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Articles

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Transfer of Oxygen from Percarboxylic Acids and Alkyl Hydroperoxides to (*meso*-Tetraphenylporphinato)cobalt(III) Chloride

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The reaction of percarboxylic acids and alkyl hydroperoxides (YOOH) with (*meso*-tetraphenylporphinato)cobalt(III) chloride ((TPP)Co^{III}Cl) (CHCl$_3$ solvent, 30 °C) is first order in both [YOOH] and [(TPP)Co^{III}Cl]. A plot of the log of the second-order rate constants vs. the pK_a of YOH shows a break in slope at about pK_a 9.0 (from −0.72 to −0.15) in going from percarboxylic acids to alkyl hydroperoxides. Percarboxylic acids are shown to undergo heterolytic O–O bond scission on 2e oxidation of (TPP)Co^{III}Cl, and in the presence of CH$_3$OH a species is formed that exhibits the spectral characteristics of an isoporphyrin. The product of the reaction of (TPP)Co^{III}Cl with *t*-BuOOH has been isolated and characterized as the cobalt(III) isoporphyrin expected from the nucleophilic addition of *t*-BuOOH to the cobalt(III) porphyrin dication. These results show that the dynamics of the reaction of a YOOH species with (TPP)Co^{III}Cl, as well as the linear free energy relationship of the logarithm of the derived second-order rate constants vs. the pK_a of YOH, resemble the behavior of an iron(III) porphyrin. While the products of 2e oxidation of chromium(III) and manganese(III) tetraphenylporphyrins are metal(V) porphyrins, with iron(III) tetraphenylporphyrin the product is an Fe(IV) porphyrin π-cation radical and it is now suggested that with cobalt(III) tetraphenylporphyrin the product formed is a Co(III) porphyrin dication. These findings are discussed.

Introduction

Both peroxidase and cytochrome P-450 enzymes react with alkyl hydroperoxides and percarboxylic acids to generate enzyme-bound high-valent iron porphyrins. The reactive species so generated from cytochrome P-450 is capable of selective epoxidations and hydroxylations. The potential of simple metalloporphyrins to act as selective oxidation catalysts without the apoprotein has prompted extensive investigations.[1]

We have recently turned our attentions to a study of the dynamics and mechanisms of the oxygen-transfer reaction from alkyl hydroperoxides and percarboxylic acids to chromium(III),[2] manganese(III),[3] and iron(III)[4] tetraphenylporphyrin chlorides ((TPP)M^{III}Cl, M = metal). The products generated by oxygen atom transfer to (TPP)Cr^{III}Cl,[2] (TPP)Mn^{III}Cl,[5] and (TPP)Fe^{III}Cl[6] have been isolated and partially characterized. Very little is known about oxygen atom transfer to cobalt porphyrins.[7a] At first glance there would appear to be little reason do so since oxidation above the Co^{III} state is rather rare.[7b] Indeed, most bioinorganic cobalt porphyrin work has focused on the activity of cobalt complexes to carry out reductive alkylations.[8] We have posed three questions: Can a 2e oxidation of (TPP)Co^{III}Cl occur via oxygen atom transfer even though cobalt(III) complexes only reluctantly undergo 1e oxidation, and if so, what are the products and what is the relationship of the free energies of activation for the oxygen-transfer reactions when compared to those of other metalloporphyrins?

Experimental Section

Instrumentation. UV–vis spectra and absorbance vs. time measurements were recorded on a Perkin-Elmer 553 spectrophotometer equipped with a constant-temperature cell holder maintained at 30 °C. Rapid-mixing experiments were carried out on a Durrum stopped-flow spectrophotometer thermostated at 30 °C interfaced to a North Star computer equipped with OLIS 3820 data acquistion and processing software (On-Line Instruments Systems, Inc.). ^{1}H NMR spectra were recorded on a Nicolet NT-300 spectrometer (300 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane (Me$_4$Si). Spectra were run in methylene-d_2 chloride with Me$_4$Si as an internal reference. IR spectra were recorded as paraffin oil mulls on a Perkin-Elmer 283 spectrophotometer. Cyclic voltammetry and controlled-potential electrolysis experiments were carried out with a three-electrode potentiostat (Bioanalytical Systems Model CV-27 voltammograph). Cyclic voltammograms were recorded on a Houston Instruments Model 100 x-y recorder. The electrochemical cells were equipped with a Bioanalytical Systems platinum-inlay electrode, a platinum-flag auxiliary electrode that was separated from the main compartment by a medium-porosity glass frit, and a Ag–AgCl reference electrode filled with aqueous tetramethylammonium chloride adjusted to 0.00 V vs. the saturated calomel electrode. For controlled-potential electrolysis, a platinum-mesh working electrode was employed. Gas chromatographic analyses were performed with a Varian Model 3700 gas chromatography equipped with a flame ionization detector, a Varian WCOT capillary column (0.2 mm i.d., 18-m length), and an HP 3392 A integrator. Elemental analyses were done by Galbraith Laboratories (Knoxville, TN).

