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SELECTIVE AIR OXIDATION OF LIGHT ALKANES CATALYZED BY ACTIVATED METALLOPORPHYRINS - THE SEARCH FOR A SUPRABIOTIC SYSTEM

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SUMMARY

Halogenated metalloporphyrins have been examined as catalysts for the air oxidation of propane and isobutane at low temperature. Room temperature oxidation of isobutane with air gives > 13,000 turnovers with > 90% selectivity to tert-butyl alcohol.

INTRODUCTION

The catalytic conversion of alkanes directly to alcohols using molecular oxygen has become increasingly important as a means of converting these available and inexpensive hydrocarbons to valuable chemical and fuel products. Currently there exist no effective catalysts for the selective and efficient conversion of the light alkanes - methane, ethane, propane, and the butanes - *to alcohols* using air or oxygen as the sole reagent. Heterogeneous catalysts, normally employed at elevated temperatures, are able to effect the oxidation of alkanes with air or oxygen but promote deeper oxidation to products such as carboxylic acids or anhydrides [1,2]. Homogeneous catalysts have also proved to be ineffective and have led researchers to closely examine enzymatic systems which are capable of promoting the oxidation of light alkanes, including methane, at ambient temperature and pressure. For this reason, there has been a sizeable effort over the past twenty years aimed at elucidating the mechanism of these enzymatic systems, applying enzyme catalysis to hydrocarbon oxidation in vitro, and studying models of the enzymes with synthetic or biomimetic systems.

A number of biological systems including cytochrome P-450 and methane monooxygenase are able to convert alkanes to alcohols in vitro [3-9]. An increased understanding of the enzymes themselves together with the growing need for catalysts which can activate aliphatic C-H bonds for selective hydroxyla-

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tion has stimulated intense activity in attempting to mimic biological systems with synthetic or biomimetic analogs. In addition, this work has brought into focus the problems associated with enzymic systems in abiotic media. While these problems may find solutions in the future, currently, an acceptable catalyst will be one which effectively applies relevant aspects of biological systems while circumventing the problems.

Probably the most useful information derived from attempts to mimic enzymatic systems is the likelihood that high oxidation state iron intermediates are the active sites for alkane oxidation [10]. In the case of cytochrome P-450, an iron oxo complex has been implicated [6]. Many iron porphyrins have been examined as models for the active site of this enzyme with the addition of single oxygen atom transfer reagents such as iodosylbenzene or organic peroxides to form the iron-oxo active intermediate [11-17]. The high oxidation state iron-oxo complex presumably hydroxylates aliphatic hydrocarbon substrates to alcohols. It appears, therefore, that if one can generate these active species in situ, alkanes will be converted to alcohols.

Other biomimetic work concerned with the enzyme cytochrome P-450 has used molecular oxygen as the oxidant with sacrificial reductants to deliver the electrons normally supplied in the enzyme by NADH [18]. Biomimetic alkane hydroxylation using iron porphyrins with dioxygen has been practically ignored and has been unsuccessful even with the use of expensive co-reductants [19]. Herein lies the major problem with the biomimetic and biological catalyst systems for the commercial application of light alkane hydroxylation to alcohols for fuels and commodity chemicals. The stoichiometric addition of electrons and protons to an operating catalytic alkane oxidation is not economically viable for the production of fuel additives or commodity chemicals. Even the use of the least expensive source of two electrons and two protons, molecular hydrogen, is unacceptable economically. Therefore a useful industrial catalyst must avoid this requirement.

