

limit, $\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2$ displays a ${}^1(\delta \rightarrow \delta^*)$ transition at $12\,500\text{ cm}^{-1}$, only 4700 cm^{-1} red shifted from that of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$. The sum of this red shift and the ${}^3(\delta\delta^*)$ energy of $\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2$, $\sim 5200\text{ cm}^{-1}$ (15 kcal/mol), which approximates the position of the ${}^3(\delta\delta^*)$ state of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ (Figure 3), is an experimental measure of the δ -bond component of the barrier to rotation about a quadruple bond.

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Registry No. $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$, 67619-17-4; $\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2$, 85115-86-2.

Mechanism of "Oxygen Atom" Transfer to (Tetraphenylporphinato)chromic Chloride

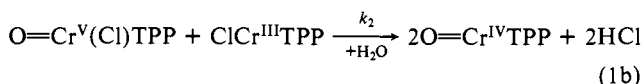
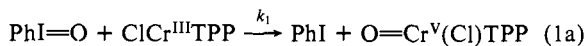
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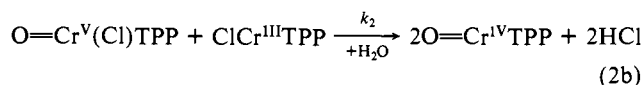
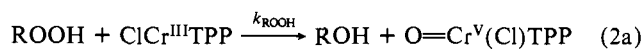
Herein are described results obtained in a study of the reaction of $\text{ClCr}^{\text{III}}\text{TPP}$ with a variety of oxygen-donor molecules. This investigation is an extension of studies of oxygen transfer from aniline *N*-oxides to (porphinato) $\text{Fe}^{\text{III}}\text{X}$ and (porphinato) $\text{Mn}^{\text{III}}\text{X}$ salts¹⁻³ and to cytochrome P-450 enzymes.⁴ The objectives of the present study are to ascertain the effect of donor structure on the ease and the mechanism of oxygen transfer.

The reaction of iodosylbenzene with $\text{ClCr}^{\text{III}}\text{TPP}$ is not well understood.⁵⁻⁸ In this study, the reaction of $\text{ClCr}^{\text{III}}\text{TPP}$ with PhIO was initiated (spectral grade dichloromethane, 25°C , N_2 atmosphere) by mixing various volumes of a freshly prepared solution saturated in PhIO with a solution of $\text{ClCr}^{\text{III}}\text{TPP}$ ($1 \times 10^{-5}\text{ M}$). As the ratio of $\text{PhIO}/\text{ClCr}^{\text{III}}\text{TPP}$, present at the time of mixing, was increased from 1 to 20 the Soret band of the product was found to shift from 429 ($\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$) to 415 nm ($\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$). Thus, at high concentrations of PhIO relative to $\text{ClCr}^{\text{III}}\text{TPP}$, there is obtained as product $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$. An investigation of the kinetics of the reaction was not attempted due to the known polymeric nature of PhIO etc.⁹ Nevertheless, it would appear that the logical explanation for these experimental results is found in eq 1. When the product $k_1[\text{PhIO}]$ is sufficiently



large, all $\text{ClCr}^{\text{III}}\text{TPP}$ is converted into $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$. At lower concentrations of PhIO the oxidant $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$ competes with PhIO for $\text{ClCr}^{\text{III}}\text{TPP}$ and a disproportionation reaction ensues to yield $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$. (Traces of moisture in the solvent were

sufficient to supply the water molecules for the disproportionation reaction.) Thus, $\text{ClCr}^{\text{III}}\text{TPP}$ may be used as a trap for $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$. The rapid trapping of the chromium(V) species by the chromium(III) species has allowed us to study oxygen transfer from percarboxylic acids and hydroperoxides to $\text{ClCr}^{\text{III}}\text{TPP}$ (eq 2).