Materials. Mallinckrodt spectrophotometric grade chloroform was used for all kinetic experiments. Burdick and Jackson "Distilled-in-Glass" grade methylene chloride was used as the solvent in the electrochemical studies. Tetrabutylammonium perchlorate from G. Frederick Smith was used as the supporting electrolyte. Argon (Linde Gas Co.) passed through an Oxiclear Gas Purifier (Labclear) was used to provide an inert atmosphere for the electrochemical experiments. Column chromatography was done on silica gel (Woelm, activity III).

Tetraphenylporphyrin was purchased from Aldrich Chemical Co. and used as supplied. *m*-Chloroperbenzoic acid (MCPBA), *p*-nitroperbenzoic acid, and *tert*-butyl hydroperoxide (3 M in toluene) were also purchased from Aldrich. Cumene hydroperoxide was purchased from Sigma Chemical Co. Phenylperacetic acid,[9] perlauric acid,[10] diphenylhydroperoxyacetonitrile,[11] diphenylhydroperoxyacetic acid,[12] and trityl hydroperoxide[13] were synthesized by literature procedures. All peracids and peroxides were subjected to standard iodometric analysis[14] prior to use.

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Cobalt(II) acetate was obtained from Alfa Inorganics. Diazomethane was generated from Diazald (Aldrich) by standard procedures.[15]

Cobalt was inserted into tetraphenylporphyrin by literature methods.[16] The resultant $(TPP)Co^{II}$ was air oxidized in methanolic HCl by the procedure of Sakurai.[17] During the recrystallization, $(TPP)Co^{III}Cl$ was partially converted back to $(TPP)Co^{II}$, as detected by the visible spectrum. The $(TPP)Co^{III}Cl$ was then isolated by column chromatography on silica gel. Methylene chloride was used to elute the $(TPP)Co^{II}$, and 5% methanol in methylene chloride eluted the $(TPP)Co^{III}Cl$, which was isolated by removing the solvent under reduced pressure. The electronic spectrum matched that for $(TPP)Co^{III}(CH_3OH)Cl$ reported in the literature.[18] The ϵ_{546} value ($(1.3 \pm 0.1) \times 10^4$ cm^{-1} M^{-1}) was similar to that reported by Stillman[19] (1.38×10^4 cm^{-1} M^{-1}).

Methods. The kinetics of oxygen atom transfer to $(TPP)Co^{III}Cl$ were determined by monitoring the decrease in absorbance of the $(TPP)Co^{III}Cl$ visible band at 546 nm at 30 °C. For the hydroperoxides, each kinetic run was carried out by adding 2–20 μL of a stock hydroperoxide solution (~0.1 M) to a 3-mL stock solution of $(TPP)Co^{III}Cl$ ($\sim 10^{-4}$ M) in $CHCl_3$ in a 1 cm path length quartz cuvette. The method of initial rates was employed to analyze the absorbance vs. time data with use of the equation

$$(\Delta A/\Delta t)/\Delta\epsilon_{546} = k[\mathrm{ROOH}][(\mathrm{TPP})\mathrm{Co^{III}Cl}]$$

For the hydroperoxides, the second-order rate constant, k, was obtained by varying the hydroperoxide concentration over an 8–10-fold range and averaging the resulting k values. The initial rate was calculated from the slope of the curve at less than 5% decomposition of $(TPP)Co^{III}Cl$.

The second-order rate constants for oxygen atom transfer from the percarboxylic acids were determined by rapid mixing on the Durrum stopped-flow bench ($[(TPP)Co^{III}Cl] = 2.3 \times 10^{-6}$ M; $[RCO_3H] = 3.7 \times 10^{-5}$–$2.6 \times 10^{-4}$ M). The absorbance vs. time data were analyzed by pseudo-first-order methods using the software described above.

To determine the mechanism of oxygen atom transfer from phenylperacetic acid, 1 mL of a stock $CHCl_3$ solution of phenylperacetic acid (1.17×10^{-2} M) and 100 μL of a stock solution of $(TPP)Co^{III}Cl$ in $CHCl_3$ (9.29×10^{-2} M) were added to each of five 2-mL glass vials sealed with a rubber septum and a metal cap. The reaction mixtures were allowed to sit for 30 min, and then 200 μL of a freshly prepared diazomethane solution was added via a microliter syringe to the vial. The concentration of methyl phenylacetate was then determined by GC. Each vial was sampled five times.

Preparation of Cobalt Isoporphyrin (1) from $(TPP)Co^{III}Cl$ and *tert*-Butyl Hydroperoxide. To a stirred solution of 25 mg (3.52×10^{-5} mol) of $(TPP)Co^{III}Cl$ in 60 mL of $CHCl_3$ was added 2 mL of a stock solution (2.46×10^{-2} M) of *tert*-butyl hydroperoxide (6.92×10^{-5} mol) in toluene. The solution was stirred for 16 h. TLC on silica gel eluted with $CHCl_3$ showed a very small amount of material at the origin and the major product with an R_f value of 0.8. This major product was taken up in $CHCl_3$ and flash chromatographed on a silica gel column, resulting in partial decomposition of the main green fraction to yield $(TPP)Co^{II}$ and a spot at the origin. The solvent was removed from the main green product fraction by blowing an N_2 stream over the solution. The solid material was recrystallized from 0.5 mL of $CHCl_3$ and 4 mL of heptane (yield 12 mg). Anal. Calcd for $C_{48}H_{37}O_2CoCl(OH)\cdot CHCl_3$: C, 63.06; H, 4.08; N, 6.00; Co, 6.32. Found: C, 63.74; H, 4.14; N, 5.98; Co, 5.92. ^{1}H NMR (CD_2Cl_2): δ 7.60–7.40 (m, 20 H), 7.22 (d, J = 5.1 Hz, 2 H), 7.04 (d, J = 5.1 Hz, 2 H), 6.58 (d, J = 4.8 Hz, 2 H), 6.30 (d, J = 4.8 Hz, 2 H), 1.29 (s, 9 H). IR (paraffin oil): 755, 790, 815, 842, 970, 1023, 1075, 1205, 1232, 1300 cm^{-1}.

