# Oxygen Transfer from Percarboxylic Acids and Alkyl Hydroperoxides to (*meso*-Tetraphenylporphinato)iron(III) and -chromium(III)

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Abstract: The second-order rate constants (k_{YOOH}) for the reaction of (*meso*-tetraphenylporphinato)iron(III) chloride ((TPP)Fe^{III}(Cl)) with a series of percarboxylic acids and alkyl hydroperoxides (species YOOH) were determined in methanol by the trapping of the hypervalent iron–oxo porphyrin species with 2,4,6-tri-*tert*-butylphenol. The oxygen donors, YOOH, were chosen so that the leaving species, YOH, possessed pK_a values spaced between 3.8 and 16.7. Values of k_{YOOH} for oxidation of (TPP)Cr^{III}(Cl) to (TPP)Cr^{V}(O) have been determined in dichloromethane by following the formation of ((TPP)Cr^{IV})$_2$O. The latter arises by non-rate-determining trapping of (TPP)Cr^{V}(O) by unreacted (TPP)Cr^{III}(Cl). A plot of log k_{YOOH} for (TPP)Fe^{III}(Cl) versus the log of k_{YOOH} for (TPP)Cr^{III}(Cl) exhibits two linear portions. A slope of about unity is seen when YOOH represents percarboxylic acids. This reflects the similarity in mechanism for the reactions of percarboxylic acids with (TPP)Fe^{III}(Cl) and (TPP)Cr^{III}(Cl). Since phenylacetic acid is obtained as the product in the reaction of both (TPP)Fe^{III}(Cl) and (TPP)Cr^{III}(Cl) with phenylperacetic acid, the common mechanism is one of heterolytic scission of the percarboxylic acid O–O bond. With (TPP)Cr^{III}(Cl), a linear free-energy plot of log k_{YOOH} versus the pK_a of the leaving YOH is shared by both percarboxylic acids and hydroperoxides. This finding is to be expected if oxygen transfer from hydroperoxides to (TPP)Cr^{III}(Cl) shares with the percarboxylic acids the common mechanism of O–O bond heterolysis. A change in mechanism of oxygen transfer in the reactions of (TPP)Fe^{III}(Cl) with percarboxylic acids and alkyl hydroperoxides is shown by the breaks in plots of the log k_{YOOH} versus either the pK_a of YOH or log k_{YOOH} for (TPP)Cr^{III}(Cl). The rate-limiting step on reaction of the less acidic alkyl hydroperoxides with (TPP)Fe^{III}(Cl) is suggested to involve homolytic O–O bond scission to provide an intimate [(TPP)Fe^{IV}(OH)(X)–•O-alkyl] pair which may then dissociate as such or after H• transfer dissociate to (+•TPP)Fe^{IV}(O)(X) + HO-alkyl. Differentiation of mechanism on the basis of the products of YOH oxidation cannot be made. Details are discussed in the paper. The various linear free-energy plots exhibit a surprising independence of steric effects in the hydroperoxides.

Cytochrome P-450 is a monooxygenase that utilizes molecular oxygen and two reducing equivalents supplied by specific reductases to hydroxylate and epoxidize organic molecules (eq 1). At its active site, cytochrome P-450 contains an iron(III) proto-

$$R—H + O_2 \xrightarrow[\text{P-450}]{2e^-, 2H^+} R—OH + H_2O \qquad (1)$$
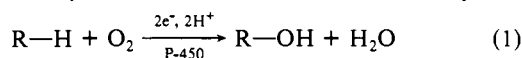
porphyrin IX bound axially to a cysteine residue from the apoprotein. In general, biomimetic approaches toward mimicking the chemistry of the enzyme have focused primarily on the metalloporphyrin and its interactions with oxygen donors, solvents, and substrates.[1] It is possible to "fine-tune" the electronic and steric properties of the porphyrin moiety and also to vary the central metal atom. Chromium,[2a,3] manganese[1g-i,l] iron,[1a-f,j,k,2b] cobalt,[4] rhodium,[5] and molybdenum[6] have been substituted into

various porphyrin ligands, and their catalytic properties have been investigated.

In this paper we describe kinetic and product studies for the reaction of percarboxylic acids and alkyl hydroperoxides with (*meso*-tetraphenylporphinato)iron(III) chloride and -chromium-(III) chloride.[2]

Experimental Section

Materials. Methanol (Mallinkrodt spectral grade) was used as received. Dichloromethane and benzonitrile (Aldrich, Gold Label) were degassed under N_2 and stored over $CaCl_2$ and molecular sieves (3A), respectively. (*meso*-Tetraphenylporphinato)iron(III) ((TPP)Fe^{III}(Cl)) was prepared by literature procedures.[7] (*meso*-Tetraphenylporphinato)chromium(III) chloride ((TPP)Cr^{III}(Cl)) was prepared and purified by literature procedures,[8] and (TPP)Cr^{III}(OH)(H$_2$O)$_2$ was obtained by vigorous stirring of a (TPP)Cr^{III}(Cl) chloroform solution with 1.0 M NaOH.[9] *m*-Chloroperbenzoic acid, *p*-nitrobenzoic acid, *tert*-butyl hydroperoxide (70% aqueous solution or 3 M in toluene), and iodosobenzene diacetate were purchased from Aldrich. Cumene hydroperoxide (Sigma) was used as received. Phenylperacetic acid,[10] perlauric acid,[11] diphenylhydroperoxyacetonitrile[12] (DPHA), diphenylhydroperoxyacetate[13] (DPHAC), trityl hydroperoxide,[14] 5-chloropervaleric acid,[15] and 3-chloroperpropionic acid[15] were prepared as reported previously. Hy-

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drogen peroxide (30% solution) was obtained from Fischer Scientific Co. The *tert*-butyl hydroperoxide/dichloromethane and H_2O_2/dichloromethane solutions were obtained by extracting ~ 2 mL of aqueous oxidant three times with 10-mL portions of dichloromethane in an N_2 glovebox. The combined extracts were dried over calcium chloride, filtered, and then diluted to 50 mL. All peracids, peroxides, and other oxygen donors were subjected to iodometric analysis[16] prior to use.

2,4,6-Trimethylpyridine (Sigma, purified grade) was used as supplied. 2,4,6-Trimethylpyridine hydrochloride was prepared by passing dry HCl gas through an ether solution of 2,4,6-trimethylpyridine and isolation of the white precipitate by vacuum filtration. 2,4,6-Tri-*tert*-butylphenol (Aldrich) was recrystallized three times from ethanol–water. All other compounds were obtained from standard suppliers.

Instrumentation. UV–vis spectra and absorbance versus time measurements were recorded on a Perkin-Elmer 553 spectrophotometer or on a Cary 118 spectrophotometer, both equipped with constant temperature cell holders. Infrared spectra were recorded on a Perkin-Elmer 553 spectrophotometer. HPLC was carried out with an Altex Model 100 pump equipped with a Hewlett Packard HP1040A diode array detector. Gas chromatographic analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector, a Varian WCOT capillary column (0.2-mm i.d.,25-m length), and an HP3392A integrator. Rapid-mixing experiments were carried out on a Durrum-Gibson Model 130d stopped-flow spectrophotometer. Kinetic analysis of absorbance versus time data were obtained with use of a Hewlett Packard 9820A computer/9864A digitizer and appropriate kinetic software (in house).

