These experiments are being extended to other aqueous-organic systems with the objective of studying sulfur reactivities for other radiation-produced organic radicals.

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Reduction and Alkylation of Cobalt(II) Tetrakis(4-sulfonatophenyl)porphyrin in Aqueous Solutions. A Kinetic Spectrophotometric Study¹

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The reactions of $Co^{II}TPPS$ (TPPS = tetrakis(4-sulfonatophenyl)porphyrin) with alkyl and hydroxyalkyl radicals have been studied by pulse radiolysis. The alkyl radicals undergo axial addition with rate constants of (1.2-1.9) \times 10⁹ M⁻¹ s⁻¹ to form R-Co^{III}TPPS complexes which either are stable (R = CH₃) or undergo decomposition $(R = CH(CH_3)_2)$ to Co^ITPPS and an olefin via a β -proton elimination mechanism ($k_1 = 0.3 \text{ s}^{-1}$ at pH 8 and 3 s^{-1} at pH 13). The hydroxyalkyl radicals also form R–Co^{III}TPPS with rate constants of (1.1–1.2) × 10⁹ M⁻¹ s^{-1} . These adducts undergo heterolytic cleavage of the cobalt-carbon bond to form Co^ITPPS and a carbonyl compound, with rate constants of 3.6×10^2 s⁻¹ (R = CH₂OH) and 6.2×10^3 s⁻¹ (R = C(OH)(CH₃)₂). The radicals $(CH_3)_2 \dot{C}O^-$ and $\dot{C}O_2^-$ reduce $Co^{II}TPPS$ to $Co^{I}TPPS$ by an outer-sphere mechanism with rate constants 7×10^8 and $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Co^ITPPS is oxidized to CH₃Co^{III}TPPS by CH₃I ($k_2 = 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) and to Co^{III}TPPS (probably through intermediate formation of Co^{III}TPPS) by N₂O ($k_2 \leq 3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$). The reactivities of the present systems have been compared with those of other models suggested for vitamin B_{12} like cobaloximes, cobalamins, and other macrocyclic Co^{II} complexes.

Introduction

Redox reactions of metalloporphyrins have been extensively studied as models for electron-transfer metalloproteins, photosynthetic pigments, and other related biological systems. An important group is the cobalt porphyrins which have been explored as models for (1) ironheme proteins involved in oxygen transport and storage,² (2) nitrogenase involved in the reduction of dinitrogen to ammonia,³ and (3) cobalt corrinoids such as vitamin B_{12} .⁴⁻⁶ In the last two cases, in particular, the lower valence states of cobalt make an important contribution toward the ability of the metalloporphyrin to mimic biological reactions occurring in vivo. This stresses the importance of obtaining a detailed understanding of the electron-transfer behavior of lower valence cobalt porphyrins.

Blackburns et al.⁷ have studied the reduction of cyanoand hydroxocobalamins and vitamin B_{12} coenzyme to Co^{II} and Co^I species by pulse radiolysis. However, their results were complicated by the presence of several centers in these molecules which undergo reduction concurrently. Reduction of a simple model like cobalt(II) porphyrin

 $(Co^{II}P)$ is expected to provide more easily interpretable results. One-electron reductions of several water-soluble Co^{III}P to Co^{II}P have been recently investigated by pulse radiolysis.⁸ In the present study we examine further one-electron reduction of Co^{II}P.

Formation of cobalt-carbon bonds and their homolysis is believed to be involved in the catalytic activity of vitamin B_{12} in a number of biochemical rearrangement reactions.^{9,10} Hence, the reaction of Co^{II}P with alkyl and hydroxyalkyl radicals, which leads to the formation of such a bond, is of considerable interest. Kinetic studies on this type of reaction have been carried out by flash photolysis^{11,12} and pulse radiolysis.^{13,14} A kinetic study on the reaction of methyl radicals with some iron porphyrins had appeared recently and preliminary work on similar reactions with Co^{II}P has been recorded.⁸ In the present study we have investigated the reactions of several alkyl and hydroxyalkyl radicals with Co^{II}P leading to alkylcobalt compounds. In addition to these, the reaction between the strong nucleophile Co^IP and methyl iodide has also been examined by kinetic spectrophotometry.

Experimental Section

Materials. The metalloporphyrin used in this study, Co^{II}TPPS (TPPS = tetrakis(4-sulfonatophenyl)porphyrin), was freshly produced in aqueous solution just prior to each experiment by quantitatively reducing (monitored spectrophotometrically) a deoxygenated solution of Co^{III}TPPS (Midcentury Chemical Co., purity checked by absorption

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and NMR spectra), with a freshly made aqueous solution of sodium dithionite (Aldrich).¹⁶ A 5-10% excess of sodium dithionite was used. This excess does not affect the results of subsequent experiments. Further handling of the Co^{II}TPPS solutions was done in strict anaerobic conditions and in the dark. At the concentrations and solution compositions used in this study the Co^{II}TPPS is in the monomeric state.^{3,17}

Methyl and isopropyl iodides were obtained from Aldrich Chemical Co. and were purified by passing through a column of basic aluminum oxide (Woelm Pharma) and degassed under vacuum by repeated freezing, pumping, and thawing cycles. Diisopropyl sulfoxide was prepared by oxidation of the corresponding sulfide with liquid N_2O_4 .¹⁸ A purity > 99% as checked by gas chromatography was obtained by fractional distillation under vacuum. Sodium borohydride from Aldrich Chemical Co. was purified by recrystallization from diglyme at 40 °C.¹⁹ All other chemicals used in this study were Baker Analyzed reagents and were used without further purification. Water was purified with a Millipore Milli-Q system.

