The spectra were similar to those of the corresponding $(N\text{-Me})TPP^2$ and $(N\text{-Me})TSPP^{8,9}$ complexes reported previously. At pH > 6 the complexes were stable for months, with no evidence for demetalation or demethylation. By addition of 1 M HCl to these solutions, the metal ions were rapidly removed, and since the molar absorptivities of the $(N\text{-Me})H_3TSPP$ are known under these conditions,[8] those of metallo-$(N\text{-Me})TSPP$ could be calculated. For $Co^{II}(N\text{-Me})TSPP$: λ_{max} 436 (1.5×10^5), 450 (sh), 560 (9.6×10^3), 610 (1.2×10^4), and 652 nm (7.6×10^3 M^{-1} cm^{-1}). For $Ni^{II}(N\text{-Me})$-TSPP: λ_{max} 434 (1.5×10^5), 440 (sh), 542 (1.0×10^4), 604 (9.0×10^3), and 654 nm (6.6×10^3 M^{-1} cm^{-1}). For $Cu^{II}(N\text{-Me})TSPP$: λ_{max} 432 (2.6×10^5), 442 (2.4×10^5), 552 (1.3×10^4), 600 (1.6×10^4), and 650 nm (8.9×10^3 M^{-1} cm^{-1}). We refer to species reduced or oxidized by one electron on the ligand as π-radical anions and cations, disregarding their overall negative charge due to the four sulfonate groups.

Water was purified with a Millipore Super-Q system.[10] Other solvents and reagents were of analytical grade purity. Aqueous solutions containing 10^{-5}–10^{-4} M of the metalloporphyrin (MP) and 1% 2-PrOH were deoxygenated by bubbling with ultrahigh purity Ar and irradiated either in a Gammacel 220 ^{60}Co source (dose rate 85 Gy/min) for observation of stable products or examined by kinetic spectrophotometric pulse radiolysis for monitoring transient species and their rate of formation and decay, as described before.[11] Under these conditions, the MP is reduced by the reactions

$$H_2O \rightsquigarrow e_{aq}^-, H^{\cdot}, OH^{\cdot}, H^+, H_2, H_2O_2 \qquad (2)$$

$$(CH_3)_2CHOH + OH^{\cdot}(H^{\cdot}) \rightarrow (CH_3)_2\dot{C}OH + H_2O(H_2) \qquad (3)$$

$$MP + e_{aq}^- \rightarrow (MP)^- \qquad (4)$$

$$MP + (CH_3)_2\dot{C}OH \rightarrow (MP)^- + (CH_3)_2CO + H^+ \qquad (5)$$

Radiolytic oxidation was performed most conveniently with $CCl_3O_2^{\cdot}$ radicals produced in aqueous/2-PrOH/CCl_4 solutions under air.

$$CCl_4 + e_{aq}^- \rightarrow CCl_3^{\cdot} + Cl^- \qquad (6)$$

$$CCl_4 + (CH_3)_2\dot{C}OH \rightarrow CCl_3^{\cdot} + Cl^- + (CH_3)_2CO + H^+ \qquad (7)$$

$$CCl_3^{\cdot} + O_2 \rightarrow CCl_3O_2^{\cdot} \qquad (8)$$

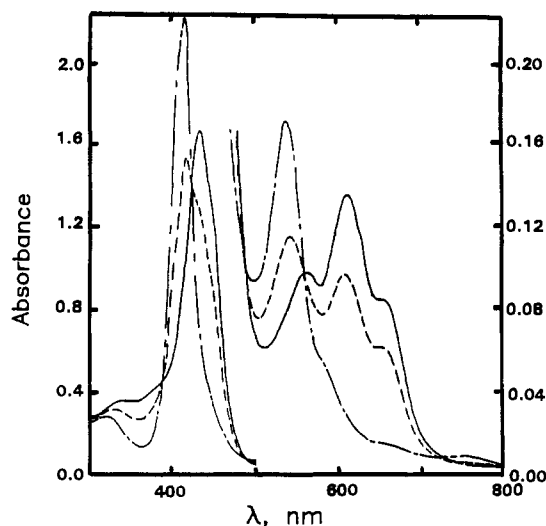$$MP + CCl_3O_2^{\cdot} \rightarrow (MP)^+ + CCl_3O_2^- \qquad (9)$$
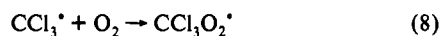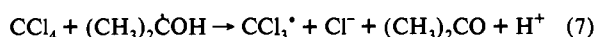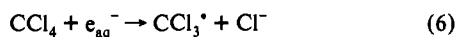
Gas chromatographic determination of methane and ethane production was carried out by sampling the head space on a vacuum line and transferring a constant fraction with He into the GC column, 6 ft. $\times$ $^1/_8$ in. stainless steel packed with Porapak R from Supelco, run at 75 °C with He as a carrier gas, in a Hewlett-Packard 5840A gas chromatograph with a flame ionization detector.