Iodometric titration of 1 was carried out by two procedures: The first method, reported by Bruice,[20] requires dissolving the peroxide in buffered 95% ethanolic NaI. The compound is not stable in ethanol, and the reduction of the peroxo linkage begins immediately. From the absorbance of I_3^- at 358 nm ($\epsilon = 2.5 \times 10^4$), 60% of the theoretical 4 equiv/mol of **1** was titrated. In the second method, the decrease in the isoporphyrin absorbance band at 824 nm was monitored upon addition of NBu_4I in $CHCl_3$. Reduction by I^- in $CHCl_3$ yields $(TPP)Co^{II}$ plus a small amount of unidentified product. On the basis of a stoichiometry of 5 equiv/mol of **1**, 110% of the equivalents were titrated. (Note: 4 equiv of I^- is required to reduce t-BuOO–$(TPP)Co^{III}(OH)Cl$ to H_2O, t-BuOH, and $(TPP)Co^{III}(OH)Cl$ and an additional 1 equiv to reduce the latter to $(TPP)Co^{II}$.)

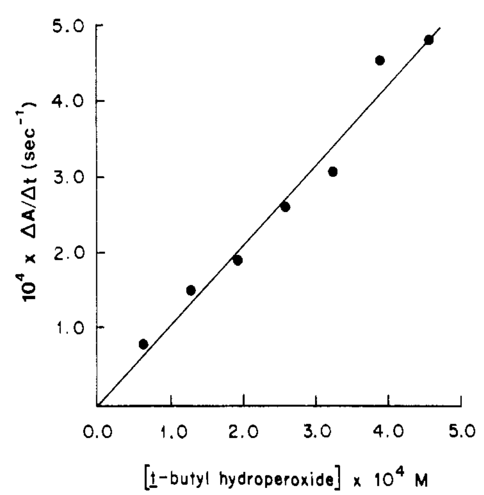

Figure 1. Initial rate of decrease in $[(TPP)Co^{III}Cl]$ at 545 nm as a function of *tert*-butyl hydroperoxide concentration ($[(TPP)Co^{III}Cl] = 2.18 \times 10^{-5}$ M, $\Delta\epsilon_{545} = 9.5 \times 10^3$, $CHCl_3$ solution at 30 °C).

Results and Discussion

The reactions of percarboxylic acids and alkyl hydroperoxides with $(TPP)Co^{III}Cl$ were followed spectrophotometrically by monitoring the decrease in the visible spectrum of $(TPP)Co^{III}Cl$ at 546 nm ($CHCl_3$ solvent at 30 °C). Kinetic studies with percarboxylic acids were carried out under pseudo-first-order conditions with percarboxylic acid in excess. The reaction was clearly biphasic, and the observed rate constants were determined by fitting the absorbance vs. time data to the equation for two sequential first-order reactions. The first and more rapid reaction, resulting in >80% of the absorbance change, was first-order in percarboxylic acid and independent of $(TPP)Co^{III}Cl$ concentration. With alkyl hydroperoxides, biphasic kinetics were also observed, but the rate of the second reaction was of a magnitude equal to the first, resulting in large errors when the data were fit to the above equations. Therefore, the rate constants were determined by the method of initial rates. A plot of the initial rate as a function of *tert*-butyl hydroperoxide concentration is shown in Figure 1. The rate law for the transfer of an oxygen atom from percarboxylic acids and alkyl hydroperoxides (YOOH) to $(TPP)Co^{III}Cl$ in $CHCl_3$ is

$$-d[(\mathrm{TPP})\mathrm{Co^{III}Cl}]/dt = k[(\mathrm{TPP})\mathrm{Co^{III}Cl}][\mathrm{YOOH}]$$
$$k_{\mathrm{obsd}} = k[\mathrm{YOOH}] \qquad (1)$$