Measurements. Steady-state radiolyses were carried out in a Gammacell 220 ⁶⁰Co source with a dose rate of 4 krd min⁻¹. Absorption spectra were recorded in a Cary 219 spectrophotometer interfaced with a PDP 11/55 computer. Kinetic spectrophotometric measurements were made with the computer-controlled pulse radiolysis apparatus described previously.²⁰ The linear accelerator (ARCO LP-7) supplies 5-50-ns pulses of 8-MeV electrons. The dose used (300–500 rd per pulse) produced 2–3 μ M concentration of radicals. At this concentration, the radical-radical recombination reaction does not take place to any significant extent compared to the process under investigation. Special precautions were taken to suppress photolysis of Co^{II}P, such as using the xenon lamp in a continuous rather than pulsed mode and placing a computer-controlled shutter (which remains open only for the minimum time for measurement before and after the pulse) as well as narrow band-pass (10-20 nm) interference filters between the xenon lamp and the cell. The dose was calibrated with an aqueous N₂O-saturated KSCN solution before each set of experiments. The differential extinction coefficients for the transient spectra $(\Delta \epsilon')$ were calculated from the relation $\Delta \epsilon' = AK/(DG)$ where A is the differential absorbance after and before the pulse, D the dose supplied by the pulse, G the radiation yield, and K a calibration factor chosen such that $\Delta \epsilon'$ for the $(SCN)_2^-$ radical is 7600 M⁻¹ cm⁻¹ at 480 nm in N₂O-saturated solution of 10⁻² M KSCN and G = 6. All experiments were carried out at room temperature, 21 ± 1 °C.

Results and Discussions

Production of Reducing Species. Radiolysis of water or aqueous solution results in the formation of e_{aq} , OH, H, and molecular products.

$$H_2O \longrightarrow (2.8)e_{aq}^- + (2.8)OH + (0.6)H$$
 (1)

Hydrated electrons reduce metalloporphyrins at either the ligand or the metal with diffusion-controlled rates.^{8,21} On

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the other hand, H and OH radicals usually add on to the porphyrin ring. In order to study a clean reduction, it is necessary to scavenge²² these radicals and convert them into reducing species. Isopropyl alcohol (i-PrOH) and formate ion have been used for this purpose.

$$OH + (CH_3)_2 CHOH \rightarrow (CH_3)_2 COH + H_2 O \qquad (2)$$

$$H + (CH_3)_2 CHOH \rightarrow (CH_3)_2 COH + H_2 \qquad (3)$$

$$CH_3)_2\dot{C}OH \xrightarrow{pR_a = 12.00} (CH_3)_2\dot{C}O^- + H^+ \qquad (4)$$

$$OH + HCO_2^- \rightarrow H_2O + \dot{C}O_2^-$$
(5)

$$H + HCO_2^- \rightarrow H_2 + \dot{C}O_2^- \tag{6}$$

The radicals $(CH_3)_2\dot{C}OH$, $(CH_3)_2\dot{C}O^-$, and $\dot{C}O_2^-$ are known to be efficient one-electron reducing agents. In N_2 -purged solution one observes rapid reduction by e_{aq} followed by a slower reduction with the organic radicals.

(

$$P + e_{ao} \rightarrow P^{-} (or M^{n+}P \rightarrow M^{(n-1)+}P)$$
 (7)

$$P + \dot{C}O_2^- \rightarrow P^- + CO_2 \tag{8}$$

$$P + (CH_3)_2 \dot{C}O^- \rightarrow P^- + (CH_3)_2 CO$$
(9)

where the reduction of P to P⁻ represents also $M^{n+}P \rightarrow$ $M^{(n-1)+}P$.

In order to determine the rate of the latter reactions, it is advantageous to use N₂O as an electron scavenger

$$N_2O + e_{ac}^- \rightarrow N_2 + OH^- + \dot{O}H$$
(10)

so that reduction takes place via reaction 8 or 9 only.

One-Electron Reduction of Co^{II}TPPS. Pulse radiolysis of an aqueous 5×10^{-5} M Co^{II}TPPS solution containing 1.5 M *i*-PrOH at pH 13 showed the expected occurrence of the reactions with e_{aq}^{-} and $(CH_3)_2CO^{-}$. From the rapid decay of e_{aq}^{-} absorption around 600 nm the rate constant of reaction 7 for (H₂O)Co^{II}TPPS²³ at pH 13 was deter-mined to be 1.4 × 10¹⁰ M⁻¹ s⁻¹ (Table I). The slower reduction by $(CH_3)_2\dot{C}O^-$ could be observed on a longer time scale (~400 μ s). Difference spectra (Figure 1a) were monitored at two time intervals, following the decay of e_{a0} and at the end of the second reduction step. The product from the reaction with e_{aq}^{-} is expected to be either Co^IP or Co^{II}P⁻. Lack of considerable absorption above 600 nm, a characteristic of porphyrin anion radicals,^{8,24} suggests the formation of Co^IP rather than Co^{II}P⁻. A previous molecular orbital calculation of charge density distribution in $Co^{I}TPP$ (TPP = tetraphenylporphyrin) indicates that the electron added in going from Co^{II}P to Co^IP is largely confined on the cobalt atom.²⁵

The spectral changes associated with the reduction by the $(CH_3)_2\dot{C}O^-$ radical were found to be qualitatively very similar to those produced by e_{aq}^{-} and thus indicate the product to be Co^IP. The slight difference between the two may arise from a small residual e_{aq}^- absorption²⁶ and also from a possibly different axial coordination in the products