Oxygen Transfer to (TPP)Fe^{III}(Cl) (without Buffer). All experiments were carried out at 30 °C under anaerobic conditions. Typically, 5 mL of (TPP)Fe^{III}(Cl) (10^{-3}–10^{-4} M) solution in CH_2Cl_2 was diluted to 50 mL with a 0.25 M TBPH solution in CH_3OH. The acidity of the stock solution was adjusted with μL quantities of 0.1 M HCl/CH_3OH and a 0.1 M solution of NBu_4OH/CH_3OH to obtain >90% monomeric (TPP)Fe^{III}(Cl). A solution of approximately 10^{-6} M HCl was required to obtain these conditions. Under basic conditions, the spectrum of the iron porphyrin matches that of the μ-oxo dimer[17] [In CH_3OH/CH_2Cl_2 (9:1) under acidic conditions $\lambda_{max} = 396$ nm (log $\epsilon = 5.11$), 531 nm (4.015), 690 nm (3.18), under basic conditions $\lambda_{max} = 415$ nm (5.08), 600 nm].

Three milliliters of TBPH/(TPP)Fe^{III}(Cl) solution was pipetted into the cell portion and 50–350 μL of oxidant ($\sim 6.0 \times 10^{-2}$ M) into the side arm of a Thunberg cuvette. Both cell chamber and side arm were outgassed with solvent saturated argon for 10 min and thermostated in the cell holder for 15 min before mixing. Upon mixing, the absorbance change due to TBP* (630 nm; ϵ 202 cm^{-1} M^{-1}) was monitored over 7 half-lives. The spectrum of the (TPP)Fe^{III}(Cl) was recorded before and after the reaction.

Oxygen Transfer to (TPP)Fe^{III}(Cl) (with Buffer). A 200-mL stock solution of pH$_{app}$ = 6.5 was prepared by dissolving 0.305 g (2.52 mmol, 0.0126 M) of 2,4,6-trimethylpyridine and 3.153 g (20.0 mmol, 0.10 M) of 2,4,6-trimethylpyridine–HCl in 200 mL of CH_3OH.[18] Aliquots of the buffer solutions were prepared such that [2,4,6-trimethylpyridine] = 1.01 $\times 10^{-2}$, 0.756×10^{-2}, 0.504×10^{-2}, 0.252×10^{-2}, and 0.126×10^{-2} M and [TBPH] = 0.01 M. (TPP)Fe^{III}(Cl) (5–25 μL) was taken in each 3 mL of buffer solution, and the kinetics followed as given in the previous section.

The kinetics were monitored at 630 nm at each buffer dilution at constant (TPP)Fe^{III}(Cl) and oxidant concentration. The uncatalyzed rate constant, k_1, at pH$_{app}$ = 6.5 was then determined from the intercept of a plot of k_{obsd}/[(TPP)Fe^{III}(Cl)] versus [2,4,6-trimethylpyridine].

Product Analysis: Trityl Hydroperoxide and (TPP)Fe^{III}(Cl). The products from the reaction were quantified by GC. In a Thunberg cuvette, a 3-mL solution of TBPH (7.85×10^{-2} M), (TPP)Fe^{III}(Cl) (10^{-4} M), and trityl hydroperoxide (6.1×10^{-3} M) was mixed. Upon completion of the reaction, 20 μL of 0.5 M HCl was added to the reaction mixture, and the mixture was injected directly into the GC. The concentration of TBP* was calculated from the ΔA at 630 nm. The concentration of the various products was determined from standard curves. The percentage yields of products based upon [Ph$_3$COOH], are as follows: TBP*, 15%; benzophenone, 85%; phenol, 81%; tritylalcohol, 32%. Note: Trityl alcohol decomposes during GC analysis, and its concentration is subject to large error. In an independent experiment carried out on a preparative scale with [TBPH] = 0.13 M; [(TPP)Fe^{III}(Cl)] = 7 $\times 10^{-5}$ M; [trityl hydroperoxide] = 0.89 mmol in 27 mL of CH_3OH/CH_2Cl_2. There was found at completion of the reaction the

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three major products: phenol, benzophenone (IR 1665 cm^{-1}) and trityl alcohol (mp 156–160 °C (lit. mp 162–163 °C)). These were isolated by silica gel preparative TLC plate (hexane/ethyl acetate 1/10) and identified by comparison to known standards.

Product Analysis: 1,1-Diphenylhydroperoxyacetonitrile (DPHAC) and (TPP)Fe^{III}(Cl). In an identical procedure as above 1,1-diphenylhydroperoxyacetonitrile (7.73×10^{-3} M) was mixed with TBPH (0.126 M) and (TPP)Fe^{III}(Cl) (7×10^{-5} M) in a Thunberg cuvette. Final product analysis: [TBP*] = 4.63×10^{-3} M; [methylbenzoate] = 3.9×10^{-3} M; [benzophenone] = 3.3×10^{-3} M; [phenol] = 5.1×10^{-3} M.
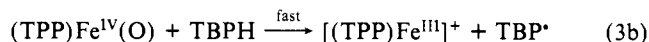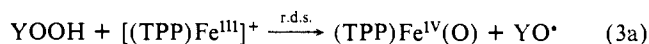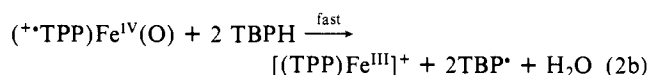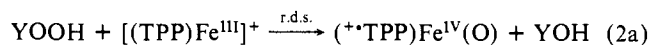
Oxygen Atom Transfer from Iodosylbenzene to (TPP)Cr^{III}(Cl). Under anaerobic conditions (N_2 atmosphere), a suspension of iodosylbenzene was vigorously stirred for 20 min in CH_2Cl_2. The suspension was then filtered, and the filtrate was analyzed by iodometric titration to determine the concentration of dissolved iodosylbenzene. The solution of PhIO was used within 1 h. Reactions were initiated by mixing 2.9 mL of PhIO (0.12–7.2×10^{-6} M) and 0.10 mL of (TPP)Cr^{III}(Cl) (1.05×10^{-5} M) in Thunberg cuvettes, and the spectrum from 800 to 350 nm was recorded at constant time intervals (25 °C).

Mechanism of O–O Bond Cleavage on Reaction of Phenylperacetic Acid with (TPP)Cr^{III}(Cl). To a 1-mL CH_2Cl_2 solution 2.6×10^{-3} M in phenylperacetic acid (under N_2) in a 2-mL sealed bottle, there was added 200 μL of a solution of (TPP)Cr^{III}(Cl) (final concentration 3.3×10^{-2} M). The reaction was allowed to stand at room temperature for 60–90 min, and an excess of an etherial solution of CH_2N_2 (200–300 μL) was then added. GC analysis detected greater than 90% PhCH$_2$CO$_2$CH$_3$. The yield of PhCH$_2$CO$_2$CH$_3$ was determined by use of a standard plot.

Oxidation of CH$_3$OH and TBPH by (TPP)Cr^{IV}(O) in CH_2Cl_2. All reactions were carried out in CH_2Cl_2 at 25 °C with use of Thunberg cuvettes in a dry N_2 glovebox. The reaction was initiated by mixing 2.9 mL of a CH$_3$OH solution (0.52–0.17 M) or TBPH (1.92×10^{-2} to 3.85 $\times 10^{-3}$ M) in CH_2Cl_2 and 0.1 mL of a CH_2Cl_2 solution of (TPP)Cr^{IV}(O) (4.67×10^{-5} M after mixing), and the ΔA at 544 nm was monitored. The reactions were first order over 7 half-lives, and the second-order rate constants were calculated from the slopes of a plot of k_{obsd} versus [TBPH] or [CH$_3$OH].