Results

Reduction of [N-methyltetrakis(4-sulfonatophenyl)porphinato]cobalt(II), -nickel(II), and -copper(II) has been studied by γ-radiolysis to examine stable products and by pulse radiolysis to monitor the rates of formation and reactions of the intermediates. Since the three complexes gave different results, we describe each one separately.

$Co^{II}(N\text{-Me})TSPP$. Radiolytic reduction of $Co^{II}(N\text{-Me})TSPP$ (1) results in the disappearance of the peaks at 436, 560, 610, and 652 nm and formation of a stable product absorbing at 416 and 538 nm (Figure 1). The isosbestic points (at 338, 424, 488,

(10) The identification of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technologies nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

(11) Nahor, G. S.; Neta, P.; Hambright, P.; Robinson, L. R.; Harriman, A. *J. Phys. Chem.* **1990**, *94*, 6659.

Figure 1. Radiolytic reduction of $Co^{II}(N\text{-Me})TSPP$ (5×10^{-5} M) in deoxygenated aqueous solutions containing 10% 2-PrOH at pH 8.4: (solid line) spectrum before irradiation; (dashed lines) spectra after irradiation in the Gammacell with a total dose of 140 and 220 Gy.

and 560 nm) indicate quantitative conversion. The product is identified as $MeCo^{III}TSPP$, which has been produced previously by reaction of methyl radicals with $Co^{II}TSPP$ or MeI with Co^ITSPP.[12]

Pulse radiolysis experiments indicate that the first reduction step takes place on the ligand to yield the π-radical anion $[Co^{II}(N\text{-Me})TSPP]^{\cdot-}$ (2), as is evident from the broad absorption with λ_{max} at 730 and 810 nm (Figure 2), typical of metalloporphyrin π-radical anions.[13] This radical anion undergoes subsequent reactions (within ~ 1 s) which are dependent on the dose per pulse, i.e. porphyrin radical concentration. At high dose (40 Gy/pulse, giving 2.4×10^{-5} M radicals), the absorption in the long-wavelength region shifts to λ_{max} 780 nm, ascribed to a stable phlorin anion (3), produced by disproportionation and protonation.[14] At low dose (13 Gy/pulse), the radical anion absorption at long wavelengths decays almost completely and the absorption of the $MeCo^{III}TSPP$ (4) at 530 nm becomes apparent. This process takes place with a rate constant of $(2.0 \times 0.8) \times 10^2$ s^{-1}. At much lower dose rates, and subsequently radical concentrations, as used in the γ-radiolysis experiments, $MeCo^{III}TSPP$ is the main product with little trace of the phlorin anion. Thus, the radical anion undergoes two competing processes, whose relative contributions are dependent on the radical concentration (Scheme I, where TSPP is abbreviated as P).

The reverse alkyl group migration takes place upon oxidation of 4. As reported for the TPP derivative,[3b,d] this oxidation is rather slow as compared with the reduction processes. Oxidation of 4 by the $CCl_3O_2^{\cdot}$ peroxyl radicals in the pulse radiolysis (in aerated solution containing 10% 2-PrOH and 0.1% CCl_4) shows that this reaction occurs via initial formation of a transient π-radical cation, 5 (absorbing at 660 nm, Figure 3a).[15] This π-radical cation decays within seconds, but it is not clear from