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$\dot{R} + Co^{II}TPPS$			
Ŕ	main products	pH	rate constant, M ⁻¹ s ⁻¹
$\begin{array}{c} e_{aq} \\ e_{aq} \\ (CH_{3})_{2}\dot{C}O^{-} \\ CO_{2}^{-} \\ CO_{2}^{-} \\ CH_{3}[CH_{3}I]^{a} \\ CH_{3}[CH_{3}I]^{a} \\ CH_{3}[CH_{3}I]^{a} \\ CH_{3}[CH_{3}]_{2} \\ CH(CH_{3})_{2} \\ CH(CH_{3})_{2} \\ CH_{2}OH \\ (CH_{3})_{2}COH \end{array}$	$\begin{array}{c} Co^{I}TPPS\\ Co^{I}TPPS\\ Co^{I}TPPS\\ Co^{I}TPPS\\ Co^{I}TPPS\\ Co^{I}TPPS\\ CH_{3}Co^{III}TPPS\\ CH_{3}Co^{III}TPPS\\ CH_{3}Co^{III}TPPS\\ CH_{3}Co^{III}TPPS\\ (CH_{3})_{2}CHCo^{III}TPPS^{b}\\ (CH_{3})_{2}CHCo^{III}TPPS^{b}\\ HOCH_{2}Co^{III}TPPS^{b}\\ (HO)(CH_{3})_{2}CCo^{III}TPPS^{b} \end{array}$	8 13 13 8 13 13 13 13 8 8 8 13 8 8 8 8 8	$\begin{array}{c} (1.2 \pm 0.4) \times 10^{10} \\ (1.4 \pm 0.5) \times 10^{10} \\ (6.9 \pm 0.8) \times 10^8 \\ (1.7 \pm 0.3) \times 10^8 \\ (2.6 \pm 0.3) \times 10^8 \\ (1.5 \pm 0.3) \times 10^9 \\ (1.2 \pm 0.2) \times 10^9 \\ (1.7 \pm 0.2) \times 10^9 \\ (1.4 \pm 0.2) \times 10^9 \\ (1.9 \pm 0.2) \times 10^9 \\ (1.1 \pm 0.2) \times 10^9 \\ (1.2 \pm 0.2) \times 10^9 \end{array}$
othe	reactions		
$\frac{\text{reactants}}{\begin{array}{c} \text{Co}^{\text{I}}\text{TPPS} + \text{N}_{2}\text{O}\\ \text{Co}^{\text{I}}\text{TPPS} + \text{CH}_{3}\text{I}\\ (\text{CH}_{3})_{2}\text{CHCo}^{\text{III}}\text{TPPS}\\ (\text{CH}_{3})_{3}\text{CHCo}^{\text{III}}\text{TPPS}\\ \text{HOCH}_{2}\text{Co}^{\text{III}}\text{TPPS}\\ (\text{HO})(\text{CH}_{3})_{2}\text{CCo}^{\text{III}}\text{TPPS} \end{array}}$	$\begin{array}{c} \mbox{main products} \\ \hline Co^{II}TPPS \\ CH_3Co^{III}TPPS \\ Co^{I}TPPS + CH_3CH=CH_2 \\ Co^{I}TPPS + CH_3CH=CH_2 \\ Co^{I}TPPS + CH_2O \\ Co^{I}TPPS + (CH_3)_2CO \\ \hline b \mbox{ Unstable products, see their of } \end{array}$	pH 13 8 8 13 8 8 decomposition rates	$\begin{tabular}{ c c c c c } \hline $$ rate constant $$ $$ $$ $$ $$ $$ $$ 10^2 M^{-1} s^{-1} $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$$
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4 2 0 -2 20 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	a = 20 15 10 5 0 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 20 -5 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -20 -5 -2 -2 -2 -20 -5 -2 -2 -20 -5 -2 -2 -20 -5 -2 -20 -5 -2 -20 -20 -5 -2 -20		b 4 2 4 2 0 0 4 2 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1

Figure 1. Differential absorption spectra recorded upon pulse radiolytic reduction of Co^{II}TPPS to Co^{II}TPPS in aqueous solutions: (a) 2.0×10^{-5} M Co^{II}TPPS, 1.5 M *i*-PrOH, pH 13, N₂, 23 μ s after the pulse (O) and 1.5 ms later (Δ); (b) 6.5×10^{-5} M Co^{II}TPPS, 0.01 M HCO₂⁻, pH 13, N₂O, 250–300 μ s after the pulse; (c) 5.0×10^{-5} M Co^{II}TPPS, 0.01 M HCO₂⁻, pH 8.2, 3×10^{-4} M borate buffer, N₂O, 700 μ s after the pulse; (d) 5.0×10^{-5} M Co^{II}TPPS, 1.5 M *i*-PrOH, pH 13, N₂O, 250–300 μ s after the pulse; (e) 2.0×10^{-5} M Co^{II}TPPS, 1.5 M *i*-PrOH, pH 3, N₂O, 250–300 μ s after the pulse; (e) 2.0×10^{-5} M Co^{II}TPPS, 1.5 M *i*-PrOH, pH 8 with borate, N₂O, 250–300 μ s after the pulse; (f) differential spectrum calculated from steady-state radiolysis (Figure 2). One unit on the relative absorbance scale corresponds to $\epsilon = 1000$ M⁻¹ cm⁻¹ for species produced with G = 6, calibrated with SCN⁻ dosimetry.

from the two reactions. A possible alternative reaction between the $(CH_3)_2\dot{C}O^-$ radical and $Co^{II}P$ is the addition of the former to the axial position of the complex resulting in alkyl-Co^{III}P. However, the differential spectrum ob-

served is not in agreement with this possibility (see below).