Results

The kinetics of oxygen transfer from percarboxylic acids and alkyl hydroperoxides to (TPP)Fe^{III}(Cl) were followed in CH$_3$OH at 25 °C by trapping the products of oxygen transfer with 2,4,6-*tert*-butylphenol (TBPH)[1d] and following with time the formation of the blue (630 nm) 2,4,6-tri-*tert*-butylphenoxyl radical (TBP*) (eq 2 and 3). The compounds YOOH were chosen such

$$\text{YOOH} + [(TPP)Fe^{III}]^+ \xrightarrow{\text{r.d.s.}} (^{+\bullet}TPP)Fe^{IV}(O) + YOH \quad (2a)$$

$$(^{+\bullet}TPP)Fe^{IV}(O) + 2\ TBPH \xrightarrow{\text{fast}}$$
$$[(TPP)Fe^{III}]^+ + 2TBP^\bullet + H_2O \quad (2b)$$

$$\text{YOOH} + [(TPP)Fe^{III}]^+ \xrightarrow{\text{r.d.s.}} (TPP)Fe^{IV}(O) + YO^\bullet \quad (3a)$$

$$(TPP)Fe^{IV}(O) + TBPH \xrightarrow{\text{fast}} [(TPP)Fe^{III}]^+ + TBP^\bullet \quad (3b)$$

$$YO^\bullet + TBPH \xrightarrow{\text{fast}} YOH + TBP^\bullet \quad (3c)$$

that the pK_a's of the respective leaving groups (YOH) formed by oxygen atom transfer ranged from 3.8 to 16.7. All reactions were carried out under the pseudo-first-order conditions of [TBPH] > [YOOH] $\gg$ [(TPP)Fe^{III}(Cl)]$_i$ = 10^{-4} to 10^{-5} M such that there were between 10 and 100 turnovers of the iron(III) porphyrin catalyst. Appearance of TBP* followed the first-order rate law to completion of reaction. The observed pseudo-first-order rate constants (k_{obsd}) exhibited a first-order dependence upon the initial concentration of the catalyst and an independence upon both [YOOH] and [TBPH].

The iron(III) porphyrin spectrum in slightly basic methanol matches that reported for the μ-oxo dimer species [((TPP)-Fe^{III})$_2$O][17] while in slightly acidic methanol (addition of HCl) the spectrum resembles that of the Cl$^-$ ligated species in CH_2Cl_2. It is likely in CH$_3$OH that the chloro species has a weakly bound CH$_3$OH as a sixth ligand. The kinetics of oxygen transfer from all percarboxylic acids and alkyl hydroperoxides were studied under two sets of experimental conditions. In the first, the ratio [(TPP)Fe^{III}(Cl)]: [((TPP)Fe^{III})$_2$O] was adjusted to greater than 9:1 by the addition of methanolic HCl (10^{-6} to 10^{-5} M in [H$^+$]).

Reaction of (TPP)Fe^III(Cl) with Percarboxylic Acids

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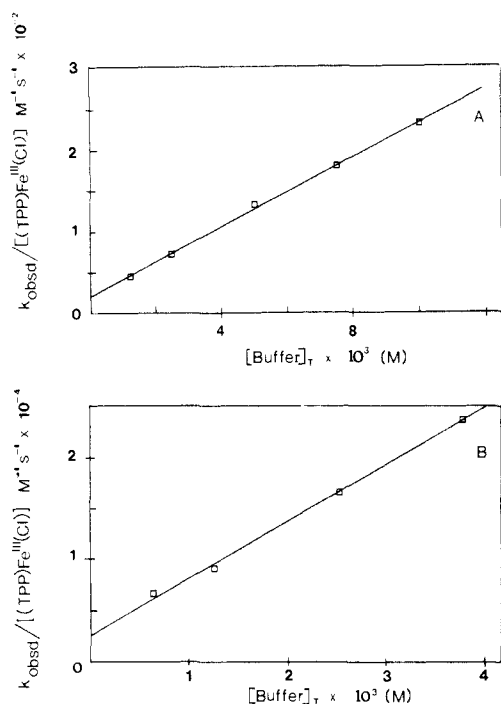
Figure 1. Dependence of the second-order rate constants (k_{obsd}/ [(TPP)Fe^III(Cl)]), determined by following the formation of TBP•, upon the concentration of collidine buffer at a calculated pH* of 6.5. In plot A YOOH represents triphenylmethyl hydroperoxide, in plot B YOOH is m-ClC$_6$H$_5$CO$_3$H. The buffer-independent second-order rate constant, k_{YOOH}, is calculated as the intercepts of such plots.

The second-order rate constants (k_{YOOH}) where calculated as k_{obsd}/[(TPP)Fe^III(Cl)]$_i$. The second set of experimental conditions employed buffering by 2,4,6-trimethylpyridine/2,4,6-trimethyl-pyridine•HCl (ratio of 1:7.9) to maintain the acidity at an apparent pH* of 6.5.[19] Since 2,4,6-trimethylpyridine buffer has a pronounced effect upon k_{obsd}, the values of k_{YOOH} were obtained by dividing the intercepts of the plots of k_{obsd} versus buffer concentration by [(TPP)Fe^III(Cl)]$_i$. For this purpose a 10-fold range of buffer concentrations at constant ratios of buffer base to buffer acid were employed (Figure 1). A linear dependence of k_{obsd} on 2,4,6-trimethylpyridine buffer concentration was found to be typical of all hydroperoxides and m-ClC$_6$H$_5$CO$_3$H. For phenylperacetic acid, perlauric acid, and 5-chloropervaleric acid, the dependence of k_{obsd} on the buffer concentration was not linear but showed distinct upward curvature. The intercept at zero buffer concentration was approximated by fitting the points to a curved line as shown for phenylperacetic acid in Figure 2. Plots of the log of k_{YOOH} versus the pK_a of YOH leaving groups obtained under both the buffered and unbuffered experimental conditions are shown in Figure 3. The plots are quite similar showing a break in the linear dependence of the log of the second-order rate constants, k_{YOOH}, on the pK_a of the leaving groups.

Products Formed on Reaction of 1,2-Diphenylhydroperoxy-acetonitrile (DPHAC) and Trityl Hydroperoxide with (TPP)-Fe^III(Cl). In the oxygen-transfer reactions to (TPP)Fe^III(Cl) from DPHA, DPHAC, and trityl hydroperoxide only 15–35% of the expected changes in A_{630}, due to TBP•, were observed. In order to account for the missing oxygen equivalents, the reaction mixtures were analyzed upon completion. By this means it was possible to account for 100% of the reaction products with trityl hydroperoxide and >90% with DPHAC.

With trityl hydroperoxide, four principal reaction products (TBP• (15%), phenol (81%), benzophenone (85%), and trityl alcohol (32%)) were identified. The yield of Ph$_3$COH is higher than expected due to Ph$_3$COH impurities in the trityl hydroperoxide. With DPHAC as oxygen transfer agent the major
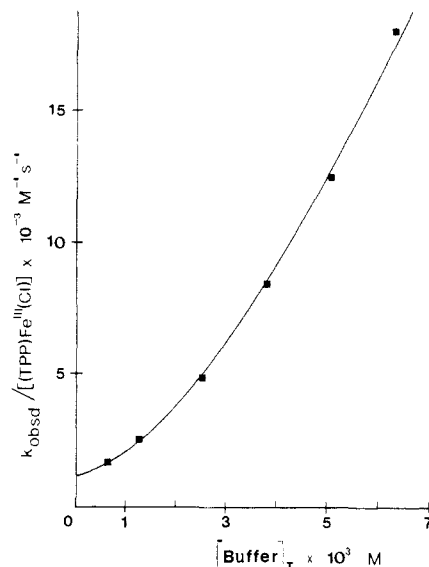
(19) pH apparent is the calculated pH value based on the quantity of HCl added or the buffer ratio as the case may be (see ref 25).