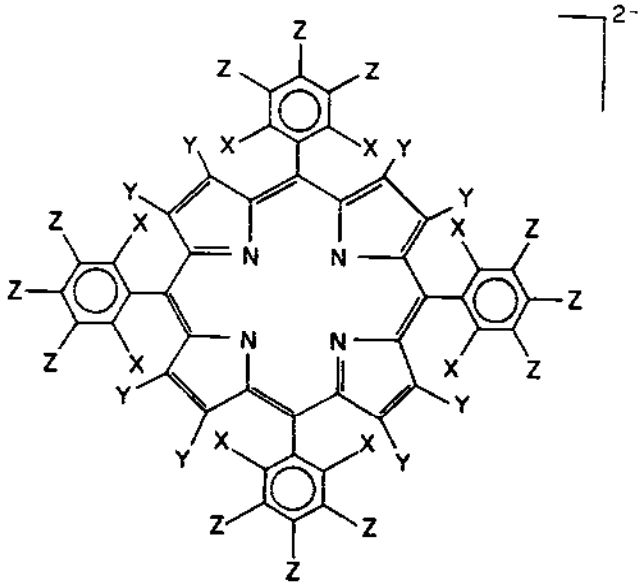
Another serious problem with biomimetic oxidation systems is their vulnerability to oxidative and thermal destruction. Although nature has the ability to replace and regenerate dysfunctioning proteins no such mechanism will be available in a commercial process based on an abiotic synthetic catalyst. Any major destruction of the ligand system would result in loss of both selectivity and reactivity.

Therefore a practical oxidation catalyst which employs an active metal oxo intermediate must have several features that are above and beyond the capability of biological and current biomimetic systems. First it must be able to generate the metal oxo species directly from molecular oxygen without the prohibitive requirement of a stoichiometric added co-reductant. Secondly, since no regeneration or repair mechanisms are possible, it must be resistant to catalytic deactivation both at the metal center and at the ligand system. A catalyst that meets these requirements could truly be called *suprabiotic*.

Such a *suprabiotic* catalyst might operate via metal oxo intermediates for converting alkanes to alcohols. We envision a new type of catalyst that realizes the following criteria:

a. It could generate metal oxo (X-M=O) from reaction of the metal center (X-M) with molecular oxygen ONLY. No co-reductant or external source of protons or electrons would be required.
b. Reaction with molecular oxygen should access the extraordinarily high metal oxidation states believed to be responsible for the high oxidation activity of biological systems (i.e., Fe(V)=O or Fe(IV)=O).
c. The metal oxo center should attract the alkane, promote facile C-H bond cleavage, but be resistant to oxidative self-destruction. The ligand system must be similarly resistant to oxidative degradation.
d. After converting the alkane to alcohol the center should expel the product from the coordination sphere and regenerate the metal center (X-M) for starting another catalytic cycle.

In this paper we will describe initial results with a catalyst system designed to address these requirements. Recent communications from our laboratory [20-23] have described a series of metalloporphyrin complexes that efficiently catalyze the oxidation of light alkanes with air or oxygen under mild conditions of temperature and pressure without the need for added co-reductants or oxygen atom transfer reagents. In this paper, we will specifically examine the effect of halogen substitution on the porphyrin skeleton and in the axial position of the metal upon the reactivity of these catalysts for alkane oxidation. We will report in this paper that, in general, the greater the extent of halogenation of the tetraphenylporphyrinato (TPP) ligand system, Figure 1, the greater is the catalytic activity of the complex for air-oxidation of alkanes.



LIGAND	X	Y	Z
(TPP)	8H	8H	12H
(TPPβ-Br_4)	8H	4H,4Br	12H
(TPPCl_8)	8Cl	8H	12H
(TPPCl_8β-Br_4)	8Cl	4H,4Br	12H
(TPPF_{20})	8F	8H	12F
(TPPF_{20}β-Br_8)	8F	8Br	12F

Fig. 1. Halogenated porphyrin ligand system for iron(III) oxidation catalysts.

EXPERIMENTAL

Iron(III)porphyrin azide and halide complexes were prepared by metathesis of the corresponding iron(III)porphyrin chloride or μ-oxo complex with the appropriate acid. HX (X = F, Cl, Br, N_3)(10% aqueous solution) in methylene chloride. Iron(III) porphyrin hydroxide complexes were prepared by treatment of the iron(III) porphyrin chloride with aqueous KOH in methylene chloride [24]. The μ-oxo complex, $[Fe(TPP,\beta\text{-}Br_4)]_2O$, was prepared using the method of Callot [25]. Preparation of $(TPPCl_8,\beta\text{-}Br_4)$ complexes was achieved by bromination of $Zn(TPPCl_8)$ with NBS [14] followed by iron insertion using the $FeCl_2$/DMF method [26]. $Fe(TPPF_{20},\beta\text{-}Br_8)Cl$ was prepared by the direct reaction of $Fe(TPPF_{20})Cl$ with 6 M Br_2 in carbon tetrachloride at reflux.