The kinetics of the reactions of percarboxylic acids and hydroperoxides with $\text{ClCr}^{\text{III}}\text{TPP}$ were carried out in CH_2Cl_2 (25°C , N_2 atmosphere), under the pseudo-first-order conditions of $[\text{ROOH}] \gg [\text{ClCr}^{\text{III}}\text{TPP}]$. The reactions were monitored by observing the decrease in $\text{ClCr}^{\text{III}}\text{TPP}$ at 446 nm and were found to follow the first-order rate law to 6 to 7 half-lives. Plots of initial $[\text{ROOH}]$ vs. the determined pseudo-first-order rate constant (k_{obsd}) were linear. The slopes of such plots provided the second-order rate constants k_{ROOH} of eq 2a. In Figure 1 there is plotted the $\log k_{\text{ROOH}}$ values for the reaction of ROOH species with $\text{ClCr}^{\text{III}}\text{TPP}$ vs. the $\text{p}K_a$ of ROH. The lack of a break in the plot is in accord with consistency of mechanism for species of great monoxygen-donation potential (*m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$) and little oxygen-donation potential (*t*- BuOOH). That this mechanism involves RO-OH bond heterolysis follows from the recovery of >90% phenylacetic acid (as methyl ester with CH_2N_2) when ROOH is phenylperacetic acid. Homolysis would yield phenylacetoxyl radical which decarboxylates rapidly.¹¹

The log of the second-order rate constants (k_{Nuc}) for heterolytic-nucleophilic cleavage of the O-O bond of a series of hydroperoxides and percarboxylic acids $[\text{ROOH}]$ have previously been shown to be a linear function ($\beta_{\text{lg}} = -0.6$) of the $\text{p}K_a$ of the leaving groups (ROH) when the nucleophilic species are thioxane, *N,N*-dimethylbenzylamine, and I^- .¹⁰ The reaction of $\text{ClCr}^{\text{III}}\text{TPP}$ with ROOH follows the same linear free energy relationship with $\beta_{\text{lg}} = -0.34$. If one wishes to ignore the difference in solvent for nucleophilic attack by I^- , $:\text{N}^-$, $:\text{S}^-$ (*t*- BuOH) and by $\text{ClCr}^{\text{III}}\text{TPP}$ (CH_2Cl_2), though probably not wise, one would conclude that O-O bond cleavage has not proceeded as far in the transition state in the instance where the Cr^{III} moiety of $\text{ClCr}^{\text{III}}\text{TPP}$ is the nucleophile. With the percarboxylic acids the product is a mixture of porphinato Cr^{IV} and Cr^{V} species, whereas with all the hydroperoxides the λ_{max} of the Soret peak at t_∞ corresponds to the Cr^{IV} species. This result is as should be expected from the results with iodosylbenzene. As the $\text{p}K_a$ of ROH increases the ease of oxygen-oxygen bond breaking in RO-OH decreases as does the value $k_{\text{ROOH}}[\text{ROOH}]$ (eq 2a) and this allows the term $k_2[\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}]$ to compete for the $\text{ClCr}^{\text{III}}\text{TPP}$ species to yield $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$.

2-(Phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine (Oxa) has been employed in the epoxidation of alkenes¹² (60°C , CHCl_3) and on this basis would appear as a worthy agent to explore as an oxygen donor to metalloporphyrins. The kinetics of reaction of Oxa (1.9×10^{-2} to $1.9 \times 10^{-3}\text{ M}$) with $\text{ClCr}^{\text{III}}\text{TPP}$ ($1.3 \times 10^{-5}\text{ M}$) to provide $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$ were followed at 429 nm (CH_2Cl_2 , 20°C). Reactions were first order to at least 6 half-lives and plots of k_{obsd} vs. $[\text{Oxa}]$ were linear with slope $8.25\text{ M}^{-1}\text{ s}^{-1}$. The appearance of $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$ rather than $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$ as product is expected since the rate constant is but ~ 2 times greater than that for the reaction of triphenylmethyl hydrogen peroxide with $\text{ClCr}^{\text{III}}\text{TPP}$ (Figure 1).