Figure 2. Dependence of the second-order rate constants (k_{obsd}/ [(TPP)Fe^III(Cl)]), determined by following the formation of TBP•, upon the concentration of collidine buffer at a calculated pH* of 6.5 in the reaction of phenylperacetic acid with (TPP)Fe^III(Cl). The buffer-independent second-order rate constant k_{YOOH} is calculated as the intercepts of such plots.
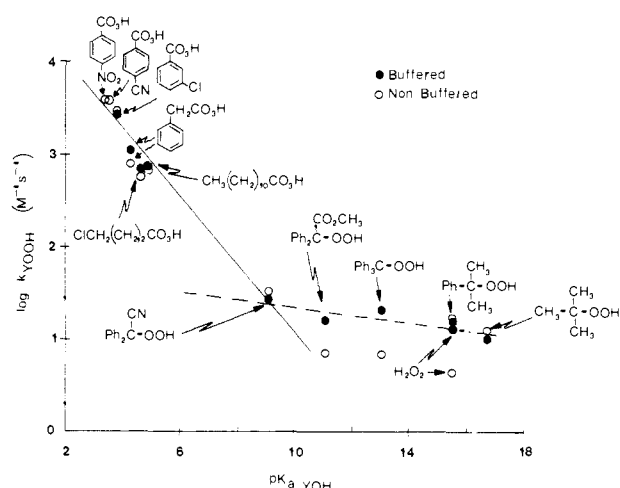

Figure 3. Plots of the calculated second-order rate constants (k_{YOOH}) for oxygen transfer from percarboxylic acids and hydroperoxides to (TPP)-Fe^III(Cl) versus the pK_a of the carboxylic acid and alcohol (for H$_2$O$_2$, water) leaving groups (YOH). (O) Values of k_{YOOH} were obtained from intercepts of buffer dilution plots (as in Figures 1 and 2). (●) The pH* was adjusted (6.5) prior to initiation of the reaction and buffering was not employed.

products were TBP• (30%), methyl benzoate (50%), benzophenone (43%) and phenol (66%).

Several experiments were carried out to determine if the product, benzophenone, might not have arisen by the trapping of (+•TPP)Fe^IVO(X) by Ph$_3$COH. Upon addition of m-ClC$_6$H$_5$CO$_3$H (to 3.03 × 10⁻³ M) to a methanolic solution of trityl alcohol (0.10 M) and (TPP)Fe^III(Cl) (10⁻⁵ M) immediate destruction (bleaching) of the porphyrin ligand is observed. Since the porphyrin moiety of (+•TPP)Fe^IVO is known to rapidly decompose to nonporphyrin products, the experiment demonstrates the inability of trityl alcohol to trap (even at 0.10 M) the reactive intermediates (+•TPP)Fe^IVO. In contrast, TBPH is an effective trap for (+•TPP)Fe^IV(O) at 10⁻³ M. Likewise, the addition of an excess of trityl alcohol to a solution of TBP• does not result in hydrogen atom exchange, so that trityl alcohol is not oxidized by TBP•. Finally, Ph$_3$COOH (to 0.044 M) was added to a solution of (TPP)Fe^III(Cl) (10⁻⁴ M) in CH$_3$OH/CH$_2$Cl$_2$ (9:1), and the effect on the electronic spectrum of (TPP)Fe^III(Cl) was observed. No bleaching of the porphyrin spectrum was observed! These
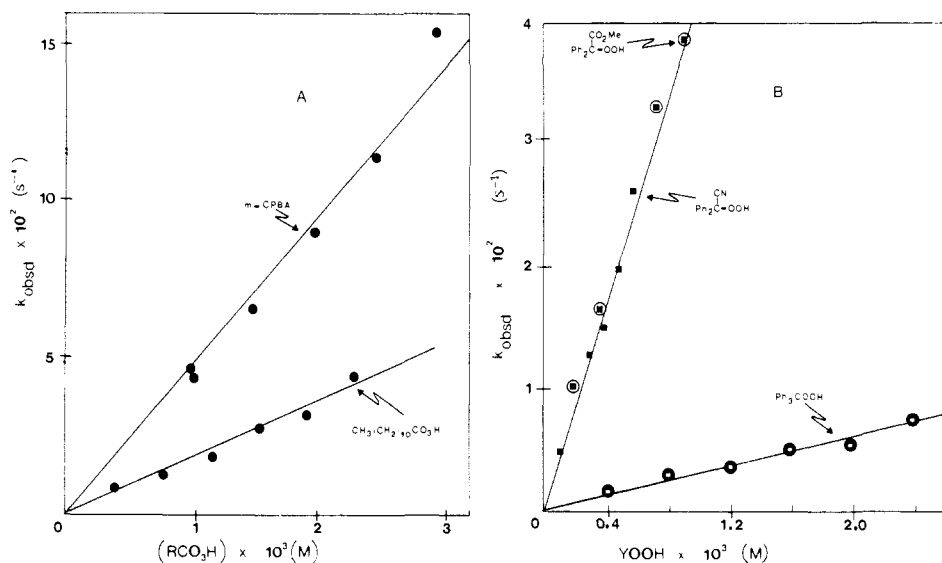
Figure 4. Plots of the observed pseudo-first-order rate constant (k_{obsd}) for the oxidation of (TPP)Cr^{III}(Cl) versus the concentration of the oxidant.

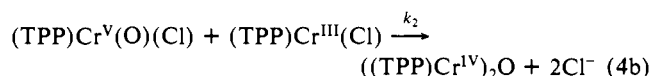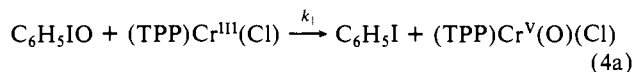Table I. The Dependence of λ_{max} Shift on the Ratio of $C_6H_5IO/(TPP)Cr^{III}(Cl)$

PhIO/(TPP)Cr^{III}(Cl)^a	λ_{max}	Cr species
19.81	416	V
11.90	416	V
6.35	418	V (main) + IV
4.49	419	V + IV
3.93	420	V + IV (main)
3.36	426	V + IV
2.80	428	IV
1.68	428	IV
1.11	428, 447 (sh)	IV (main) + III
0.32	428, 447	IV + III

^{a} [(TPP)Cr^{III}(Cl)] = 1.05 × 10^{-5} M in CH$_2$Cl$_2$ at 25 °C.

experiments demonstrate that the leaving group, trityl alcohol, must undergo oxidation prior to its dissociation from the formed higher valent iron–oxo porphyrin species or within a solvent cage.

Reaction of (TPP)Cr^{III}(Cl) with C$_6$H$_5$IO. Freshly prepared solutions of CH$_2$Cl$_2$ saturated with C$_6$H$_5$IO are required for reproducible results. In Table I the identity of the higher valent chromium intermediate, as a function of the ratio of C$_6$H$_5$IO to (TPP)Cr^{III}(Cl), is shown (i.e., (TPP)Cr^{III}(Cl), λ_{max} 447 nm; ((TPP)Cr^{IV})$_2$O, λ_{max} 428; (TPP)Cr^V(O)(X) 416 nm). Examination of Table I shows that at high concentrations of C$_6$H$_5$IO relative to (TPP)Cr^{III}(Cl), the (TPP)Cr^V(O)(Cl) was obtained as the exclusive product. With a lower concentration of C$_6$H$_5$IO, relative to (TPP)Cr^{III}(Cl), ((TPP)Cr^{IV})$_2$O was formed. When the ratio of C$_6$H$_5$IO/(TPP)Cr^{IV}(Cl) is less than 1, a mixture of Cr(III) and Cr(IV) species was observed. The logical explanation for the results in Table I is found in eq 4. When the product of k_1[C$_6$H$_5$IO] is sufficiently large, the rate of reaction of (TPP)-

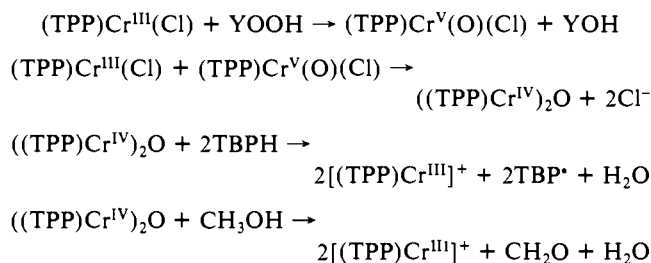$$C_6H_5IO + (TPP)Cr^{III}(Cl) \xrightarrow{k_1} C_6H_5I + (TPP)Cr^V(O)(Cl)$$
(4a)

$$(TPP)Cr^V(O)(Cl) + (TPP)Cr^{III}(Cl) \xrightarrow{k_2}$$
$$((TPP)Cr^{IV})_2O + 2Cl^- \quad (4b)$$

Cr^{III}(Cl) with C$_6$H$_5$IO exceeds the rate of comproportionation of (TPP)Cr^{III}(Cl) with (TPP)Cr^V(O)(Cl) so that the product observed is (TPP)Cr^V(O)(Cl). As the concentration of C$_6$H$_5$IO is decreased, comproportionation of (TPP)Cr^{III}(Cl) with (TPP)Cr^V(O)(Cl) becomes more important until the sole product is ((TPP)Cr^{IV})$_2$O.[20] When freshly prepared solutions are used, a molarity of 2.5 × 10^{-4} in C$_6$H$_5$IO is required to convert 1.05 × 10^{-4} M (TPP)Cr^{III}(Cl) to (TPP)Cr^V(O)(Cl) free of ((TPP)-

(20) Listen, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568.