The reactive intermediate generated upon oxygen atom transfer could not be trapped by high concentrations (>1 M) of 2,4,6-tri-*tert*-butylphenol, which has been very effective in trapping out the intermediates formed in similar experiments with $(TPP)Mn^{III}Cl$[3] and $(TPP)Fe^{III}Cl$.[4,21] The rate of oxygen transfer, as well as the spectrum of the final product, was found to be insensitive to the presence of dioxygen. The addition of CH_3OH drastically slowed the rate of oxygen transfer to $(TPP)Co^{III}Cl$ and influenced the final spectrum of the product. Methanol presumably competes (eq 2) with the oxidants for the vacant axial site

$$(\mathrm{TPP})\mathrm{Co^{III}}(\mathrm{CH_3OH})\mathrm{Cl} \underset{\mathrm{CH_3OH}}{\rightleftharpoons} (\mathrm{TPP})\mathrm{Co^{III}Cl} \overset{\mathrm{ROOH}}{\rightleftharpoons} (\mathrm{TPP})\mathrm{Co^{III}}(\mathrm{ROOH})\mathrm{Cl} \xrightarrow{\mathrm{rds}} \text{intermediate} \xrightarrow{\mathrm{CH_3OH}} \text{product} \qquad (2)$$

on the cobalt. The spectrum of the product obtained in the presence of CH_3OH is shown in Figure 2. Inspection of this

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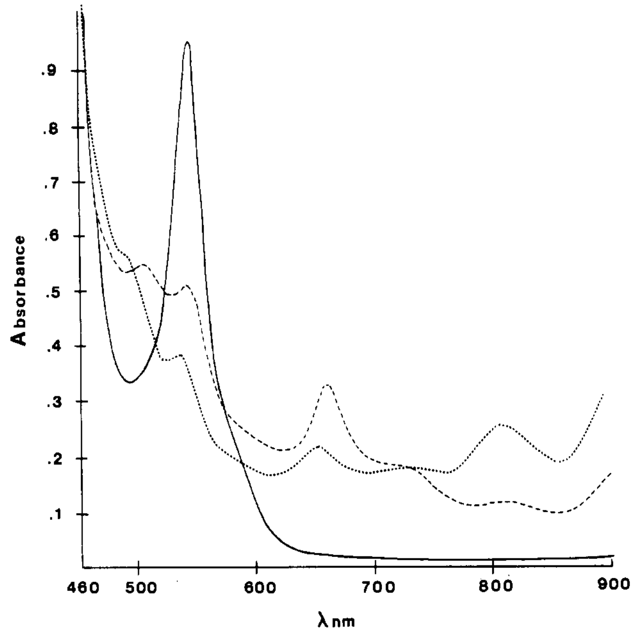


Figure 2. Initial spectrum of 1.03×10^{-4} M (TPP)$Co^{III}Cl$ in $CHCl_3$ (—) and final spectra of 1.03×10^{-4} M (TPP)$Co^{III}Cl$ with 3.45×10^{-4} M MCPBA in $CHCl_3$ (---) and in 3% $CH_3OH/CHCl_3$ (···).

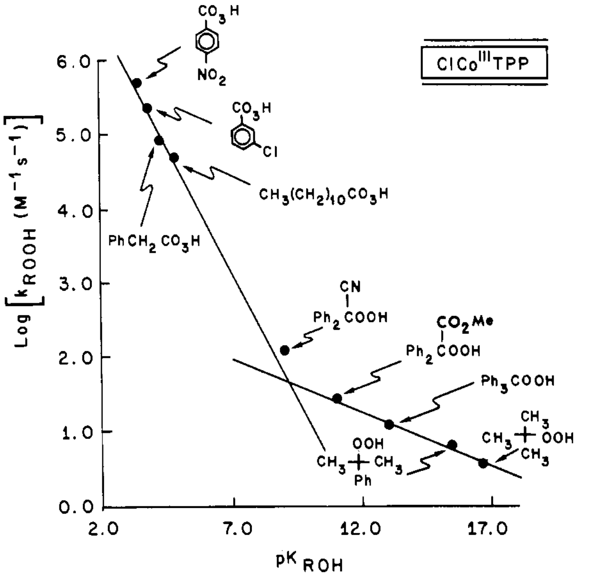


Figure 3. Logarithm of the second-order rate constants for oxygen transfer to (TPP)Co–Cl in $CHCl_3$ at 30 °C as a function of the leaving-group acidity.

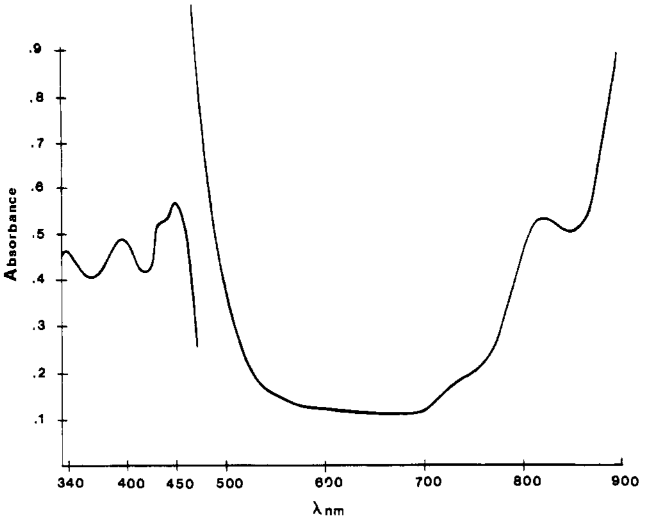
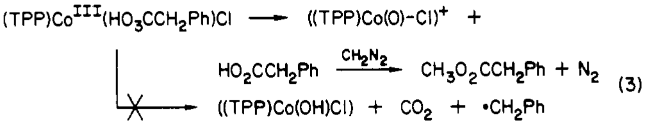


Figure 4. Electronic spectrum of the cobalt(III) isoporphyrin **1** isolated from the reaction of 2 mol of *tert*-butyl hydroperoxide with 1 mol of (TPP)$Co^{III}Cl$ in $CHCl_3$ (340–475 nm, 1 mm path length; >475 nm, 1-cm path length).

spectrum shows that it resembles that of an isoporphyrin (vide infra).