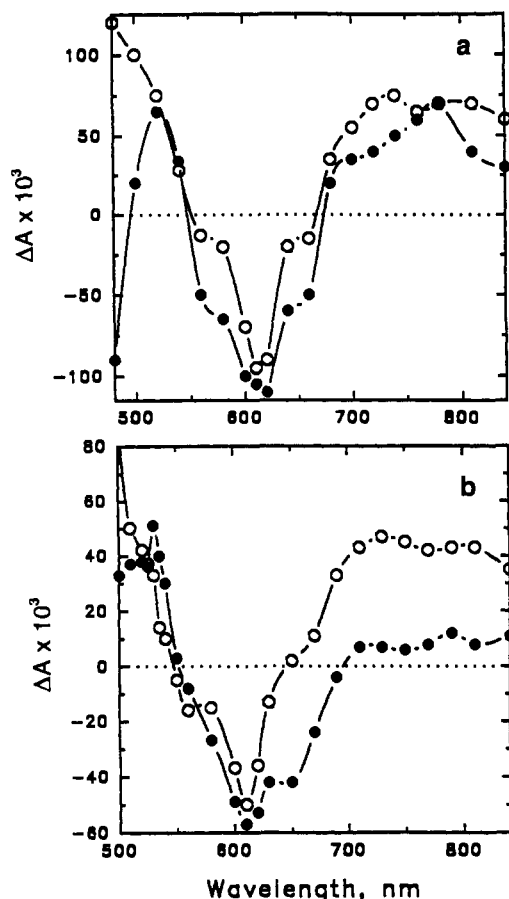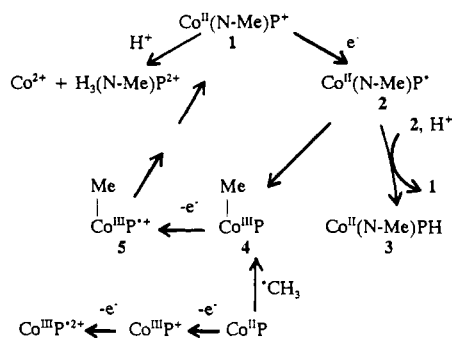(12) Baral, S.; Neta, P. *J. Phys. Chem.* **1983**, *87*, 1502.

(13) See, e.g.: Neta, P.; Scherz, A.; Levanon, H. *J. Am. Chem. Soc.* **1979**, *101*, 3624. Neta, P. *J. Phys. Chem.* **1981**, *85*, 3678. Baral, S.; Hambright, P.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 1595. Richoux, M.-C.; Neta, P.; Harriman, A.; Baral, S.; Hambright, P. *J. Phys. Chem.* **1986**, *90*, 2462.

(14) $Co^{II}TSPP$ and $Co^{II}TMPyP$ [tetrakis(N-methyl-4-pyridyl)porphyrin] are reduced to the Co^I state before they undergo further reduction to give the phlorin anions, in contrast with the present case of the N-methylporphyrin. For details on this and on the typical spectra of phlorin anions see, e.g., ref 13 and: Baral, S.; Neta, P.; Hambright, P. *Radiat. Phys. Chem.* **1984**, *24*, 245.

(15) The species is identified as the π-radical cation based on the similarity of its spectrum with that observed upon pulse radiolytic oxidation of $Co^{III}TSPP$ under the same conditions (Figure 3b) and with spectra of other π-radical cations reported before (e.g.: Harriman, A.; Richoux, M.-C.; Neta, P. *J. Phys. Chem.* **1983**, *87*, 4957).