Cr^{IV})$_2$O. Excess C$_6$H$_5$IO is required so that (TPP)Cr^V(O)(Cl) is not trapped by (TPP)Cr^{III}(Cl), since C$_6$H$_5$IO does not oxidize ((TPP)Cr^{IV})$_2$O to (TPP)Cr^V(O)(Cl). The finding of rapid trapping of the Cr(V) species by the Cr(III) species provided us with a means to study oxygen transfer from percarboxylic acids and hydroperoxides to (TPP)Cr^{III}(Cl).

Oxygen Transfer from RCO$_3$H and ROOH to (TPP)Cr^{III}Cl in CH$_2$Cl$_2$. Attempts to use TBPH as a trap for either (TPP)Cr^V-(O)(Cl) or ((TPP)Cr^{IV})$_2$O intermediates, generated upon oxygen transfer to (TPP)Cr^{III}(Cl), resulted in less than the theoretical 2 equiv of stable phenoxyl radical (TBP•) per equivalent of oxidant. The oxidation of both TBPH and CH$_3$OH by ((TPP)Cr^{IV})$_2$O (4.67 × 10^{-5} M) in CH$_2$Cl$_2$ was followed by the appearance of (TPP)Cr^{III}(Cl). Values of [TBPH]$_i$ and k_{obsd} × 10^3 s^{-1} were as follows: 0.004 M, 3.25; 0.008 M, 4.5; 0.012 M, 6.5; 0.0158 M, 8.3; and 0.0193 M, 9.5. Values of [CH$_3$OH] and k_{obsd} × 10^4 s^{-1} were as follows: 0.17 M, 1.0; 0.26 M, 2.37; 0.35 M, 3.44; and 0.53 M, 5.8. The second-order rate constants are calculated to be ca. 0.4 and 1 × 10^{-3} M^{-1} s^{-1}, respectively. The overall reaction is depicted in Scheme I.

Scheme I

$$(TPP)Cr^{III}(Cl) + YOOH \rightarrow (TPP)Cr^V(O)(Cl) + YOH$$

$$(TPP)Cr^{III}(Cl) + (TPP)Cr^V(O)(Cl) \rightarrow$$
$$((TPP)Cr^{IV})_2O + 2Cl^-$$

$$((TPP)Cr^{IV})_2O + 2TBPH \rightarrow$$
$$2[(TPP)Cr^{III}]^+ + 2TBP• + H_2O$$

$$((TPP)Cr^{IV})_2O + CH_3OH \rightarrow$$
$$2[(TPP)Cr^{III}]^+ + CH_2O + H_2O$$

Thus, methanol is an inappropriate solvent for the investigation of the reaction of (TPP)Cr^{III}(Cl) with oxygen transfer agents because ((TPP)Cr^{IV})$_2$O is reduced by this solvent. Also, as stated, TBPH is an inefficient trap for ((TPP)Cr^{IV})$_2$O. However, (TPP)Cr^V(O)(X) and ((TPP)Cr^{IV})$_2$O are stable in CH$_2$Cl$_2$, and the appearance of (TPP)Cr^V(O)(X) and ((TPP)Cr^{IV})$_2$O and disappearance of (TPP)Cr^{III}(Cl) can be monitored directly during the reaction of (TPP)Cr^{III}(Cl) with RCO$_3$H and ROOH species. The kinetics of oxygen atom transfer to (TPP)Cr^{III}(Cl) from a series of percarboxylic acids and alkyl hydroperoxides (YOOH) whose leaving group (YOH) pK_a's are between 3.8 and 16.7 were studied in CH$_2$Cl$_2$ at 25 °C. Reactions were carried out under the pseudo-first-order conditions of [YOOH] ≫ [(TPP)Cr^{III}(Cl)]. Appearance of ((TPP)Cr^{IV})$_2$O and (TPP)Cr^V(O)(X) followed the first-order rate law to over 7 half-lives. Plots of the pseudo-first-order rate constants (k_{obsd}) versus [YOOH] were linear and provided (Figure 4A,B) as slopes the second-order rate constants
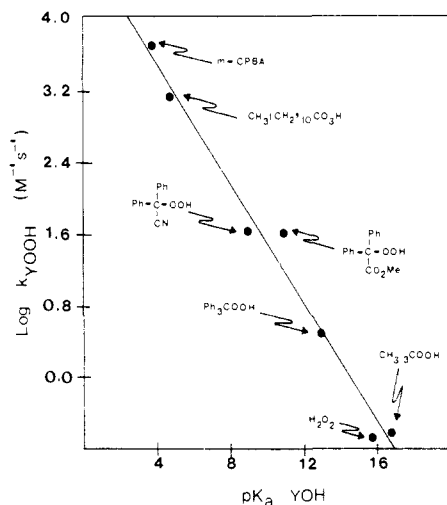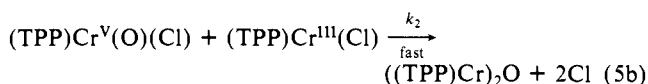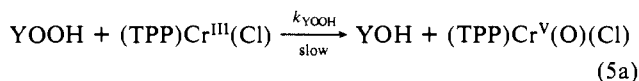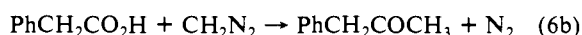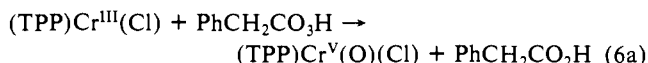
Figure 5. A plot of the log of the second-order rate constants (k_{YOOH}) for oxygen transfer from percarboxylic acid and hydroperoxide YOOH compounds to (TPP)Cr^{III}(Cl) versus the pK_a of the YOH leaving groups.