In Figure 3 a plot of the log of the second-order rate constants for oxygen transfer from a series of percarboxylic acids and alkyl hydroperoxides vs. the corresponding pK_a of the respective leaving group;[20] i.e., the carboxylic acid or the alcohol is shown. The plot clearly shows two distinct linear regions which intersect at a pK_a value of ~9. The slope values (β_{lg}) are a measure of the sensitivity of the oxygen-transfer reaction to the nature of the leaving group. We previously observed a break in such a linear free-energy plot for the reaction of percarboxylic acids and alkyl hydroperoxides with (TPP)$Fe^{III}Cl$ in CH_3OH.[4] With phenylperacetic acid, the oxygen-transfer experiment to (TPP)$Co^{III}Cl$ was run to completion, as evidenced by the visible spectrum, and an excess of diazomethane then added to the reaction mixture. Methyl phenylacetate was shown to be present in >70% yield, and this establishes that the oxygen-transfer mechanism involves a heterolytic O–O bond scission of the percarboxylic acid. A reaction involving O–O bond homolysis with HO· transfer would result in decarboxylation, since C–C bond and O–O bond rupture are simultaneous and, therefore, no methyl phenylacetate would be detected (eq 3).[22] Since all of the percarboxylic acids fall on the same linear free energy line, we conclude that the mechanism of oxygen transfer with the percarboxylic acids involves a heterolytic O–O bond cleavage. The mechanism of the oxygen transfer from the alkyl hydroperoxides is less clear. A homolytic cleavage of the O–O bond can be rationalized, thus explaining the different sensitivities between the leaving group pK_a's for percarboxylic acids ($\beta_{lg} = -0.72$) and alkyl hydroperoxides ($\beta_{lg} = -0.15$).



$$(TPP)Co^{III}(HO_3CCH_2Ph)Cl \longrightarrow ((TPP)Co(O){-}Cl)^+ + HO_2CCH_2Ph \xrightarrow{CH_2N_2} CH_3O_2CCH_2Ph + N_2$$
$$\not\longrightarrow ((TPP)Co(OH)Cl) + CO_2 + {\cdot}CH_2Ph \qquad (3)$$

The electronic spectra of the final products obtained upon addition of the alkyl hydroperoxides to (TPP)$Co^{III}Cl$ resemble the spectra of the ferric[23] and zinc[24] isoporphyrins. The electronic spectrum of the product upon addition of *tert*-butyl hydroperoxide to (TPP)$Co^{III}Cl$ is shown in Figure 4. The near-IR absorbances at 824 and >900 nm are characteristic of an isoporphyrin species. The electronic spectrum of the final product, obtained with MCPBA, does not appear to be that of an isoporphyrin (Figure 2). Attempts to isolate this product from preparative-scale reactions resulted in its decomposition. Interestingly, carrying out the reaction with MCPBA in 3% $CH_3OH/CHCl_3$ does result in the formation of a product with long-wavelength isoporphyrin-like bands (Figure 2).

The cyclic voltammogram of (TPP)Co^{II} in CH_2Cl_2, shown in Figure 5, exhibits three reversible waves anodic of the rest potential. These waves correspond to the (TPP)Co^{II}/(TPP)Co^{III}, (TPP)Co^{III}/$\cdot^+$(TPP)Co^{III}, and $\cdot^+$(TPP)Co^{III}/$^{2+}$(TPP)Co^{III} couples [$\cdot^+$TPP = porphyrin π cation radical; $^{2+}$TPP = porphyrin dication).[25] Controlled-potential electrolysis of (TPP)Co^{II} at 1.30 V removes 3 electron equiv, resulting in the formation of a $^{2+}$(TPP)Co^{III} species. Addition of an excess of CH_3OH to this species yields a new cyclic voltammogram that indicates the irreversible addition of CH_3OH to the product of the 3e oxidation

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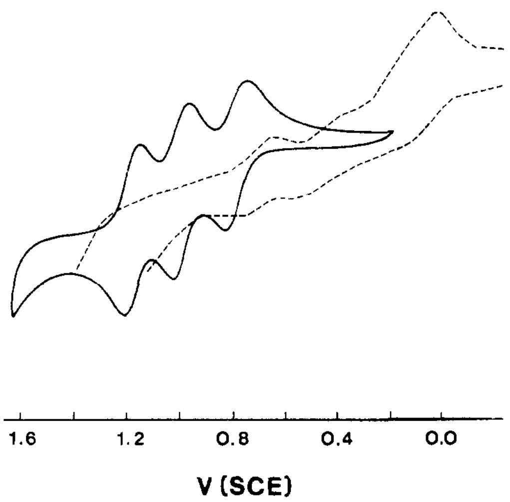


Figure 5. Cyclic voltammograms of 3.1 × 10^{-4} M $(TPP)Co^{II}$ (—) and the product (---) after removal of 0.456 C and addition of 100 μL of CH_3OH (0.1 M $TBAP/CH_2Cl_2$).