Oxidations were carried out in a barricaded laboratory equipped for experimentation at high pressure since many reactions were conducted within the explosion limits. Reactions reported in Table 1 were carried out in 50 cc Fisher-Porter glass aerosol tubes with magnetic stirring. Reactions reported in Tables 2 and 3 were conducted in a glass lined stirred autoclave with Teflon coated internals (impeller, dip-tube, etc.). Gas and liquid products were analyzed by a combination of standardized gc, ms, and gcms analyses.

In-situ absorption spectroscopy was performed using a Guided Wave Model 200 spectrometer equipped with an optical transmission wand probe which is inserted into the bottom of a stirred autoclave, using high pressure fittings and is fixed 1 cm below the impeller blades.

RESULTS AND DISCUSSION

Table 1 shows that replacement of four of the β- (pyrrolic) hydrogen atoms with bromine substituents in $Fe(TPP\beta\text{-}Br_4)Cl$ increases the catalytic activity of these porphyrinato complexes toward hydroxylation of isobutane. Replacement of the eight ortho-hydrogens of the meso-phenyl groups with chloro substituents in $Fe(TPPCl_8)Cl$ gives complexes with even greater activity. If four of the β-hydrogens in the octachlorotetraphenylporphyrin are replaced with bromine atoms in $Fe(TPPCl_8,\beta\text{-}Br_4)Cl$ activity is enhanced still further. The complex in which all twenty hydrogens in the meso-phenyl groups have been replaced by fluorine atoms, $Fe(TPPF_{20})Cl$, has even higher activity. Furthermore, the complex, $Fe(TPPF_{20},\beta\text{-}Br_8)Cl$, in which all twenty-eight of the C-H bonds have been halogenated has the highest activity of this series sustaining the high selectivity to the alcohol.

TABLE 1

EFFECT OF RING HALOGENATION ON THE ISOBUTANE OXIDATION ACTIVITY OF PORPHYRINATO IRON (III) COMPLEXES[a]

Catalyst	mmoles	O_2 Uptake, mmoles	TON[b]	Selectivity[c] To TBA, %
Fe(TPP)Cl	0.025	0.0	0	-
Fe(TPPβ-Br_4)Cl	0.013	2.0	155	-
Fe(TPPCl_8)Cl	0.019	5.0	260	89
Fe(TPPCl_8,β-Br_4)Cl	0.020	17.3	865	83
Fe(TPPF_{20})Cl	0.016	32.6	2040	90
Fe(TPPF_{20},β-Br_8)Cl	0.013	40.2	3090	89
Fe(TPP)N_3	0.013	1.7	130	92
Fe(TPPβ-Br_4)N_3	0.013	2.3	180	-
Fe(TPPCl_8)N_3	0.023	15.0	650	80
Fe(TPPCl_8,β-Br_4)N_3	0.023	21.5	930	82
Fe(TPPF_{20})N_3	0.016	33.0	2060	89
[Fe(TPP)]$_2$O	0.019	0	0	-
[Fe(TPPβ-Br_4)]$_2$O	0.013	0	0	-
Fe(TPPCl_8)OH	0.013	9.2	710	83
[Fe(TPPF_{20})]$_2$O	0.013	24.0	1,850	84
Fe(TPPF_{20})OH	0.013	29.2	2,245	82

[a] A solution of the catalyst in 25 ml benzene containing 6 grams of isobutane was stirred at 80°C under 100 psig of O_2 for 6 hours.

[b] moles O_2 consumed/mole catalyst used.

[c] (moles t-butyl alcohol produced/total moles liquid product) x 100

Table 2 shows the very same trend for propane oxidation, however, since the less reactive secondary C-H bonds put a more severe demand on catalytic activity, many complexes with low activity for isobutane oxidation are not catalysts for propane oxidation under mild conditions.