(k_{YOOH}) for oxygen transfer (eq 5a). In Figure 5 the log of k_{YOOH} versus the pK_a of the leaving YOH groups is plotted. The fit of

$$YOOH + (TPP)Cr^{III}(Cl) \xrightarrow[slow]{k_{YOOH}} YOH + (TPP)Cr^V(O)(Cl)$$
(5a)

$$(TPP)Cr^V(O)(Cl) + (TPP)Cr^{III}(Cl) \xrightarrow[fast]{k_2}$$
$$((TPP)Cr)_2O + 2Cl \quad (5b)$$

the experimental points to a linear plot is satisfactory. Phenyl-peracetic acid was employed in order to determine the mechanism of oxygen transfer from percarboxylic acids to (TPP)Cr^{III}(Cl). After treating the spent reaction solution with diazomethane, >90% of phenylacetic acid was accounted for as its methyl ester (eq 6),

$$(TPP)Cr^{III}(Cl) + PhCH_2CO_3H \rightarrow$$
$$(TPP)Cr^V(O)(Cl) + PhCH_2CO_2H \quad (6a)$$

$$PhCH_2CO_2H + CH_2N_2 \rightarrow PhCH_2COCH_3 + N_2 \quad (6b)$$

Discussion

A large body of data (NMR,[21] UV–vis,[22] Mössbauer,[23] ESR,[24] ENDOR[25]) supports an iron(IV)–oxo porphyrin π-cation radical structure for the primary intermediate generated upon oxygen transfer to the iron(III) porphyrin of horseradish peroxidase and the catalases. A similar intermediate has been isolated and characterized[26] from the reaction of (tetramesitylporphinato)-iron(III) porphyrin with iodosobenzene or MCPBA. Thus, oxygen atom transfer to an iron(III) porphyrin results in both 1e⁻ oxidation of the iron(III) and a 1e⁻ oxidation of the porphyrin ligand. Both the 1e⁻ and 2e⁻ oxidized species have also been generated electrochemically.[27] In the case of (TPP)Cr^{III}(Cl), the hypervalent metal complexes ((TPP)Cr^{IV})_2O and (TPP)Cr^V(O)(X) are known.[3]

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(26) Groves, J. T.; Haunshalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884. Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613.
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2,4,6-Tri-*tert*-butylphenol (TBPH) has been employed as a trapping agent in order to determine the second-order rate constants for oxygen atom transfer by percarboxylic acids and alkyl hydroperoxides (YOOH) to (TPP)Fe^{III}(Cl). In our hands, TBPH is not an efficient trap for (TPP)Cr^V(O)(Cl) which is the initial product of oxygen atom transfer to (TPP)Cr^{III}(Cl). The reaction of a variety of oxygen atom donors (hydroperoxides[28], percarboxylic acids[28], alkaline hypochlorite,[3a] and 2-(benzenesulfonyl)-3-(*p*-nitrophenyl)oxaziridine[2a]) with (TPP)Cr^{III}(Cl) yields (TPP)Cr^{IV}(O). The formation of ((TPP)Cr^{IV})_2O rather than (TPP)Cr^V(O)(X) is due to the comproportionation reactions shown in eq 5a and 5b. In such cases the formation of Cr(IV) species may be followed spectrophotometrically. Thus, the rate constants for oxygen transfer to (TPP)Cr^{III}(Cl) can be determined in a one-turnover experiment. The second-order–rate constant of 0.433 M⁻¹ s⁻¹ for the oxidation of TBPH by (TPP)Cr^{IV}(O) (solvent CH_2Cl_2) reflects the difference in its reactivity and that of (⁺•TPP)Fe^{IV}(O) (solvent CH_3OH) where the rate of TBPH oxidation has been estimated to be >10⁶ M⁻¹ s⁻¹.[29] The difference in reactivity between the hypervalent Cr and Fe oxo intermediates is also apparent in the oxidation of TBPH by (TPP)Cr^{IV}(O) and (⁺•TPP)Fe^{IV}(O)(Cl) in methanol solvent. (TPP)Cr^{IV}(O) oxidized CH_3OH (1.09 × 10⁻³ M⁻¹ s⁻¹) in competition with TBPH oxidation whereas in oxygen transfer from percarboxylic acids to (TPP)Fe^{III}(Cl) the hypervalent iron–oxo porphyrin species is completely trapped at 10⁻³ M TBPH in CH_3OH. The large difference in rate constants for TBPH oxidation by (TPP)Cr^{IV}(O) and (⁺•TPP)Fe^{IV}(O) is at least partially explained by the smaller redox potential for the former.[27,30] Convincing evidence has been presented to indicate that TBPH is oxidized by (⁺•TPP)Fe^{IV}-(O)(Cl) via an outersphere electron-transfer mechanism.[1e] Perhaps the oxidations by (TPP)Cr^{IV}(O) may be innersphere reactions, possibly involving hydrogen atom abstraction.

Linear Free-Energy Relationships for the Transfer of Oxygen to Metalloporphyrins. The log of the second-order rate constants for nucleophilic attack by thioxane, *N,N*-dimethylbenzylamine, and iodide on a series of hydroperoxides and percarboxylic acids (YOOH) has previously been shown to be a linear function of the pK_a of the corresponding leaving groups (YOH).[31]

$$\log k_{YOOH} = -\beta_{lg}pK_{YOH} + C \quad (7)$$

Thus, for the heterolytic cleavage of the O–O bonds by nucleophilic displacement, percarboxylic acids and alkyl hydroperoxides follow the same linear free-energy relationship of $\Delta G^\ddagger$ versus ΔG° for proton ionization of the leaving group. Oxygen transfer from a percarboxylic acid or an alkyl hydroperoxide to a metalloporphyrin can also be formally viewed as a nucleophilic displacement, the rate of which is dependent both upon the metal and the oxygen donating species.

The log of the second-order rate constants for oxygen atom transfer (k_{YOOH}) from percarboxylic acids and alkyl hydroperoxides to (TPP)Cr^{III}(Cl) is correlated to the pK_a of YOH by a single linear free-energy relationship (eq 7; Figure 4) with β_{lg} equal to −0.34. There are a number of considerations that make this observation important. First, a common linear free-energy relationship is highly suggestive of a common mechanism for both percarboxylic acids and alkyl hydroperoxides. We show that heterolytic O–O bond cleavage is involved in the reaction of phenylperacetic acid with (TPP)Cr^{III}(Cl). Second, the value of β_{lg} is important, for its provides a means of assessing the extent of O–O bond cleavage in the transition state. The maximum value of β_{lg} for oxygen transfer is not known. The value of β_{lg} for oxygen transfer to (TPP)Mn^{III}(X) by percarboxylic acids has been determined as −1.27[32] while that for oxygen transfer by percarboxylic acid and hydroperoxides to I⁻, thioxane, and *N,N*-dimethyl-