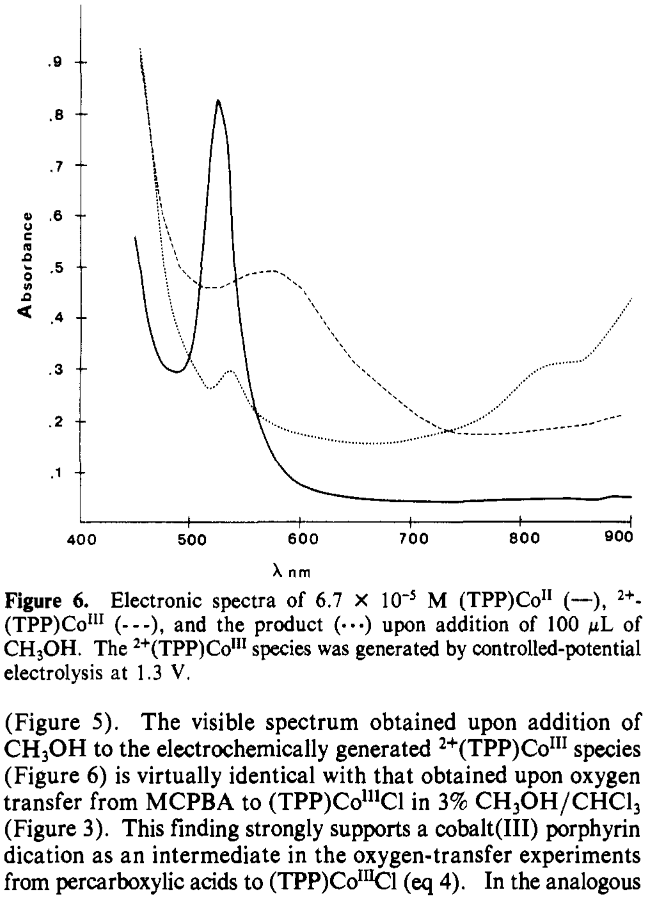
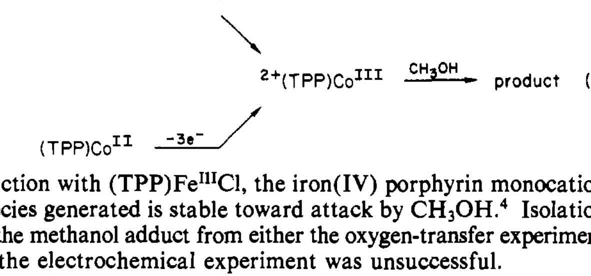


Figure 6. Electronic spectra of 6.7 × 10^{-5} M $(TPP)Co^{II}$ (—), $^{2+}(TPP)Co^{III}$ (---), and the product (···) upon addition of 100 μL of CH_3OH. The $^{2+}(TPP)Co^{III}$ species was generated by controlled-potential electrolysis at 1.3 V.

(Figure 5). The visible spectrum obtained upon addition of CH_3OH to the electrochemically generated $^{2+}(TPP)Co^{III}$ species (Figure 6) is virtually identical with that obtained upon oxygen transfer from MCPBA to $(TPP)Co^{III}Cl$ in 3% $CH_3OH/CHCl_3$ (Figure 3). This finding strongly supports a cobalt(III) porphyrin dication as an intermediate in the oxygen-transfer experiments from percarboxylic acids to $(TPP)Co^{III}Cl$ (eq 4). In the analogous



$$\begin{array}{l}(TPP)Co^{III}Cl + RCO_3H \searrow \\ \qquad\qquad {}^{2+}(TPP)Co^{III} \xrightarrow{CH_3OH} \text{product} \\ (TPP)Co^{II} \xrightarrow{-3e^-} \nearrow \end{array} \qquad (4)$$

reaction with $(TPP)Fe^{III}Cl$, the iron(IV) porphyrin monocation species generated is stable toward attack by CH_3OH.[4] Isolation of the methanol adduct from either the oxygen-transfer experiment or the electrochemical experiment was unsuccessful.

A stable product was isolated in the reaction of 2 equiv of *tert*-butyl hydroperoxide with 1 equiv of $(TPP)Co^{III}Cl$. The electronic spectrum, shown in Figure 4, is highly indicative of an isoporphyrin structure. The presence of a peroxide bond is also suggested by iodometric titrations, which required approximately 4 equiv of I^- to reduce the cobalt isoporphyrin structure. Two bands at 815 and 842 cm^{-1} in the infrared spectrum also support the presence of a peroxo linkage.[23a] The elemental analysis requires the presence of a *tert*-butylperoxy-substituted product (see Experimental Section). The proposed structure for the cobalt isoporphyrin is analogous to that obtained by Gold with iron(III) tetrakis(4-methoxyphenyl)porphyrin chloride and *tert*-butyl hydroperoxide[23a] and is shown by **1**. The ^1H NMR spectrum