Pulse radiolysis experiments have also been carried out with N₂O-saturated solutions to study the reduction of $Co^{II}TPPS$ by the $(CH_3)_2CO^-$ and CO_2^- radicals, under

conditions where these radicals are the only reducing species present. The rates of reduction, determined from the absorbance changes with time at several wavelengths, were found to follow first-order kinetics. From the pseudo-first-order rates for three or four concentrations of $Co^{II}P$, the second-order rate constants were calculated and found to be 7×10^8 and $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Table I). The rate constants show that the tendency of electron transfer is greater with $(CH_3)_2\dot{C}O^-$ than with $\dot{C}O_2^-$ as expected from the reduction potentials of these radicals.²⁷

The difference spectra monitored in each case after complete reduction are shown in Figure 1b–d. Again, it is observed that, although the major features remain the same, these spectra are not quite identical. It should be noted that these difference spectra are actually small differences (~10% or less) between two large quantities. Hence, a small change in the absorption band of initial or final products or both can show up strongly in the difference spectra. The difference between spectra 1b and 1c,d may arise from the different solution composition and ionic strength. The change in the nature of the difference spectrum in going from pH 8 to pH 13 for $\dot{\rm CO}_2^-$ reduction may also arise from a small contribution by the conjugate base of (H₂O)Co^{II}TPPS at pH 13.

Pulse radiolysis experiments in N₂O-saturated 1.5 M *i*-PrOH solution at pH 8 have also been carried out to examine the reduction of Co^{II}TPPS by the $(CH_3)_2\dot{C}OH$ radical. However, unlike the case of the $(CH_3)_2\dot{C}O^-$ and $\dot{C}O_2^-$ radicals, where only one reaction step occurs leading to the formation of Co^I species (which should, therefore, involve an outer-sphere electron transfer), an initial formation of an intermediate was observed with $(CH_3)_2\dot{C}OH$ which then decomposed to a Co^I species. As will be described later, this intermediate is an alkyl-Co(III) complex formed by the axial addition of $(CH_3)_2\dot{C}OH$ to Co^{II}TPPS. The differential spectrum monitored after complete formation of the more stable Co^I product is shown in Figure 1e.

Steady-state radiolyses of a 5×10^{-5} M solution of $Co^{II}TPPS$ in N₂-bubbled water containing 1.5 M *i*-PrOH at pH 8 or 13 do not show any systematic changes in absorption spectrum except for a very gradual broadening of all bands into featureless spectra suggesting a gradual decomposition. The formation of Co^ITPPS in this case is not observed because of its subsequent oxidation by water. Thus, $Co^{I}TPPS$ is more easily oxidized than cob-(I)aloxime^{28,29} or vitamin B_{12S}^{29} which can be obtained in aqueous solutions. The ease of oxidation of these compounds, in general, is determined to a large extent by the electron-donating ability of the peripheral ligating atoms. Obviously the fully conjugated porphyrin ligand with two acidic NH groups is a better electron donor than corrin with only one acidic NH group or dimethylglyoxime with electronegative oxygens attached to donor N atoms. On the other hand, Co^I complexes with some macrocyclic ligands³⁰ with two acidic NH groups and two sp³ nitrogen atoms are also as strongly reducing as the present compound.

In order to avoid reoxidation by water, we have carried out experiments in neat methanol. Steady-state radiolysis of a 7×10^{-5} M solution of Co^{III}TPPS in deoxygenated



Figure 2. Radiolytic reduction of Co^{II}TPPS in methanol. Solution containing 7×10^{-5} M Co^{II}TPPS and 6.8×10^{-3} M sodium methoxide, N₂ bubbled, was irradiated in the Gammacell. Absorption spectra taken after 0 (solid line), 2 (dashed line), and 4 (dotted line) min irradiation (dose rate = 2.3×10^{17} eV g⁻¹ min⁻¹).

methanol (N₂ bubbled) in the presence of 6.8×10^{-3} M sodium methoxide results in an initial formation of Co^{II}-TPPS with G = 5.2. On further radiolysis Co^ITPPS is formed with G = 4.9. The spectrophotometric monitoring of the later step is shown in Figure 2. The presence of well-defined isosbestic points at 548, 535, 519, 427, and 384 nm indicates the occurrence of a clean reduction. The observed G value definitely suggested the participation of e_s^- as well as CH_2OH radicals in the reduction process. The reduction is reversible and Co^{II}TPPS is instantly and quantitatively regenerated by bubbling N_2O . The mechanism of reduction of Co^{II}TPPS with CH₂OH radicals will be discussed later. Further irradiation of the solution beyond the Co^ITPPS stage, however, results in a gradual broadening of all the absorption peaks into featureless spectra and reduces the yield of Co^{II}TPPS or Co^{III}TPPS which can be recovered on subsequent oxidation by N_2O or O_2 , respectively.

Chemical reduction of $Co^{II}TPPS$ in methanolic solution with NaBH₄ also results in spectral changes identical with those observed in the γ -radiolysis experiment (Figure 2). The difference spectrum obtained from Figure 2 for the $Co^{II}TPPS \rightarrow Co^{I}TPPS$ reduction is shown in Figure 1f. Despite the difference in the solvent, the similarities in the spectra shown in Figure 1a-f leave little doubt that the products obtained in the pulse radiolysis experiments described so far are all $Co^{I}TPPS$ species.

Oxidation of $Co^{I}TPPS$. The presence of an excess electron density on the cobalt atom in $Co^{I}TPPS$ makes it strongly nucleophilic in character.²⁹ We have already referred to its oxidation by water and we discuss below its oxidation with other oxidants, i.e., N₂O and CH₃I.