Figure 2. Pulse radiolytic reduction of Co^{II}(N-Me)TSPP. Solutions as in Figure 1 were irradiated at different dose rates, and spectra were monitored at different times after the pulse. (a) 40 Gy/pulse: (O) 360 μs after the pulse, (●) 3.3 s later. (b) 13 Gy/pulse: (O) 80 μs after the pulse; (●) 1.3 s later.
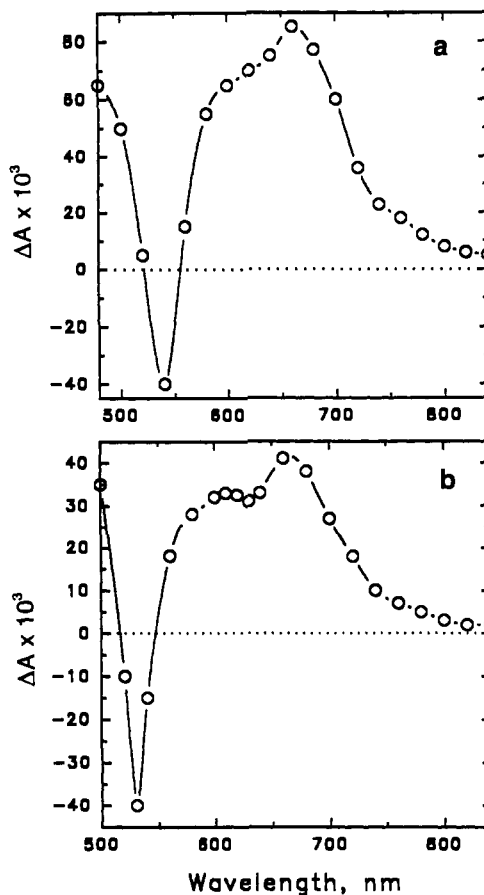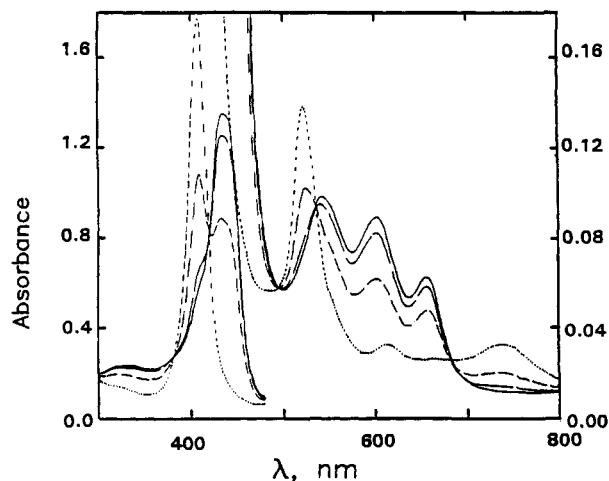
Scheme I

Figure 3. Pulse radiolytic oxidation of MeCo^{III}TSPP (a) and Co^{III}TSPP (b) in aqueous solutions containing 20% 2-PrOH and 0.1% CCl$_4$ under air at pH 8.4. The dose was 13 Gy/pulse and spectra were monitored 240 μs after the pulse.

Figure 4. Radiolytic reduction of Ni^{II}(N-Me)TSPP in deoxygenated aqueous solution containing 10% 2-PrOH at pH 8.4: (solid line) 4.8 × 10^{-5} M Ni^{II}(N-Me)TSPP; (dashed lines) after irradiation with doses of 40, 130, 170 Gy to achieve full conversion to Ni^{II}TSPP.

the results whether the products contain a substantial amount of 1. Oxidation under γ-radiolysis conditions indicates that a small amount of 1 is produced during the radiolysis, but when the irradiated solution is allowed to stand for another 1 h, most of the initial compound 4 is found to convert into 1. This complexity is indicated by the double arrow between 5 and 1 in Scheme I, and it is not clear whether the delayed migration involves additional intermediates or whether the radical cation rearranges very slowly and is present in equilibrium with the dication or its hydroxylated form.

The same migration could be obtained in aerobic systems where O$_2$ is the oxidant, upon addition of trichloroacetic acid. Mineral acids, such as HClO$_4$ or HCl, were ineffective. The strongly acidic pH causes demetalation of the complex leading to H$_3$(N-Me)TSPP^{2+} with λ$_{max}$ at 446, 618, and 667 nm.

Cu^{II}(N-Me)TSPP. Reduction of Cu^{II}(N-Me)TSPP under radiolysis in deaerated aqueous 2-PrOH solutions at pH 8 did not

