

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 $\text{p}K_{\text{a}}$ 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

William A. Lee and Thomas C. Bruice*

Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106

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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

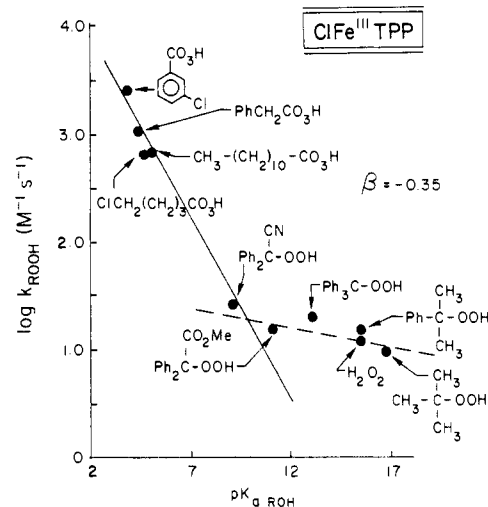
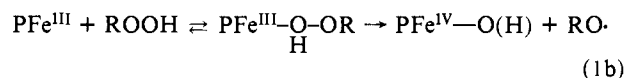
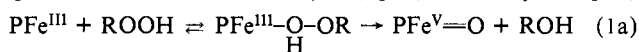


Figure 1. Plot of $\log k_{\text{ROOH}}$ vs. $\text{p}K_{\text{a}}$ of corresponding ROH. The reactions were studied under an argon atmosphere in spectral grade methanol employing collidine buffer at pH 6.5 ($[\text{collidine}]/[\text{collidine}\cdot\text{HCl}] = 0.126$). k_{ROOH} was determined from 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	$(7.5 \pm 0.1) \times 10^2$

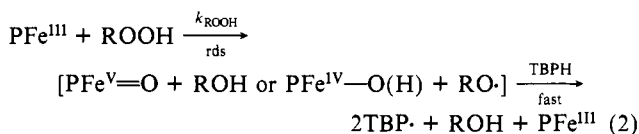
as oxygen donors to the ferric state of cytochrome P-450. The question as to whether heterolysis (eq 1a) or homolysis (eq 1b)



[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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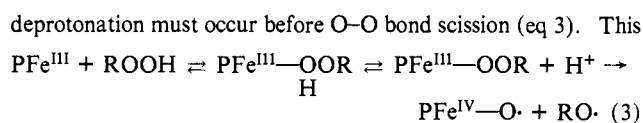
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ROOH and ClFe^{III}TPP by both initial rate and pseudo-first-order methods. In Figure 1, the log k_{ROOH} values are plotted against $\text{p}K_{\text{a}}$ for the corresponding leaving group (ROH). For comparative purposes, we also examined the oxygen-transfer rates of several other often used oxidants (Table I). Iodosobenzenediacetate reacts with a rate constant similar to the peracids while the rate of oxygen transfer from *p*-cyano-*N,N*-dimethylaniline *N*-oxide is 2X that of the most reactive hydroperoxide.

The slope of the linear free energy plot in Figure 1 shows a break at a $\text{p}K_{\text{a}}$ for ROH of 11. This behavior is highly suggestive of a change in mechanism or a change in rate-limiting step. In the transfer of an oxygen atom from ROOH to a tertiary amine, an alkyl sulfide, and iodide, plots of log k_{ROOH} vs. $\text{p}K_{\text{a}}$ (ROH) exhibited a negative slope with no break.¹⁵ Likewise, a negative slope with no break was observed in a plot of log k_{ROOH} vs. $\text{p}K_{\text{a}}$ (ROH) for oxygen transfer to (tetraphenylporphyrin)chromium chloride (ClCr^{III}TPP).¹⁶ Since the reactions of protohemin¹¹ and ClFe^{III}TPP with peracids have been shown to involve heterolytic O—O bond cleavage, we suggest that, for hydroperoxides with a $\text{p}K_{\text{a}} < 11$ for the corresponding leaving group (ROH), the mechanism of oxygen transfer to ClFe^{III}TPP involves a heterolytic cleavage of the O—O bond. For hydroperoxides of lower acidity, we propose the mechanism of oxygen transfer involves a homolytic cleavage of the O—O bond. We are unable to rationalize the data in Figure 1 by assuming a heterolytic mechanism and a change in rate-determining step.