The half-life of Co^ITPPS in a solution saturated with N₂O at pH 13 has been found to be ~100 ms while in the absence of N₂O no appreciable decay was observed for a period of 400 ms. This finding suggests a rate constant of $\leq 3 \times 10^2$ M⁻¹ s⁻¹ for the oxidation of Co^ITPPS by N₂O, but no accurate determination was possible for such a low rate. At pH 8 a slow decay was observed with a half-life ~250 ms in the absence of N₂O and is probably due to the oxidation of Co^IP by H⁺. Unfortunately, since the stability of the signal in these pulse radiolytic experiments did not allow measurements at times longer than 1 s, we could not monitor the spectra of the products formed from such oxidation reactions. The oxidation by N₂O is believed³¹ to proceed through a formal two-electron-transfer inner-

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sphere mechanism:

$$Co^{IP} + N_2O \xrightarrow{slow} (N_2O) - Co^{IIP} \xrightarrow{H^+} HO - Co^{IIIP} + N_2$$
(11)

followed by

$$Co^{III}P + Co^{I}P \xrightarrow{IBSL} 2Co^{II}P$$
 (12)

However, an intermediate formation of Co^{III} species has not yet been proved. A one-electron-transfer mechanism such as reactions 13 and 14 is possible, provided that OH

$$Co^{I}P + N_{2}O + H^{+} \xrightarrow{\text{slow}} Co^{II}P + N_{2} + \dot{O}H$$
 (13)

$$Co^{I}P + \dot{O}H \xrightarrow{\text{rask}} Co^{II}P + OH^{-}$$
 (14)

reacts at the Co and not at the ligand. The reaction of OH with cobalamins at pH 6-9 was suggested to involve addition to the ligand.⁷ At pH 13, on the other hand, Co^{II}TPPS has been found to undergo quantitative oxidation to Co^{III}TPPS in N₂O-saturated solutions, with a second-order rate constant of $5.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This oxidation is probably owing to reaction with O⁻ rather than OH (p $K_a = 11.8$), since the former is known to oxidize but not form adducts. Therefore, mechanisms 13 and 14, although they may be possible at high pH involving O⁻, are not likely to be important at pH 8.

Oxidation of Co^ITPPS by CH₃I was sufficiently rapid to be accurately followed by the pulse radiolysis technique. Experiments were carried out with $(2-7) \times 10^{-5} \text{ M Co}^{II}\text{T}$ -PPS solutions in water containing 1.5 M i-PrOH, (0.5–1) \times 10⁻³ M CH₃I, buffered at pH 8 with 3 \times 10⁻⁴ M borate and deoxygenated by bubbling N2O. At pH 8 the reaction between $(CH_3)_2$ COH and CH_3I is too slow¹⁵ to compete with the reaction of the radical with Co^{II}TPPS which ultimately produces Co^ITPPS. Figure 3 shows the kinetic traces of the subsequent reaction of Co^ITPPS with CH₃I followed at several wavelengths. The rate of decay of Co^ITPPS absorption at 495 and 510 nm and the rate of the buildup of product absorption at 550 nm were measured for various CH_3I concentrations. (At higher CH_3I concentrations acetone was added to the solution to prevent CH_3I from scavenging any e_{aq} . From the pseudofirst-order rates, a second-order rate constant of 3×10^5 $M^{\text{--}1}\ s^{\text{--}1}$ was calculated (Table I).

The difference spectra monitored about 1 and 18 ms after the pulse (Figure 3) show the formation of Co^ITPPS and its reaction product with CH₃I, respectively. The latter could be identified as CH₃Co^{III}TPPS from its spectral characteristic. CH₃Co^{III}TPPS is known to be formed by the reactions of Co^{II}TPPS with either CH₃ radical (to be discussed below) or CH₃I (in strongly alkaline aqueous solutions, along with an equivalent of Co^{III}TPPS, see reaction 19). An identical difference spectrum was also obtained by first reducing CoIITPPS under steady-state radiolysis condition in methanolic solution to Co^ITPPS and then adding CH_3I . It should be noted, however, that steady-state radiolysis of a solution similar in composition to the one used for pulse radiolysis did not result in the formation of $CH_3Co^{III}TPPS$ probably because of further reduction of the CH₃Co^{III}TPPS by (CH₃)₂COH radicals.

The reaction of Co^ITPPS with CH₃I can proceed through either a two-electron or one-electron transfer step leading respectively to a nucleophilic displacement (reaction 15) or a free-radical process (reactions 16 and 17).

$$CH_{3}I + Co^{I}TPPS \rightarrow CH_{3}Co^{III}TPPS + I^{-}$$
(15)

$$CH_3I + Co^{I}TPPS \xrightarrow{\text{slow}} Co^{II}TPPS + \dot{C}H_3 + I^-$$
 (16)

alor

$$\dot{C}H_3 + Co^{II}TPPS \xrightarrow{fast} CH_3Co^{III}TPPS$$
 (17)



Figure 3. Reaction of Co¹TPPS with CH₃I. Pulse radiolysis of an aqueous solution containing 2 \times 10⁻⁵ M Co¹¹TPPS, 1.5 M /-PrOH, 6 \times 10⁻⁴ M CH₃I, pH 8.2 with 3 \times 10⁻⁴ M borate buffer, N₂O bubbled. The differential spectrum for formation of Co¹TPPS (Δ) was monitored $\sim\!0.8$ ms after the pulse and that for formation of $\rm CH_3Co^{111}TPPS$ (O) 20 ms later. The kinetic traces show absorption changes owing to these two processes at several wavelengths.

Although the two-electron-transfer mechanism has been suggested for several reactions of cobalt(I) complexes (vitamin B_{12S} + alkyl halides),²⁹ a rate constant of the magnitude of $\sim 10^5$ M⁻¹ s⁻¹, observed in the present case, is difficult to explain from such a mechanism. The fast reactions with alkyl iodides are believed to take place by a free-radical mechanism.^{30,32,33} It should be noted that a free-radical mechanism has also been suggested for reactions of alkyl iodides with Co^{II} complexes in aqueous solution.34

Reactions of Co^{II}TPPS with Alkyl Radicals. Alkyl radicals were produced by two different methods:

(1) Addition of OH to dialkyl sulfoxides followed by fragmentation of the adduct to yield sulfinic acids and alkyl radicals.35

$$\dot{O}H + R_2SO \rightarrow RSO_2^- + H^+ + \dot{R}$$

For R = Me and *i*-Pr, used in the present study, 92% and 79% of the OH radicals, respectively, react in this manner. The remaining OH probably abstract a hydrogen atom. There is a possibility that the sulfinic acid formed may act as a reducing agent toward Co^{II}TPPS or R-Co^{III}TPPS. However, this has not been observed in any of the present experiments.