result in Me group migration but in reduction of the ligand to the phlorin anion. This product exhibits a broad absorption with λ$_{max}$ 755 nm and is quantitatively reoxidized by O$_2$ back to the starting material within minutes. Pulse radiolysis experiments indicated that the initial product of one-electron reduction of Cu^{II}(N-Me)TSPP is the π-radical anion (λ$_{max}$ 740, 780 nm shoulder), which subsequently disproportionates and protonates to form the phlorin anion. These reduction processes are parallel to those of 1 → 2 → 3 in Scheme I for the Co derivative, but with no evidence for methyl migration to give either MeCu^{III}TSPP or Cu^{II}TSPP. To increase the probability of methyl migration by
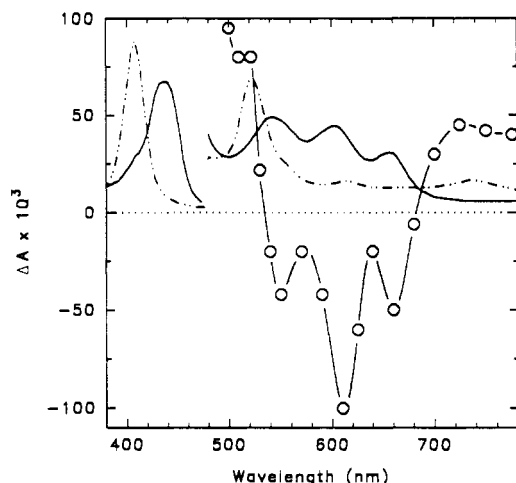
Figure 5. Radiolytic reduction of $Ni^{II}(N\text{-Me})TSPP$ in deoxygenated aqueous solution containing 10% 2-PrOH at pH 8.4. The solid line and dashed line are from Figure 4, showing full conversion to $Ni^{II}TSPP$. Circles show the differential spectrum following pulse irradiation, indicating bleaching of the starting material and formation of a transient π-radical anion absorbing above 700 nm (dose 40 Gy/pulse).
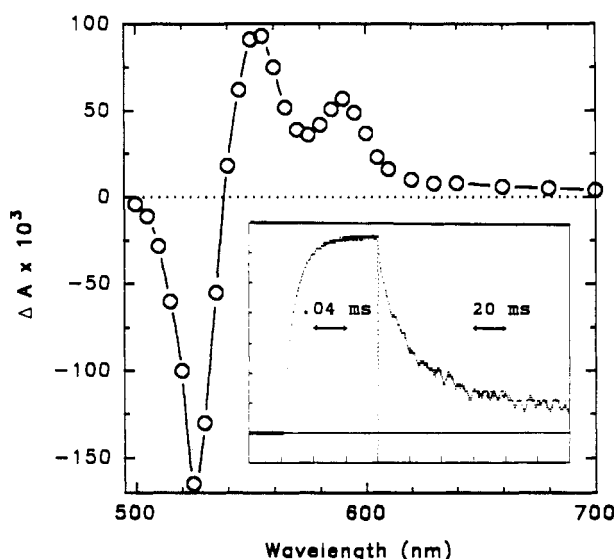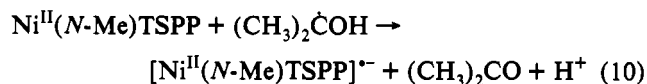

Figure 6. Reaction of the methyl radical with $Ni^{II}TSPP$: (circles) differential spectrum observed upon pulse irradiation (40 Gy/pulse) of N_2O-saturated aqueous solution containing the porphyrin (6×10^{-5} M) and 0.01 M DMSO at pH 8.4. (Insert) time profile of formation and decay of the transient absorption at 560 nm.
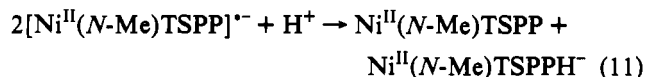
decreasing the likelihood of protonation, experiments were carried out at higher pH (12.5) and with up to 80% 2-PrOH. Even under these conditions, the only product observed was the phlorin, suggesting that methyl migration is less likely with the Cu than with the Co complex. These findings are in contrast with previous reports that $Cu^{II}(N\text{-Me})TPP$ in organic solvents shows an electrochemical wave indicating reduction to the Cu^I state;[16] the difference in behavior may be due a solvent effect.