Though *p*-cyano-*N,N*-dimethylaniline *N*-oxide (*p*- CNDMA-NO) is comparable to PhIO as an oxygen donor to $\text{ClFe}^{\text{III}}\text{TPP}$ in the epoxidation of alkenes,² it does not react with $\text{ClCr}^{\text{III}}\text{TPP}$ (25°C , CH_2Cl_2 solvent, N_2 atmosphere). With photoexcitation of the reaction mixture, *p*- CNDMA-NO does transfer an oxygen to yield $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$. The photoreaction is presumably associated

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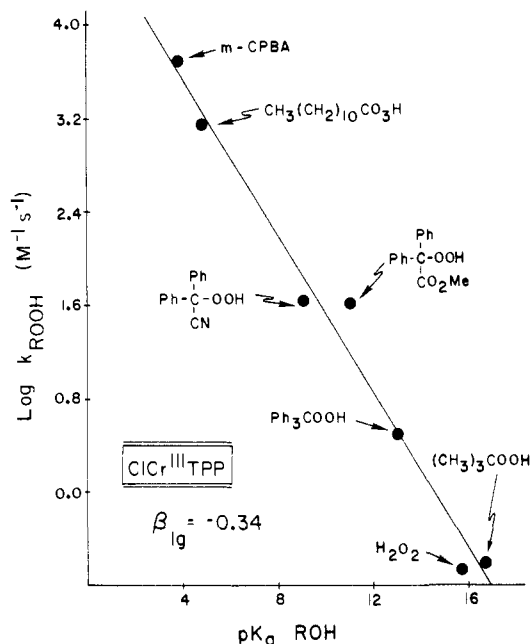


Figure 1. A plot of the log of the second-order rate constants for the reaction $\text{ClCr}^{\text{III}}\text{TPP}$ with percarboxylic acids and hydroperoxides (k_{ROOH}) vs. the pK_a of the carboxylic acid and alcohol leaving groups (see eq 2a).

with a high Φ . Thus, with diffuse room fluorescent lighting a solution containing $[\text{p-CNDMANO}] = 2.38 \times 10^{-3} \text{ M}$ and $[\text{ClCr}^{\text{III}}\text{TPP}] = 1.34 \times 10^{-5} \text{ M}$ provides $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$ in >95% yield in just a few minutes. The reactions of *p*-CNDMANO with chromium TPP species will be considered in greater detail in a full paper.

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Registry No. Oxa, 86428-23-1; *m*-CPBA, 937-14-4; *p*-CNDMANO, 62820-00-2; $\text{CH}_3(\text{CH}_2)_{10}\text{CO}_3\text{H}$, 2388-12-7; $\text{Ph}_2\text{C}(\text{CO}_2\text{Me})\text{OOH}$, 57272-44-3; $\text{Ph}_2\text{C}(\text{CN})\text{OOH}$, 5233-67-0; Ph_3COOH , 4198-93-0; $(\text{C}-\text{H}_3)_3\text{COOH}$, 75-91-2; H_2O_2 , 7722-84-1; (tetraphenylporphinato)chromic chloride, 28110-70-5; iodosylbenzene, 536-80-1.

Homolytic and Heterolytic Oxygen-Oxygen Bond Scissions Accompanying Oxygen Transfer to Iron(III) Porphyrins by Percarboxylic Acids and Hydroperoxides. A Mechanistic Criterion for Peroxidase and Cytochrome P-450

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The monooxygenase enzymes are of current interest to biochemists and pharmacologists, as well as to organic and inorganic chemists. The cytochrome P-450 enzymes have received most of the attention because of their key roles in metabolism, their inducibility by xenobiotics, and their ability to catalyze specific oxidation reactions that are not easily reproduced in purely chemical systems.^{1,2}