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Figure 4. Reaction of Co^{II}TPPS with CH₃. Radiolysis of an aqueous solution containing 7×10^{-5} M Co^{II}TPPS, 0.25 M Me₂SO, pH 8.3 with 3×10^{-4} borate buffer, bubbled with N₂O (a) γ radiolysis. Spectra recorded after 0 (solid line), 1.5 (dashed), and 2.5 (dotted) min irradiation. (b) Differential spectrum (O) monitored 70 μ s after the electron pulse. The solid line drawn with it was calculated from the steady-state radiolysis results.

(2) By the reduction of alkyl iodides with $(CH_3)_2\dot{C}O^-$ (ref 15)

$$(CH_3)_2\dot{C}O^- + RI \rightarrow (CH_3)_2CO + \dot{R} + I^-$$
 (18)

However, this method is severely limited because of two reasons: (a) the pK_a for $(CH_3)_2\dot{C}OH$ is about 12 and hence it is present in its basic form in sufficient concentration only at pH >12. The $(CH_3)_2\dot{C}OH$ reacts too slowly with CH_3I for the process to be useful at pH <12. (b) At higher pH Co^{II}TPPS is expected³⁴ to react with alkyl iodides as follows:

$$2Co^{II}TPPS + RI \rightarrow Co^{III}TPPS + R-Co^{III}TPPS + I^{-}$$
(19)

For R = Me the reaction was found to have a half-life of about 4 h at pH 13 while no reaction was found at pH 8 even after 24 h. In pulse radiolysis studies, made within 1 h after CH₃I is added to the solution, reaction 19 does not affect the result significantly. However, when R = i-Pr, reaction 19 is expected to be faster and to be followed by further decomposition of alkyl-cobalt complex (vide infra) and, therefore, this method has not been used with *i*-PrI.

Steady-state radiolysis of a 8×10^{-5} M solution of Co^{II}TPPS at pH 8 containing 0.25 M Me₂SO and saturated with N₂O yields CH₃Co^{III}TPPS with G = 5.5. The spectral changes on irradiation are shown in Figure 4a. A very similar spectral change was observed at pH 13 by using either Me₂SO or isopropyl alcohol-methyl iodide combination. Pulse radiolysis studies of CH₃ radical addition result in difference spectra similar to those obtained from steady-state irradiation. One typical result is presented



Figure 5. Reaction of Co¹¹TPPS with (CH₃)₂CH. Pulse radiolysis of a solution containing 6.1 × 10⁻⁵ M Co¹¹TPPS, 1.6 × 10⁻² M diisopropyl sulfoxide, pH 13, saturated with N₂O. Spectrum (O) monitored ~90 μ s after the pulse. Several points (∇) monitored ~2 s later.

in Figure 4b. The second-order rate constant for the addition reaction

$$Co^{II}TPPS + \dot{C}H_3 \rightarrow CH_3CO^{III}TPPS$$
 (20)

has been found to be in the range $(1.2-1.5) \times 10^9$ at pH 13 and $(1.5-1.7) \times 10^9$ at pH 8.2 (Table I). A systematically lower value was observed in experiments involving Me₂SO. Although this lowering is within the experimental error limit, it might reflect an effect of axial coordination by Me₂SO. The values obtained for the rate constant are comparable to that observed for $\dot{CH}_3 + B_{12r}$ in flash photolysis experiments.¹¹

The $CH_3Co^{III}TPPS$ obtained radiolytically was characterized from its spectral similarity with the product formed by the reaction of Co^ITPPS (produced by reduction in methanol) with CH₃I. Analogous reactions for other Co^I complexes are known to quantitatively produce alkyl-cobalt(III) complexes. CH₃Co^{III}TPPS was found to be quite stable in aqueous solution in the dark even in the presence of oxygen. In daylight, however, oxygenated solutions decompose completely to Co^{III}TPPS in about 1 day.

Pulse radiolysis of a 5×10^{-5} M solution of Co^{II}TPPS at pH 8 or 13 in the presence of 2×10^{-2} M diisopropyl sulfoxide and saturated with N₂O shows an initial pseudo-first-order formation of a product with a difference spectrum (Figure 5) very similar to that of CH₃Co^{III}TPPS (Figure 4). Because of this spectral similarity, the product is taken to be $(CH_3)_2CHCo^{III}TPPS$. The second-order rate constant for its formation is found to be $2\times 10^9~M^{-1}~s^{-1}$ (Table I). (CH₃)₂CHCo^{III}TPPS, however, undergoes a slow first-order decay at a rate (0.3-3 s⁻¹) depending on the pH of the solution (Table I). The first-order rate constant at a particular pH has been found to be independent of the Co^{II}TPPS or sulfoxide concentration or the dose. Several spectral points monitored at the end of the decay at pH 13 (Figure 5, ∇) strongly suggests that the product is Co^ITPPS (Figure 1). The decomposition process, therefore, appears as

$$(CH_3)_2CHCo^{III}TPPS \rightarrow CH_3CH=CH_2 + Co^{I}TPPS + H^+$$
 (21)

Similar spontaneous decomposition of the cobalt–carbon bond in aqueous solution has been observed recently for secondary alkyl cobalamins.³⁶ A β -proton elimination mechanism involving heterolytic cleavage of the cobalt– carbon bond has been suggested to account for the pH dependence and product analyses results. The driving force for the reaction has been attributed to steric factors.

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Figure 6. Reaction of Co^{II}TPPS with hydroxyalkyl radicals and decomposition of the adducts. Pulse radiolysis of solutions containing 5.5×10^{-5} M Co^{II}TPPS at pH 8 (borate buffer), N₂O bubbled. (a) 10% MeOH; (b) 10% *i*-PrOH.