$Ni^{II}(N\text{-Me})TSPP$. Reduction of $Ni^{II}(N\text{-Me})TSPP$ in aqueous 2-PrOH solutions led to nearly quantitative formation of $Ni^{II}TSPP$, as is evident from the changes in optical absorption following γ-radiolysis (Figure 4). The peaks $Ni^{II}(N\text{-Me})TSPP$ disappear with concomitant formation of the 408- and 524-nm peaks of $Ni^{II}TSPP$. A minor product absorbing at 740 nm is also observed and is most likely the phlorin anion of the starting material (see below). Pulse radiolysis indicated a rapid one-electron reduction of $Ni^{II}(N\text{-Me})TSPP$ to the π-radical anion absorbing above 700 nm (Figure 5). The rate constant for this

reduction by the radical derived from 2-PrOH was determined to be $k_{10} = (1.6 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.

$$Ni^{II}(N\text{-Me})TSPP + (CH_3)_2\dot{C}OH \rightarrow$$
$$[Ni^{II}(N\text{-Me})TSPP]^{\bullet-} + (CH_3)_2CO + H^+ \quad (10)$$

At longer times (10–20 ms after the pulse) the π-radical anion decays in a process that is dependent on radical concentration [R], i.e. dose per pulse. At high dose ([R] $\approx$ 24 μM), it forms mainly a phlorin anion (λ_{max} 750 nm). Only at low dose ([R] $\approx 4 \mu$M) was the formation of $Ni^{II}TSPP$ observed. This suggests that the initial π-radical anion undergoes two competing processes. Reaction 11 is second order in radical concentration whereas

$$2[Ni^{II}(N\text{-Me})TSPP]^{\bullet-} + H^+ \rightarrow Ni^{II}(N\text{-Me})TSPP +$$
$$Ni^{II}(N\text{-Me})TSPPH^- \quad (11)$$

$$[Ni^{II}(N\text{-Me})TSPP]^{\bullet-} \rightarrow MeNi^{III}TSPP \rightarrow Ni^{II}TSPP \quad (12)$$

reaction 12 is first order, with $k_{obs} = (2.0 \pm 0.6) \times 10^2 s^{-1}$. In fact, the stable product after pulse irradiation, where the radical concentration is many orders of magnitude higher than that in the γ-radiolysis experiment, was predominantly the phlorin anion rather than $Ni^{II}TSPP$. This competition is similar to that described for the Co derivative in Scheme I with regard to the transformation of **1** to **2** and subsequently to **3** and **4** in parallel, except that in the case of the Ni derivative the methyl group migration is followed by rapid release of this group from the metal center.

The first step in reaction 12 is probably the migration of the methyl group from the nitrogen to the nickel, as formulated for the cases of $Co^{2,3}$ and $Fe.^{2,4}$ To obtain evidence for the existence of $MeNi^{III}TSPP$ and to unravel the mechanism of its decomposition to $Ni^{II}TSPP$, we studied the reaction of Me radicals with $Ni^{II}TSPP$.

Reaction of Methyl Radicals with Nickel Porphyrins. The reaction of Me radicals with $Ni^{II}TSPP$ was studied by steady-state and pulse radiolysis in aqueous solutions containing 1% DMSO and saturated with N_2O at pH 8–9. Under these conditions, the hydrated electrons are converted into OH radicals

$$e_{aq}^- + N_2O \rightarrow N_2 + OH^\bullet + OH^- \quad (13)$$
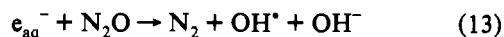
and the reaction of OH radicals with DMSO provides $^\bullet CH_3$ radicals.[17]

$$OH^\bullet + (CH_3)_2SO \rightarrow (CH_3)_2SO(OH)^\bullet \rightarrow CH_3SO_2H +$$
$$CH_3^\bullet \quad (14)$$
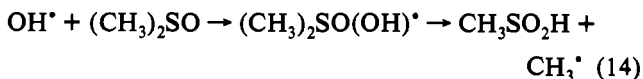
The reaction of methyl radicals with the nickel porphyrin
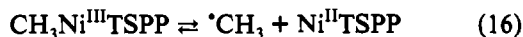
$$Ni^{II}TSPP + CH_3^\bullet \rightarrow CH_3Ni^{III}TSPP \quad (15)$$

leads to formation of a transient species absorbing at 550 and 590 nm (Figure 6) which is ascribed to $MeNi^{III}TSPP$ by comparison with other porphyrins containing metal–carbon bonds.[18] From the observed rate of formation at different concentrations we derived the second-order rate constants $k_{15} = (1.0 \pm 0.2) \times 10^9$ and $(0.9 \pm 0.2) \times 10^9$ M^{-1} s^{-1} at pH 9 and 3.3, respectively. The transient absorption disappears in a second-order process ($2k \approx 1 \times 10^7$ M^{-1} s^{-1}) leading to full recovery of the spectrum of the original material. This decay is interpreted as the decay of methyl radicals in equilibrium with the complex.[19]