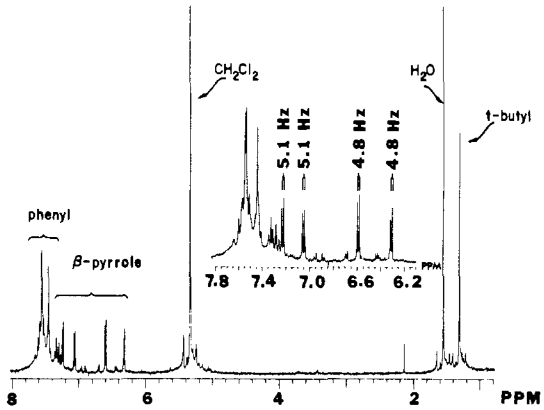
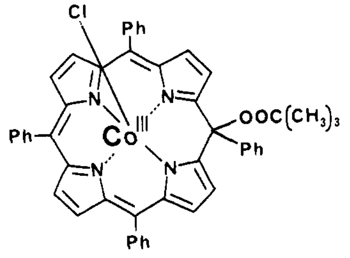


Figure 7. ^1H NMR spectrum (300 MHz) of isoporphyrin **1** in CD_2Cl_2.



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(CD_2Cl_2) of **1** supports the structure shown (Figure 7). The sharp peaks and the lack of resonances outside the 0–10 ppm range indicate that all of the cobalt is present as low-spin diamagnetic cobalt(III). The β-pyrrole protons in the 300-MHz spectrum appears as two well-separated AX patterns (δ 6.30, 6.58 (J = 4.8 Hz) and δ 7.04, 7.22 (J = 5.1 Hz)) in contrast to the 100-MHz ^1H NMR spectrum of the zinc isoporphyrin, which exhibits two overlapping AB quartets (δ 6.2–6.7).[24] The AX patterns are consistent with the C_s symmetry of the molecule. This symmetry requires the Co atom to either rapidly equilibrate between the two faces of the isoporphyrin plane or remain in the plane of the porphyrin. The two downfield doublets are assigned to the pyrrole ring adjacent to the doubly substituted meso carbon because of the greater aromaticity of this ring relative to that of the other pyrrole ring. There are only two pyrrole rings in the NMR spectrum. Each doublet integrates to 1:1:1:1:4.5 relative to a sharp singlet at 1.29 ppm assigned to the *tert*-butyl group. The phenyl region exhibits several overlaying multiplets as expected for the product, and we have not attempted further interpretation.

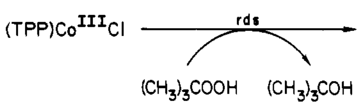
Two plausible mechanisms exist for the formation of **1**. By analogy to the mechanism of oxygen transfer to $(TPP)Fe^{III}Cl$ from *tert*-butyl hydroperoxide, a homolytic cleavage of the O–O bond yielding $\cdot^{+}(TPP)Co^{III}OH$ and *tert*-butoxide radical, eq 5, is likely.

$$(TPP)Co^{III}Cl + (CH_3)_3COOH \xrightarrow{rds} \cdot^{+}(TPP)Co^{III}(OH)Cl + (CH_3)_3CO\cdot \qquad (5a)$$

$$(CH_3)_3CO\cdot + (CH_3)_3COOH \xrightarrow{fast} (CH_3)_3COH + (CH_3)_3COO\cdot \qquad (5b)$$

$$(CH_3)_3COO\cdot + \cdot^{+}(TPP)Co^{III}(OH)Cl \xrightarrow{fast} \mathbf{1} \qquad (5c)$$

Alternatively, a heterolytic cleavage of the O–O bond would yield an intermediate with both oxidation equivalents on the porphyrin ligand and nucleophilic substitution by *tert*-butyl hydroperoxide on this dication, analogous to CH_3OH attack on the electrochemically generated $^{2+}(TPP)Co^{III}Cl$, would be possible (eq 6).



$$^{2+}(TPP)Co^{III}(O)Cl \xrightarrow{(CH_3)_3COOH} \mathbf{1} \quad (6)$$

The break in the linear free energy relationship shown in Figure 3 suggests to us a mechanistic difference between the percarboxylic acids and the alkyl hydroperoxides. On this basis we prefer the rate-determining homolytic cleavage mechanism of eq 5 for the reaction of *tert*-butyl hydroperoxide with $(TPP)Co^{III}Cl$.