The rate of decomposition observed in the present study is about 2 orders of magnitude larger than those observed for cobalamins. This reflects the presence of a greater steric repulsion with secondary alkyl–Co^{III}TPPS. At this point, however, it is not clear whether this is due to the increased planarity of the porphyrin ring or due to the presence of phenyl substitutions.

As expected from the pulse radiolysis result, steady-state radiolysis of a Co^{II}TPPS solution containing diisopropyl sulfoxide and saturated with nitrous oxide shows very little change in the absorption spectrum. The Co^ITPPS formed by addition and decomposition (reactions 20 and 21) is oxidized back to the Co^{II}TPPS by the N₂O present. Also, addition of degassed isopropyl iodide to a methanolic solution of Co^{II}TPPS produces Co^{II}TPPS, probably through simple oxidation. In any case we were not able to obtain an aqueous solution of (CH₃)₂CHCo^{III}TPPS.

Reactions of Co^{II}TPPS with Hydroxylalkyl Radicals. $\dot{C}H_2OH$ and $(CH_3)_2\dot{C}OH$ radicals are generated by the reaction of OH radical with the corresponding alcohol as shown in reaction 2. Pulse radiolysis of a 5×10^{-5} M Co^{III}TPPS solution at pH 8, containing 1.5 M CH₃OH or i-PrOH and saturated with N₂O, shows the initial formation of an alkyl-Co^{III} complex with a rate constant of $(1.1-1.2) \times 10^9$ M⁻¹ s⁻¹ (Table I). The alkyl–Co^{III} complexes then undergo first-order decay with a rate constant of 3.6 \times 10² s⁻¹ for HOCH₂Co^{III}TPPS and 6.2 \times 10³ s⁻¹ for (H- $O(CH_3)_2CCo^{III}TPPS$. These rate constants have been found to be independent of the concentration of the Co^{II}TPPS or the dose. The kinetics of the decay were monitored by following the absorbances at several wavelengths as shown in Figure 6. The product was found to be Co^ITPPS in both cases as determined from its differential absorption spectrum (Figure 1e), in accordance with the steady-state radiolysis result mentioned before (Figure 2). At longer times $Co^{I}TPPS$ decays by reaction with $N_{2}O$. From gas chromatography coupled with mass spectrometry, formaldehyde and acetone, respectively, have been identified in the γ -radiolysis products from experiments involving CH₃OH or *i*-PrOH. This indicates the decomposition reaction to be

$$HOCH_{2}Co^{III}TPPS \rightarrow Co^{I}TPPS + CH_{2}O + H^{+}$$
(22)
(HO)(CH₃)₂CCo^{III}TPPS $\rightarrow Co^{I}TPPS + (CH_{3})_{2}CO + H^{+}$ (23)

These reactions parallel that suggested for reaction of $\dot{C}H_2OH$ with other macrocyclic Co^{II}L complexes.¹⁴ A different mechanism has been suggested for reaction of $(CH_3)_2\dot{C}OH$ with B_{12r} , which involves complex formation and hydride transfer,¹⁴ while the reaction of $(CH_3)_2\dot{C}OH$ with some $Co^{II}L$ was too slow (<10⁷ M⁻¹ s⁻¹) to be observed by pulse radiolysis.^{14,30} In the case of Co^{II}TPPS the reaction with $(CH_3)_2$ COH is slightly more rapid than that with CH₂OH and leads to analogous products. The difference between this reaction (eq 23) and the mechanism suggested for some Co^{II}L¹⁴ must result from the difference in the ligand structure. In fact, with more highly unsaturated ligands, Co^{II}L was found to be rapidly reduced by (CH₃)₂COH.³⁰ Reactions 22 and 23 probably occur through an initial loss of a proton from the OH group followed by heterolysis of the cobalt-carbon bond. The 20-fold increase in the dissociation rate in going from CH₂OH to C- $(CH_3)_2OH$ adduct might reflect both the effect of electron donation from methyl groups as well as steric effect.

Summary and Concluding Remarks

The reactions of several aliphatic free radicals with $Co^{II}TPPS$ have been studied. The radicals $\dot{C}O_2^-$ and $(CH_3)_2\dot{C}O^-$ reduce $Co^{II}TPPS$ by an outer-sphere electron transfer.

$$Co^{II}TPPS + \dot{R}O^{-} \rightarrow Co^{I}TPPS + RO$$
 (24)

No formation of an unstable intermediate has been observed in this case. On the other hand, hydroxyalkyl radicals like $\dot{C}H_2OH$ and $(CH_3)_2\dot{C}OH$ initially form unstable intermediates containing a σ cobalt-carbon bond. This bond then undergoes heterolytic fission to form $Co^{I}TPPS$ and a carbonyl compound as follows:

$$Co^{II}TPPS + \dot{R}OH \rightarrow HOR-Co^{III}TPPS \rightarrow Co^{I}TPPS + RO + H^+$$
 (25)

Primary alkyl radicals such as CH_3 add on to $Co^{II}TPPS$ to form alkylcobalt compounds.

$$Co^{II}TPPS + \dot{R} \rightarrow R - Co^{III}TPPS$$
 (26)

The cobalt-carbon σ bond in this case is stable and decomposes only on photolyzing the solution. Secondary alkyl radicals like CH(CH₃)₂, on the other hand, give alkylcobalt compounds which undergo sterically induced β -hydrogen elimination to form Co^ITPPS and an olefin (reaction 21).

The reactions of Co^{II}TPPS with radicals leading to the formation of cobalt-carbon σ bonds occur with rate constants of (1-2) × 10⁹ M⁻¹ s⁻¹ (Table I), comparable to those observed in the cobalamin systems¹¹ but faster by several orders of magnitude than the analogous reactions observed with other macrocyclic Co^{II}L complexes.¹⁴ In this respect, the Co^{II}P is a better model for vitamin B_{12r} than is Co^{II}L. However, the heterolysis of the cobalt-carbon σ bond in the case of secondary alkyl adducts is several orders of magnitude faster in the present system than those for the organocobalamins.³⁶ Thus, in this reaction the Co^{II}TPPS does not serve as a very good model for vitamin B_{12r}.