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$$CH_3Ni^{III}TSPP \rightleftharpoons {}^{\bullet}CH_3 + Ni^{II}TSPP \quad (16)$$

$${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \text{ (or } {}^{\bullet}CH_3 + CH_3Ni^{III}TSPP) \rightarrow C_2H_6 \quad (17)$$

This mechanism was confirmed by determining ethane as a product. Radiolysis of aqueous DMSO[20] produced CH$_4$ and C$_2$H$_6$ with a ratio of 20:1; i.e. most CH$_3{}^{\bullet}$ radicals react with DMSO to form methane under these conditions.

$${}^{\bullet}CH_3 + (CH_3)_2SO \rightarrow CH_4 + {}^{\bullet}CH_2SOCH_3 \quad (18)$$

In the presence of Ni^{II}TSPP, the yield of methane decreased by a factor of $\sim$2 due to competition by reaction 15 and the yield of ethane increased by a factor of $\sim$2 due to reaction 17. The yield of methane was not suppressed completely since the methyl radicals present in equilibrium 16 react by reaction 18 more rapidly than by reaction 17 (due to the high concentration of DMSO relative to those of radicals and porphyrin).

When CH$_3$Ni^{III}TSPP was produced by reduction of Ni^{II}(N-Me)TSPP in aqueous 2-PrOH solutions, the methyl radicals released were found to give some ethane via reaction 17 but predominantly gave methane via reaction with 2-PrOH. Attempts to avoid the use of OH scavengers in order to increase the yield of ethane and decrease that of methane were not successful, since in the absence of OH scavengers the reduction of Ni^{II}(N-Me)-TSPP did not take place even after reasonably long irradiations.

Experiments on reactions of various alkyl radicals with other Ni porphyrins (hemato- and deuteroporphyrin) indicated that CF$_3{}^{\bullet}$ radicals gave the most stable Ni–C bonds.[21] Therefore, we reacted CF$_3{}^{\bullet}$ radicals with Ni^{II}TSPP in an attempt to obtain a more stable product than that produced by the reaction of methyl radicals. The pulse radiolysis results, however, were identical for these two radicals, giving the same transient spectrum and a similar rate of decay back to the starting material. Thus, no stable Ni–C bond was formed upon reactions of either of these radicals with Ni^{II}TSPP. In contrast with this instability of MeNi^{III}TSPP, the reduced form, MeNi^{II}TSPP, is expected to be more stable toward homolysis and may result in reduction of the methyl to methane. This possibility is being studied as a model for coenzyme F$_{430}$.[22]

Discussion

The absorption spectrum of the water-soluble N-methyltetrakis-(4-sulfonatophenyl)porphyrin at pH 7 and $I = 0.1$ (NaNO$_3$) followed[23] Beer's law from 3.0×10^{-8} to 4.0×10^{-5} M, indicating that (N-Me)TSPP is monomeric in solution. In contrast, H$_2$-TSPP has a dimerization constant of 9.6×10^4 M^{-1} under similar conditions.[24] For the protonation equilibria of (N-Me)TSPP at $I = 0.1$, a pK_{a3} of 3.0 was found for the (H$_3$P$^+$)/(H$_2$P) reaction and p$K_{a2} = 8.5$ for the (H$_2$P)/(HP$^-$) process,[23] in agreement with the results (3.0, 8.8) of Tanaka.[8] The Co^{II}, Ni^{II}, and Cu^{II} complexes of (N-Me)TSPP were stable in water for months at pH >6. With M^{II}(N-Me)TPPCl in nonaqueous solutions, the methyl group is lost more or less rapidly depending on the solvent and the identity of M^{II}. For example, Cu^{II}(N-Me)TPPCl in chloroform[25] at 25 °C spontaneously dissociates into Cu^{II}TPP

and CH$_3$Cl with a half-life of 75 min and the high-spin Ni^{II}-(N-Me)TPPCl behaves in a similar fashion.[26] Lavallee[2] noted that this demethylation reaction is substantially slower in acetonitrile and methanol, solvents which better solvate the chloride ion, thus reducing its nucleophilic character.