A variety of peracids and alkyl hydroperoxides have been used

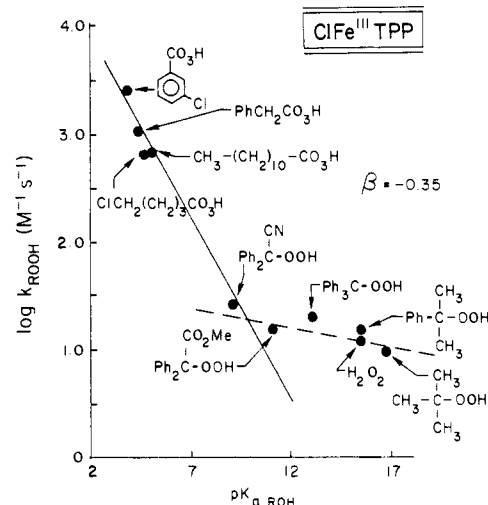
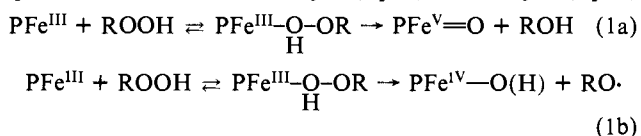


Figure 1. Plot of $\log k_{\text{ROOH}}$ vs. pK_a of corresponding ROH. The reactions were studied under an argon atmosphere in spectral grade methanol employing collidine buffer at pH 6.5 ($[\text{collidine}]/[\text{collidine}\cdot\text{HCl}] = 0.126$). k_{ROOH} was determined from the intercept of plots of k_{obsd} vs. $[\text{collidine}]$ at zero collidine buffer concentration. Values of k_{ROOH} so determined are in close agreement with rate constants determined in methanol without buffer present. $[\text{ClFe}^{\text{III}}\text{TPP}] = (0.15\text{--}1.5) \times 10^{-4} \text{ M}$; $[\text{TBPH}] = 0.1\text{--}0.3 \text{ M}$; $[\text{ROOH}] = (0.2\text{--}1.5) \times 10^{-2} \text{ M}$; $T = 30^\circ \text{C}$.

Table I. Second-Order Rate Constants for Oxygen Transfer to $\text{ClFe}^{\text{III}}\text{TPP}$ ($1.5 \times 10^{-4} \text{ M}$) by Non-Peroxidic Oxygen Donor Molecules (10^{-2} M) ($T = 30^\circ \text{C}$)

oxidant	$\text{M}^{-1} \text{ s}^{-1}$
iodosobenzenediacetate	$(3.2 \pm 0.1) \times 10^3$
<i>p</i> -cyano- <i>N,N</i> -dimethylaniline <i>N</i> -oxide	72 ± 3
2-(phenylsulfonyl)-3-(<i>p</i> -nitrophenyl)oxaziridine	$(7.5 \pm 0.1) \times 10^{-2}$

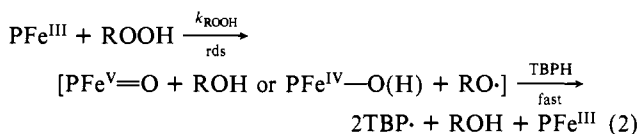
as oxygen donors to the ferric state of cytochrome P-450. The question as to whether heterolysis (eq 1a) or homolysis (eq 1b)



[P = porphyrin]

occurs in these reactions is of particular concern.³⁻¹³

We have attempted a comparative evaluation of the second-order rate constants for oxygen transfer to (tetraphenylporphyrin)iron chloride ($\text{ClFe}^{\text{III}}\text{TPP}$) from a series of peracids and hydroperoxides. An ideal method to study these reactions employs 2,4,6-*tert*-butylphenol (TBPH) to trap the reactive intermediate formed (eq 2) and has been offered by



Traylor et al.^{11,14} The reactions were shown to be first order in

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