The calculated slope (β_{1g}) for oxygen transfer to ClFe^{III}TPP via the proposed heterolytic cleavage of ROOH is -0.35. This is identical with the value obtained for oxygen atom transfer to ClCr^{III}TPP¹⁶ and may be compared to $\beta_{1g} = -0.6$ for oxygen atom transfer to thioxane, *N,N*-dimethylbenzylamine, and iodide.¹⁵ The less negative β_{1g} for heterolytic cleavage of ROOH by ClFe^{III}TPP and ClCr^{III}TPP as compared to the classical nucleophiles, :S<, :N<, and I⁻, can be loosely interpreted as an earlier transition state for the former. Interestingly, the absolute magnitude of the rate constants for oxygen transfer to ClFe^{III}TPP is greater than for the three classical nucleophiles studied earlier. This forces one to consider a "positively" charged iron(III) porphyrin a relatively strong nucleophile toward peroxide oxygen. The nucleophilicity of the iron center is conceivably due to the pairing of electrons in an axially oriented d orbital. The magnitude of the rate constant may be influenced by low-lying d orbitals capable of reducing electron-electron repulsion by forming a π bond in the transition state.¹⁷

As expected for homolytic cleavage of an O—O bond, the hydroperoxides of lowest acidity show small variations in k_{ROOH} with the $\text{p}K_{\text{a}}$ of ROH.¹⁸ We have also briefly examined the sensitivity of k_{ROOH} for *tert*-butyl hydroperoxide and diphenylhydroperoxyacetonitrile with ClFe^{III}TPP toward hydrogen ion activity in pure methanol. *tert*-Butyl hydroperoxide shows a large negative dependence on hydrogen ion concentration in the range 10⁻⁴ to 10⁻⁹ M (values were obtained by adding calculated amounts of NaOCH₃ or methanolic HCl). In contrast, k_{ROOH} for diphenylhydroperoxyacetonitrile exhibits the reverse hydrogen ion sensitivity in this concentration range. It appears that in the homolytic cleavage of a hydroperoxide bound to an iron porphyrin



differs significantly from the heterolytic mechanism where the proton must be transferred to the oxygen atom of the leaving group.¹¹

We feel our results help to clarify much of the controversy in the current literature concerning the reaction mechanism of simple iron(III) porphyrins with peracids and hydroperoxides. In examples where the mechanism of O—O bond cleavage differs from the prediction, additional catalysis could be invoked. The observed heterolysis of H₂O₂ by the peroxidases is a case in point.¹⁹ For cytochrome P-450, our results suggest that indeed both homolytic and heterolytic mechanisms can be operative depending on the structure of the oxidant.

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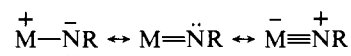
Electron-Transfer Reactions of Trivalent Uranium. Preparation and Structure of (MeC₅H₄)₃U=NPh and [(MeC₅H₄)₃U]₂[μ - η^1, η^2 -PhNCO]

John G. Brennan and Richard A. Andersen*[†]

Chemistry Department and Materials and Molecular Research Division of Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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In contrast to the large number of d-metal organoimides,¹



only one f-metal organoimide, Cp₃UNC(Me)C(H)PPh₂Me,^{2a} prepared by insertion of acetonitrile into Cp₃U(CH)PPh₂Me,^{2b} has been reported. The U—N distance of 2.06 (1) Å and the U—N—C angle of 163 (1)° suggest that the U—N bond order is between 2 and 3. Organoimides are of considerable interest relative to structure³ and reactivity studies⁴ and rational synthetic reactions need to be developed before the reaction chemistry can be explored systematically. Reaction of a trivalent uranium compound with either an organic azide or isocyanate to give a pentavalent uranium organoimide derivative with evolution of either nitrogen or carbon monoxide, respectively, is a rational and potentially general synthetic reaction for these interesting complexes.^{1,5} In this paper we describe the reaction of U-(C₅H₄Me)₃(THF) with organic azides to give U(C₅H₄Me)₃NR

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