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(30) Creager, S. E.; Murray, R. W. *Inorg. Chem.* **1985**, *24*, 3824.
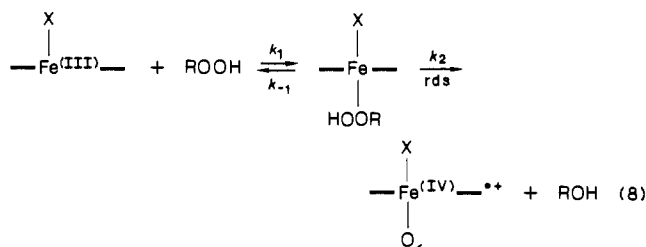(31) Bruice, T. C.; Noar, J. B.; Ball, S. S.; Venkataram, U. V. *J. Am. Chem. Soc.* **1983**, *105*, 2452.
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benzylamine is -0.6.[31] A β_{lg} value of -0.34 for (TPP)Cr^{III}(Cl) suggests an earlier transition state for this reaction compared to the other two. The third consideration is the relative unimportance of steric effects in the determination of k_{YOOH} (see Figure 4). A fourth consideration is that the log k_{YOOH} values determined with (TPP)Cr^{III}(X) may be used as a reference for oxygen transfer from YOOH species to other metalloporphyrins. In this fashion linear free-energy relationships may be created between log k_{YOOH} for a particular metal ligated to a particular porphyrin and log k_{YOOH} for the reactions with (TPP)Cr^{III}(Cl). Such relationships obviate the need to know the pK_a of YOH.
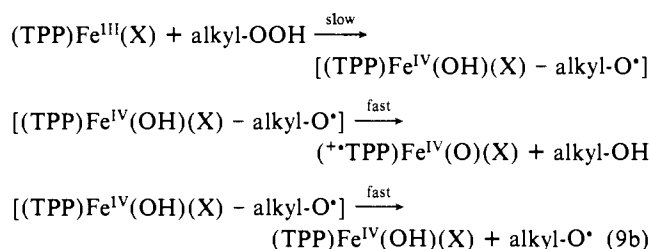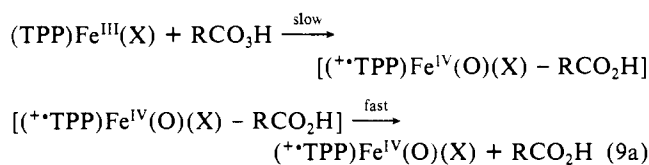
The linear free-energy plot of log k_{YOOH} versus pK_{YOH} for (TPP)Fe^{III}(Cl) (Figures 3) shows two linear regions which intersect. Plots of log k_{YOOH} for the (TPP)Fe^{III}(Cl) reactions versus log k_{YOOH} for the (TPP)Cr^{III}(Cl) reactions obviously show the same discontinuity. Thus, oxygen atom transfer reactions from percarboxylic acids and alkyl hydroperoxides to (TPP)Fe^{III}(Cl) are in marked contrast to the oxygen atom transfer reactions with the classical nucleophiles I$^-$, thioxane, and N,N-dimethylbenzylamine and with (TPP)Cr^{III}(Cl). With phenylperacetic acid the mechanism of oxygen transfer to an iron(III) porphyrin was shown to involve a heterolytic O–O bond scission.[1d] The values of β_{lg} for the percarboxylic acids are much the same for oxygen transfer to (TPP)Fe^{III}(Cl) and to (TPP)Cr^{III}(Cl) ($-\beta_{lg} = 0.34$). Heterolytic O–O bond scission has also been demonstrated in the reaction of phenylperacetic acid with (TPP)Mn^{III}(Cl),[32] (TPP)-Mn^{III}(ImH)(Cl),[32] and (TPP)Co^{III}(Cl).[4] As in the case with (TPP)Fe^{III}(Cl), breaks are seen in the plots of log k_{YOOH} versus pK_a of YOH [or if one prefers plots of log k_{YOOH} for a given metal(III) porphyrin versus log k_{YOOH} for (TPP)Cr^{III}(Cl) with (TPP)Co^{III}(Cl) and (TPP)Mn^{III}(ImH)(Cl)]. The pK_a of YOH where the break occurs is much the same with (TPP)Co^{III}(Cl) and (TPP)Fe^{III}(Cl); however, with (TPP)Mn^{III}(ImH)(Cl) the break occurs at a higher pK_a of YOH.

A break in a linear free-energy relationship may be associated with a change in the rate-limiting step of a two-step mechanism (eq 8) or a change in mechanism. We are unable to rationalize the break in the linear free-energy plot for (TPP)Fe^{III}(Cl) (and similarly for the linear free-energy plot with (TPP)Co^{III}(Cl)[10])

$$—Fe^{(III)}— \; + \; ROOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; \begin{array}{c} X \\ | \\ —Fe— \\ | \\ HOOR \end{array} \overset{k_2}{\underset{rds}{\longrightarrow}}$$

$$\begin{array}{c} X \\ | \\ —Fe^{(IV)}—^{\bullet +} \; + \; ROH \quad (8) \\ | \\ O \end{array}$$

by assuming a switch in the rate-limiting step from ligation to O–O bond breaking (eq 8). Thus, the β_{lg} values for both percarboxylic acids and the weakly acidic alkyl hydroperoxides are negative. If k_1 became rate-limiting instead of k_2, a positive value of β_{lg} would be expected, since increasing electron donation from the R group should increase k_1. An explanation for nonlinearity in the linear free-energy plot which involves oxygen transfer from ligated RCO$_3^-$ and alkyl-OOH would appear unlikely in that Groves and co-workers[26] offer evidence that it is the ligated RCO$_3$H species which transfers oxygen with concomitant O–O bond heterolysis. The decreased sensitivity of $\Delta G^\ddagger$ to the nature of the leaving group for oxygen transfer from the less acidic alkyl hydroperoxides to (TPP)Fe^{III}(Cl) can be explained if it is assumed that O–O bond breaking with RCO$_3$H is a single step heterolysis (eq 9) while with the less acidic alkyl-OOH compounds a homolytic reaction is rate-determining (eq 9b). The O–O bond strengths in alkyl hydroperoxides show only small variations as a function of the alkyl group, as opposed to the greater sensitivity of the pK_a for the corresponding alcohol.[33] The change in the oxygen-transfer mechanism observed is not only controlled by the nature of the metal ion moiety but also by the ligand. When employing (EDTA)Fe^{III}, no break in the linear free-energy plot

Scheme II

$$(TPP)Fe^{III}(X) \; + \; RCO_3H \; \xrightarrow{\text{slow}}$$
$$[(^{+\bullet}TPP)Fe^{IV}(O)(X) \; - \; RCO_2H]$$

$$[(^{+\bullet}TPP)Fe^{IV}(O)(X) \; - \; RCO_2H] \; \xrightarrow{\text{fast}}$$
$$(^{+\bullet}TPP)Fe^{IV}(O)(X) \; + \; RCO_2H \quad (9a)$$

$$(TPP)Fe^{III}(X) \; + \; \text{alkyl-OOH} \; \xrightarrow{\text{slow}}$$
$$[(TPP)Fe^{IV}(OH)(X) \; - \; \text{alkyl-O}^\bullet]$$

$$[(TPP)Fe^{IV}(OH)(X) \; - \; \text{alkyl-O}^\bullet] \; \xrightarrow{\text{fast}}$$
$$(^{+\bullet}TPP)Fe^{IV}(O)(X) \; + \; \text{alkyl-OH}$$

$$[(TPP)Fe^{IV}(OH)(X) \; - \; \text{alkyl-O}^\bullet] \; \xrightarrow{\text{fast}}$$
$$(TPP)Fe^{IV}(OH)(X) \; + \; \text{alkyl-O}^\bullet \quad (9b)$$

of log k_{YOOH} versus pK_a of YOH is observed.[34] Indeed a plot of the log of the rate constants with (EDTA)Fe^{III} versus log rate constants with (TPP)Cr^{III}(Cl) provides a straight line with slope ~ 1.0. The similarity of β_{lg} for the reaction of percarboxylic acids with (TPP)Fe^{III}(Cl) and (EDTA)Fe^{III} (solvent, methanol) and (TPP)Cr^{III}(Cl) (solvent, CH$_2$Cl$_2$) is interesting.

The hypervalent iron–oxo porphyrin species generated by using trityl hydroperoxide as an oxygen atom donor is only partially trapped by TBPH. Examination to see if the triphenylcarbinol product competes with TBPH as a trap for the iron–oxo intermediate demonstrated that added (to 0.10 M) triphenylcarbinol *is not* oxidized by the higher valent iron–oxo porphyrin intermediate at a rate sufficiently large to protect the porphyrin from oxidative destruction nor is triphenylcarbinol oxidized by TBP$^\bullet$. When trityl hydroperoxide and diphenylhydroperoxyacetonitrile are used as oxygen donors (YOOH) the major reaction products are (Ph)$_2$CO + PhOH + (Ph)$_3$COH and PhCO$_2$Me + (Ph)$_2$CO + PhOH, respectively. It is concluded that the leaving group species (YO$^\bullet$ or YOH) undergoes oxidation by hypervalent iron–oxo porphyrin species within a solvent caged pair formed on rate-determining oxygen atom transfer. The reaction sequences of Schemes III and IV are suggested. Rearrangements of the type depicted in Schemes III and IV are well-known for Ph$_3$O$^+$.[35] Since from the linear free-energy plots it would follow that diphenylhydroperoxyacetonitrile undergoes heterolytic O–O bond scission and trityl hydroperoxide initial homolytic O–O bond scission, Schemes III and IV have been constructed to reflect this difference in mechanism. It is true, however, that the nature of the oxidation products for these alkyl hydroperoxides does not confirm the mechanism of O–O bond scission. In the case of trityl hydroperoxide, identical products would be obtained if heterolysis was followed by oxidation of trityl alcohol inside the solvent cage.