When the complexes: Fe(TPPF$_{20}$)X (X = F, Cl, Br) were used as catalysts for isobutane oxidation at 80°C, 1700-1900 moles of oxygen were consumed per mole catalyst used in six hours. Catalyst turnovers using the same three halides for propane oxidation at 125°C varied from about 400-600 moles of product per mole catalyst in 4.5 hours. In fact, there was little difference between the activities of the Fe(TPPF$_{20}$) halides and the azido, μ-oxo or hydroxo complexes suggesting that Fe(TPPF$_{20}$) complexes with any of these axial anions might all go through a common intermediate in the catalytic cycle. A characteristic which

TABLE 2

EFFECT OF RING HALOGENATION ON THE PROPANE OXIDATION ACTIVITY OF PORPHYRINATO IRON (III) COMPLEXES[a]

Catalyst	mmoles	T, Hrs.	TON[b]	IPA/Acetone
Fe(TPP)Cl	0.023	3	2	na
Fe(TPPβ-Br$_4$)Cl	0.023	3	0	-
Fe(TPPCl$_8$)Cl	0.023	6	0	-
Fe(TPPCl$_8$,β-Br$_4$)Cl	0.023	3	125	1.0
Fe(TPPF$_{20}$)Cl	0.023	3	230	0.8
Fe(TPPF$_{20}$,β-Br$_8$)Cl	0.023	4.5	420	0.7
Fe(TPP)N$_3$	0.023	3	0	-
Fe(TPPβ-Br$_4$)N$_3$	0.023	3	0	-
Fe(TPPCl$_8$)N$_3$	0.023	4.5	0	-
Fe(TPPCl$_8$,β-Br$_4$)N$_3$	0.023	4.5	250	0.8
Fe(TPPF$_{20}$)N$_3$	0.023	3	330	0.8
Fe(TPPF$_{20}$,β-Br$_8$)N$_3$	0.013	4.5	540	0.9
[Fe(TPP)]$_2$O	0.023	3	0	-
[Fe(TPPβ-Br$_4$)]$_2$O	0.023	4.5	0	-
Fe(TPPCl$_8$)OH	0.023	4.5	0	-
[Fe(TPPF$_{20}$)]$_2$O	0.013	3	440	0.8
Fe(TPPF$_{20}$)OH	0.013	3	270	0.6

[a] Stirred a solution of the catalyst in 60 grams of propane in 48 ml benzene at 125°C under 1000 psig air.

[b] moles (isopropyl alcohol + acetone) formed/mole catalyst used.

appears to differentiate porphyrinatoiron(III)-catalyzed reactions of alkanes with molecular oxygen from classical radical-initiated autoxidation is that most of these reactions exhibit no apparent induction periods.

Table 3 shows that reactions of isobutane with molecular oxygen catalyzed by $Fe(TPPF_{20})OH$ proceed far faster in the absence of benzene as a solvent. Reactions carried out in neat isobutane produce more than 11,000 turnovers to tert-butyl alcohol in three hours at 80°C. Perhaps even more surprising is the fact that isobutane can be hydroxylated with dilute air at room temperature to give over 12,000 turnovers producing tert-butyl alcohol in 95% selectivity. The final entry in Table 3 shows that the perhalogenated iron porphyrin, $Fe(TPPF_{20},\beta\text{-}Br_8)Cl$ gives unprecedented room temperature productivity under the same conditions. Over 22% conversion of neat isobutane occurred in about 70 hours. (This corresponds to over 13,000 turnovers or greater than 190 moles of product per mole of catalyst per hour.) Thus the perhalogenated iron porphyrin is more than twice as active as the $Fe(TPPF_{20})OH$ for room temperature hydroxylation of isobutane.

Other workers [12-14] have shown that electron withdrawal from the porphyrin ring via halogenation enhances the rate of alkane hydroxylation using iodosylbenzene as the primary oxidant. Our results using molecular oxygen as the oxidant and halogenated porphyrinato iron complexes as catalysts show a similar trend in activity. In the iodosylbenzene work iron oxo or ferryl complexes have been implicated as the active intermediate [27]. Two reasons were suggested for the increase in catalyst activity with porphyrin halogenation. First it was argued [13] that electron-withdrawing halogen substituents may activate the ferryl intermediate and increase its reactivity toward the hydrocarbon. Secondly, by removing electron density from the ring, the halogens were thought to make the porphyrin less susceptible to electrophilic attack by the ferryl species leading to destruction of the catalyst.

Since we observe the same effects of halogenation it is tempting to speculate on the possible intermediacy of a high oxidation state iron oxo in the reactions of alkanes with molecular oxygen. Figure 2 shows a possible way in which a high oxidation state iron oxo complex might be generated by reaction with molecular oxygen and how it could participate in the catalytic oxidation of light alkanes.