Reduction of Co^{II}(N-Me) porphyrins results in the intramolecular migration of the methyl group, forming MeCo^{III} porphyrins. One postulated mechanism assumes reduction of the Co^{II} porphyrin to the Co^I state, followed by methyl migration and oxidative addition to the MeCo^{III} porphyrin. Another possibility is reduction of the porphyrin ring rather than the coordinated Co^{II} as the initial step. We find that the reduction of the Co^{II}-, Cu^{II}-, and Ni^{II}(N-Me) porphyrins in aqueous solutions does not produce the Co^I, Cu^I, and Ni^I species[14] but rather the electron in each case is added to the porphyrin ligand. The resulting π-radical anions undergo two competing processes: (a) disproportionation and protonation to yield phlorin anions, which become more important at high porphyrin radical anion concentrations and predominate in the case of the Cu^{II} complex, and (b) migration of the methyl group from the pyrrole nitrogen to the metal ion. The latter process takes place by first-order kinetics with a rate constant of 2×10^2 s^{-1} for both [Co^{II}(N-Me)TSPP]$^{\bullet-}$ and [Ni^{II}(N-Me)TSPP]$^{\bullet-}$, in the former case giving stable MeCo^{III}TSPP. MeNi^{III}TSPP, on the other hand, is short-lived and exists only in equilibrium with Me radicals and Ni^{II}TSPP. The reaction of Me radicals with Ni^{II}TSPP takes place with a rate constant of 1×10^9 M^{-1} s^{-1}, and the transient MeNi^{III}TSPP, absorbing at 550–600 nm, decays with a rate constant of 2×10^7 M^{-1} s^{-1} through the reaction of free Me radicals either with the Me–Ni complex or with other solutes, to give ethane or methane, respectively.

We have reported before that the first observed products of the radiolytic reduction of Co^{II}TSPP[12] and a variety of Ni^{II} porphyrins[11] in aqueous solution are spectrally distinct Co^I and Ni^I complexes. Co^{I}TSPP reduces water while the Ni^I porphyrins rapidly disproportionate into Ni^{II}P and the two-electron ring-reduced metallochlorins or phlorins. This is in contrast to the Ni^{II}- and Co^{II}(N-Me)TSPP reductions described above, where the first electron is added at the porphyrin ligand and not at the metal ion. For both Cu^{II}P and Cu^{II}(N-Me)P, electron addition occurs only on the ligand.

The molecular orbital to which the first electron is added in Ni^{II}- and Co^{II}(N-Me)TSPP appears to have a ligand π^* character, as judged from the spectra, but a considerable overlap with the metal d$_{x^2-y^2}$ is possible. As a result, the subsequent reaction of the initial transient can be at the ligand (disproportionation to form phlorin anion) or may involve the metal center (oxidative addition of the methyl group). The mechanism of the N-methyl group migration may be (a) via release of a methyl radical and its addition to the metal ion (M^{II} state) or (b) by a nucleophilic attack of a reduced metal ion (M^I state) on the N-Me group. The N-methyl group transfer reactions formally produce Co^{III} and Ni^{III} oxidation states, and since Co^{III} porphyrins are well-known and many Ni^{III} porphyrins can be produced radiolytically,[27] this transfer is not altogether unexpected. The finding that the N-methyl group remains with the ring-reduced Cu^{II}(N-Me)TSPP can be taken as indirect evidence for the nonexistence of the Cu^{III} oxidation state in this porphyrin.

(19) Such equilibria with Ni and Cr macrocyclic complexes have been suggested previously, see, e.g.: Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713. Meyerstein, D. *Pure Appl. Chem.* **1989**, *61*, 885. Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1991**, *30*, 4826 and references therein.

(20) In solutions for GC analysis the N$_2$O was replaced with 0.01 M H$_2$O$_2$, to convert the hydrated electrons into OH radicals, because N$_2$O masked the GC peak of ethane. The DMSO concentration was also varied between 0.1 and 1%.

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