With $(TPP)Cr^{III}Cl$, $(TPP)Mn^{III}Cl$, and $(TPP)Fe^{III}Cl$, oxygen atom transfer from percarboxylic acids and alkyl hydroperoxides results in intermediates in which the metal is raised to the oxidation state of M^V or M^{IV}. These intermediates are sufficiently stable toward nucleophiles in the presence of an appropriate substrate to function as oxygen-transfer catalysts. This is not the case with $(TPP)Co^{III}Cl$. The ready formation of isoporphyrin complexes from the cobalt intermediate in the presence of trace concentrations of nucleophiles is compatable with the localization of the oxidizing equivalents on the porphyrin ligand rather than on the metal. The cobalt is a very active participant in the oxygen-transfer reaction, as evidenced by the exceedingly large second-order rate constants for oxygen transfer from the percarboxylic acids. Although Co(III) is oxidized to Co(IV) with great reluctance, being limited primarily to fluoro and oxo complexes,[7] the rate constants for reaction of the percarboxylic acids and $(TPP)Co^{III}Cl$ are 2 orders of magnitude greater than those obtained with $(TPP)Cr^{III}Cl$ and $(TPP)Fe^{III}Cl$, a further indication that the porphyrin ligand is supplying the electrons. Electrochemical studies of organobis(dimethylglyoximato)cobalt(III) complexes demonstrate that the principal site of one-electron removal is the cobalt atom.[26] In this same study, based on kinetic measurements for the chemical oxidation of these complexes, the authors conclude that the electron may initially be removed from the ligand followed by structural rearrangement and internal electron transfer to yield the Co(IV) species. With an electron-rich porphyrin ligand, an opposite effect can be imagined wherein initial transfer of an oxygen atom to cobalt(III) yields a higher valent cobalt(V) species which by rapid internal electron transfer results in the porphyrin dication species (eq 7). On the other hand, the intermediate structures depicted

$$(TPP)Co^{III}\text{–}Cl + RCO_3H \rightarrow [(TPP)Co^{V}(O)Cl] \rightarrow {}^{2+}(TPP)Co^{III}(O)Cl \quad (7)$$

$$(TPP)Co^{V}(O)Cl \leftrightarrow {}^{\cdot+}(TPP)Co^{IV}(O)Cl \leftrightarrow {}^{2+}(TPP)Co^{III}(O)Cl \quad (8)$$

in eq 7 could also be simply limiting forms of the same structure (eq 8). The extremely high reactivity of the intermediate toward nucleophiles suggests that the porphyrin dication is the predominant intermediate structure.

Several cobalt(III) complexes with an alkyl hydroperoxide bonded directly to the cobalt have been characterized. A recent report on the thermal decomposition of the *t*-BuOO–cobalt(III) 1,3-bis(pyridylimino)isoindoline complex demonstrated a homolytic decomposition of the O–O bond of the peroxide.[27] In contrast to the electron-rich porphyrin ligand the 1,3-bis(pyridylimino)isoindole ligand was not oxidized and the oxidation equivalent resided in the cobalt–oxo moiety (species reacts as if it were $Co^{III}\text{–}O\cdot$).

The likely formation of a cobalt porphyrin dication species upon oxygen atom transfer to $(TPP)Co^{III}Cl$ completes an interesting series. Oxygen atom transfer to $(TPP)Cr^{III}Cl$, $(TPP)Mn^{III}Cl$, $(TPP)Fe^{III}Cl$, and $(TPP)Co^{III}Cl$ results in intermediate metal–oxo species that go from primarily metal-centered to what our data suggest is mainly a metal–oxo porphyrin-centered oxidation. With chromium and manganese, the pentavalent metal–oxo species are formed. In the case of iron, one oxidizing equivalent is localized on the metal and the other on the porphyrin, resulting in an iron(IV)–oxo porphyrin π cation radical, and with cobalt, the cobalt(III) porphyrin dication appears to be the primary product.

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Registry No. 1, 99604-59-8; $(TPP)Cr^{III}Cl$, 60166-10-1; *t*-BuOOH, 75-91-2; CH_3OH, 67-56-1; O_2, 7782-44-7; *m*-chlorobenzoic acid, 937-14-4; *p*-nitroperbenzoic acid, 943-39-5; cumene hydroperoxide, 80-15-9; phenylperacetic acid, 19910-09-9; perlauric acid, 2388-12-7; diphenylhydroperoxyacetonitrile, 5233-67-0; diphenylhydroperoxyacetic acid, 60538-68-3; trityl hydroperoxide, 4198-93-0.

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Synthesis and Study of Mononuclear Ruthenium(II) Complexes of Sterically Hindering Diimine Chelates. Implications for the Catalytic Oxidation of Water to Molecular Oxygen

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Bis(diimine) complexes of ruthenium(II) have been prepared. The chelates used are 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbp) or 2,9-dimethyl-1,10-phenanthroline (2,9-dmp). Due to the steric hindrance created by the methyl groups α to the nitrogen atoms, the bis chelate complexes synthesized are all cis, with respect to the two remaining coordination sites, and cannot be photoisomerized to their trans isomers, in contrast with the equivalent complexes containing unsubstituted diimines. In addition, condensation of the mononuclear species to hydroxo- or oxo-bridged species of higher nuclearity is strictly prevented. The complexes have been characterized and studied by spectroscopic methods (UV–visible, IR, and ^1H and ^{13}C NMR). Their electrochemical behavior has been investigated in relation to the oxidation of water to molecular oxygen. The most significant results are the following: dinuclear species like $(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2^{4+}$ are required for catalytic generation of O_2 from water, in agreement with previously reported data.[7] On the other hand, the complexes presently reported display no activity toward oxidation of water.

Introduction

Oxidation of water to molecular oxygen is of great importance as a means for converting light energy into chemical energy. The practical value of the artificial systems presently available as models of water photosplitting is highly dependent on the ability of future systems to efficiently use H_2O as an electron donor.[1,2]

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