Other data, besides our own, suggest that alkyl hydroperoxides react via a different mechanism with (TPP)Fe^{III}(Cl) than do percarboxylic acids. Coon has offered experimental results in support of homolytic O–O bond cleavage with cytochrome P-450.[36] A homolytic mechanism for oxygen transfer from t-BuOOH to (TPP)Mn^{III}(ImH)(Cl) is supported in a recent study by Suslick and Cooke, who report that manganese(III) porphyrins with sterically protected pockets are shape-selective hydroxylation catalysts when oxidation takes place at the metal center.[37] With iodosylbenzene, selectivity is observed for terminal hydroxylation with a number of alkanes. Employing t-BuOOH as the oxidant, a metal-initiated free radical reaction ensues with hydrocarbon

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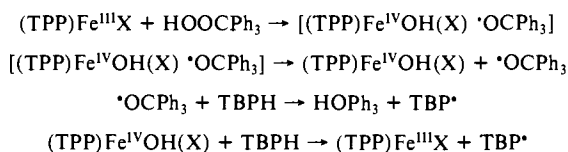
(35) (a) Bartlett, P. D.; Cotman, J. D. *J. Am. Chem. Soc.* **1950**, *72*, 3095. (b) Starnes, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 1807. (c) Gardner, H. W.; Weisleder, D.; Nelson, E. L. *J. Org. Chem.* **1984**, *49*, 508.

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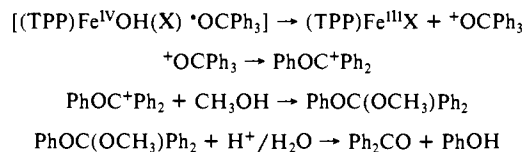
(37) Suslick, K. S.; Cook, B. R. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, NY; American Chemical Society: Washington, DC, 1986; INORG 249.

Scheme III

To provide TBP• and HOCPh$_3$:

(TPP)Fe^{III}X + HOOCPh$_3$ → [(TPP)Fe^{IV}OH(X) •OCPh$_3$]

[(TPP)Fe^{IV}OH(X) •OCPh$_3$] → (TPP)Fe^{IV}OH(X) + •OCPh$_3$

•OCPh$_3$ + TBPH → HOPh$_3$ + TBP•

(TPP)Fe^{IV}OH(X) + TBPH → (TPP)Fe^{III}X + TBP•

To provide PhOH and Ph$_2$CO:

[(TPP)Fe^{IV}OH(X) •OCPh$_3$] → (TPP)Fe^{III}X + $^+$OCPh$_3$

$^+$OCPh$_3$ → PhOC$^+$Ph$_2$

PhOC$^+$Ph$_2$ + CH$_3$OH → PhOC(OCH$_3$)Ph$_2$

PhOC(OCH$_3$)Ph$_2$ + H$^+$/H$_2$O → Ph$_2$CO + PhOH

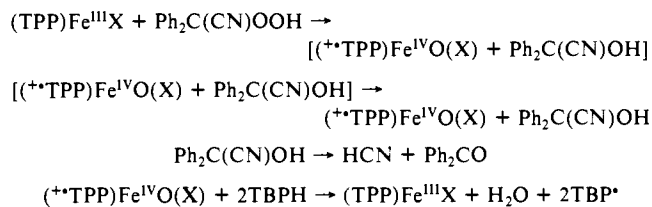oxidation occurring at a site remote from the metal center.

The Effects of Buffers on the Rates of Oxygen Transfer to (TPP)Fe^{III}(Cl). The oxidation of metalloporphyrin by per-carboxylic acids and alkyl hydroperoxides involves proton-transfer steps. With the peroxidases, an overall heterolytic mechanism has been established for oxygen transfer from both percarboxylic acids and alkyl hydroperoxides.[38] Distal ligation and proximal general-base catalysis by the imidazole moieties of histidine amino acids within the enzyme pocket has been invoked to explain the large differences in rate constant for oxygen transfer from alkyl hydroperoxides to the peroxidases versus simple model compounds.[1d,39] One must note, however, that X-ray determination of the structure of cytochrome P-450$_{cam}$ reveals that there is no basic group present that could act as a general base to assist oxygen loading by the "peroxide shunt" mechanism.[40]

Traylor and co-workers established that iron(III) hemins appropriately substituted by imidazole and carboxyl side chains exhibited enhanced reactivity and invoked intramolecular general-base catalysis.[1d] This group also introduced the use of the non-metal ligating 2,4,6-trimethylpyridine/2,4,6-trimethyl-pyridine·HCl as buffer in methanol solvent. Increases in rate with the increase in total buffer concentration was attributed to general catalysis of oxygen transfer from the YOOH species. In this study we have employed the same buffer system and have also observed buffer promoted oxygen transfer for both percarboxylic acids and hydroperoxides.
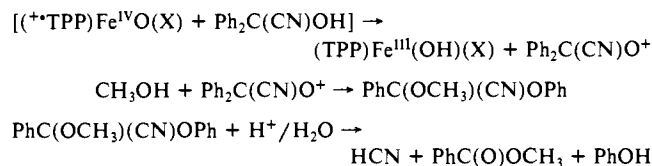
The means of promotion of the rates by 2,4,6-trimethylpyridine buffer cannot be considered to be defined from what is presently known. Thus, the influence of pH and change in the ratio of buffer base to buffer acid are not known. In organic solvents pH and the pK_a values of reactants and intermediates and the change in

Scheme IV

To provide TBP• and Ph$_2$CO:

(TPP)Fe^{III}X + Ph$_2$C(CN)OOH →
$\qquad$ [($^{+•}$TPP)Fe^{IV}O(X) + Ph$_2$C(CN)OH]

[($^{+•}$TPP)Fe^{IV}O(X) + Ph$_2$C(CN)OH] →
$\qquad$ ($^{+•}$TPP)Fe^{IV}O(X) + Ph$_2$C(CN)OH

Ph$_2$C(CN)OH → HCN + Ph$_2$CO

($^{+•}$TPP)Fe^{IV}O(X) + 2TBPH → (TPP)Fe^{III}X + H$_2$O + 2TBP•

To provide PhC(O)OCH$_3$ and PhOH:

[($^{+•}$TPP)Fe^{IV}O(X) + Ph$_2$C(CN)OH] →
$\qquad$ (TPP)Fe^{III}(OH)(X) + Ph$_2$C(CN)O$^+$

CH$_3$OH + Ph$_2$C(CN)O$^+$ → PhC(OCH$_3$)(CN)OPh

PhC(OCH$_3$)(CN)OPh + H$^+$/H$_2$O →
$\qquad$ HCN + PhC(O)OCH$_3$ + PhOH

pK_a with concentration are not known. Thus, an extension of studies directed to an understanding of the role of general catalysis should not involve organic solvents. Further investigations from this laboratory will be restricted to aqueous solutions wherein pH and μ may be accurately controlled and pK_a values understood. A start has been made in this direction using the water-soluble, nonaggregation, and non-μ-oxo-dimer forming hydrates of (5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-porphina-to)iron(III) [(1)Fe^{III}(OH$_2$) and (1)Fe^{III}(OH)] and manganese(III) [(1)Mn^{III}(OH$_2$) and (1)Mn^{III}(OH)]. With H$_2$O$_2$ as oxygen transfer agent, using the water-soluble iron(III) porphyrin, there is no catalysis by oxyanions nor their conjugate acids; however, 2,4,6-trimethylpyridine buffer acts as a catalyst at low pH. These results have been published and discussed.[1k] The reactions of H$_2$O$_2$ with the manganese(III) porphyrin[41] and t-BuOOH with the iron(III) porphyrin[42] show no catalysis, at any pH, with either oxyanion or amine bases nor their conjugate acids. These studies are being actively extended.

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