Co^{II}TPPS is reduced by e_{aq} with a diffusion-controlled rate constant (~10¹⁰ M⁻¹ s⁻¹) and by $\dot{C}O_2^-$ and $(CH_3)_2\dot{C}O^$ more slowly ((2–7) × 10⁸ M⁻¹ s⁻¹) to yield in all cases the Co^ITPPS. Reactions with $\dot{C}H_2OH$ and $(CH_3)_2\dot{C}OH$ also lead to Co^ITPPS as the final product, but the mechanism involves addition and elimination as discussed above. It is noted that the rate constant for reaction of $(CH_3)_2\dot{C}OH$ with Co^{II}TPPS at pH 8 is slightly higher than that for reaction of $(CH_3)_2CO^-$ at pH 13. This trend is opposite to the usual findings²² which indicate more rapid reduction by $(CH_3)_2CO^-$ than by $(CH_3)_2COH$ (since the former has a higher redox potential). The observations with Co^uTPPS are not due to acid-base equilibria in this complex (see reactions of CO_2^- at pH 8 and 13) but rather to the different mechanisms involved, i.e., outer-sphere electron transfer with $(CH_3)_2CO^-$ vs. addition of $(CH_3)_2COH$ and the electrostatic effect of the negative charges on the rate constant $(CH_3)_2CO^-$.

Co^ITPPS produced by the above reductions is a strong nucleophile and reacts with CH₃I and N₂O. The former reaction occurs with $k = 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and leads to the formation of CH₃Co^{III}TPPS via a mechanism which is believed to involve an electron transfer in the first stage, followed by addition of CH₃ to Co^{II}TPPS. N₂O also oxidizes Co^ITPPS to Co^{II}TPPS but more slowly, $k \le 3 \times 10^2$ M^{-1} s⁻¹. A comparison with the reactivities of other Co^I complexes indicates that the nucleophilic character of Co^ITPPS is intermediate between that of cob(I)alamin²⁹ (vitamin B_{12s}) and of some Co^IL.³⁰

Registry No. Co^ITPPS, 85028-59-7; CH₃CO^{III}TPPS, 85028-60-0; (CH₃)₂CHCo^{III}TPPS, 85028-61-1; HOCH₂Co^{III}TPPS, 85028-62-2; (HO)(CH₃)₂CCo^{III}TPPS, 85028-63-3; Co^{III}TPPS, 72282-44-1; (CH₃)₂CO⁻, 17836-38-3; CO₂⁻, 14485-07-5; CH₃, 2229-07-4; CH(CH₃)₂, 2025-55-0; CH₂OH, 2597-43-5; (CH₃)₂COH, 5131-95-3.

Effect of Lipid Chain Length Inequivalence on the Packing Characteristics of Bilayer Assemblies. Raman Spectroscopic Study of Phospholipid Dispersions in the Gel State

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The inequivalent chain configurations of diacylphosphatidylcholines lead to distortions at the methyl termini which perturb the gel-phase packing properties of the remaining hydrocarbon chain segments within the bilayer assembly. The effect on gel-state bilayer disorder resulting from methyl-group displacements at the end of the sn-1 chain is reflected by a structurally fixed, independent perturbation parameter P which is inversely proportional to the length of the acyl chain. For a homologous series of saturated symmetric phosphatidylcholines, a function involving spectral frequency differences between specific C-C stretching modes for the nearly all-trans acyl chains is shown to be linearly correlated with the perturbation parameter P. This specific frequency difference parameter is determined from Raman spectra recorded at common reduced temperatures. The quantity P also displays a linear dependence with respect to other spectral parameters reflecting changes either in the intramolecular gauche/trans conformer ratios for gel-state acyl chains or in the lateral chain packing properties which occur during the bilayer gel \leftrightarrow liquid crystalline phase transition.

Introduction

Recent discussions concerning the organization of the molecular constituents comprising biological membranes have emphasized the importance of the conformational and packing behavior exhibited by the phospholipid components of the bilayer matrix.¹⁻⁴ Since the bilayer rearrangements observed in model phospholipid systems dispersed in aqueous media are relevant to the order/disorder characteristics of natural membranes,⁵⁻⁷ the well-defined structures of assemblies of synthetic phosphatidylcholines provide tractable bilayer configurations for stipulating the critical factors that determine bilayer stability. For example, for bilayer assemblies of saturated symmetric phosphatidylcholines in the gel phase, Mason and Huang^{8,9} proposed that the inequivalent sn-1 and sn-2 acyl chain configurations for the terminal methyl groups lead to perturbations in both the intramolecular conformational statistics of the acyl chains and the intermolecular interactions existing between chains. In this model the disruption of the acyl chain packing properties is expressed quantitatively by a fixed, independent perturbation parameter $P^{8,9}$ The value of P for a given phospholipid molecule is defined by the number of bond lengths in the

interface and distorted methyl regions relative to the number of bonds in an assumed all-trans conformation for the hydrocarbon segments lying between these two molecular areas of the phospholipid derivative. Thus, the perturbation parameter, given as a percentage, is inversely related to the acyl chain length by the expression P = $[3.5/2n - 5.5)] \times 10^2$, where n represents the number of carbon atoms per chain.⁸

For the gel \leftrightarrow liquid crystalline phase transition in bilayers of a homologous series of saturated-chain, diacylphosphatidylcholines, Mason and Huang demonstrated that the accompanying transition entropy, which reflects the overall bilayer order/disorder changes, varies linearly with the perturbation parameter $P.^8$ According to these

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