TABLE 3
IRON PORPHYRIN CATALYZED ISOBUTANE OXIDATIONS[a]

Catalyst (mmole)	T,°C	t, Hrs.	Reactor Charge, mmoles $i\text{-}C_4H_{10}$	O_2	BzH(ml)	Liquid Reaction Products, mmoles TBA	Acetone	Conversion $i\text{-}C_4H_{10}$, %	Selectivity TBA,%	TON[b]
$Fe(TPPF_{20})OH$ (0.06)	80	3	1042	35	80	164	27.8	18	85	3,195
	80	3	1046	52	80	173	29.8	19	85	3,385
	80	3	1051	56	80	180	41.9	21	81	3,695
	80	3	1034	102	80	146	35.9	17	80	3,040
	80	3	1041	212	80	123	26.7	14	82	2,495
	80	3	1243	56	60	190	28.4	17	86	3,640
	80	3	1458	53	40	238	32.0	18	88	4,510
	80	3	1660	53	20	262	30.0	17	89	4,880
	80	3	1872	53	0	376	58.1	23	86	7,230
(0.03)	80	3	1869	53	0	310	45.7	17	87	11,330
(0.03)	25	143	1871	53	0	332	16.7	18	95	12,150
$Fe(TPPF_{20}Br_8)Cl$ (0.03)	25	71.5	1862	53	0	372	34.6	22	92	13,560

a Isobutane was oxidized by an oxygen-containing gas mixture (75 atm, diluent = N_2) in the liquid phase (180 ml). Oxygen added as consumed.

b moles (TBA + Acetone)/mole Catalyst used.

The postulated mechanism in Figure 2 is dependent upon a μ-oxo diiron(III) species which disproportionates in equilibrium with Fe(II) and a Fe(IV) oxo. Halogenation could shift the position of equilibrium away from the μ-oxo diiron(III) species in favor of a low oxidation state iron(II) complex and a high oxidation state iron(IV) ferryl complex. Both steric and electronic factors could destabilize the diiron μ-oxo complex toward disproportionation. It appears from

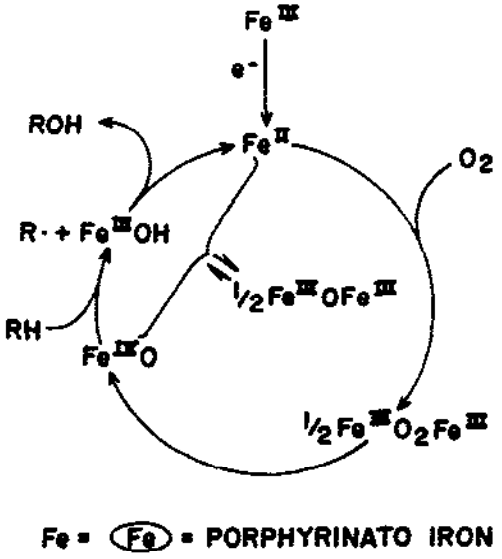


Fig. 2. Possible catalytic reaction pathway for alkane oxidations catalyzed by halogenated iron(III) porphyrins.

single crystal x-ray structural determinations [31-32], that $(FeTPPF_{20})_2O$ is relieved from the strain induced by the C-F bonds by making the Fe-O-Fe bond closer to 180° [178.4° vs. 174.5° in $(FeTPP)_2O$] and by moving the iron atoms further out of the porphyrin plane [0.673(2)Å vs. 0.50(1)Å in $(FeTPP)_2O$]. Larger halogens such as Cl or Br in the *ortho* position of the phenyl groups have prevented the synthesis of the μ-oxo diiron(III) species entirely. Electron withdrawal from the porphyrinato ligand should make it more difficult for oxidation of the ligand by electron transfer to the iron center. Thus, perhaps an iron(IV) ferryl species generated from symmetrical cleavage of a μ-peroxo dimer [30] of a halogenated tetraphenylporphyrin could survive and be effective in alkane hydroxylation. The reductant, which initially converts Fe(III), need only be present in small amounts, and might either be an adventitious impurity or, perhaps, the alkane itself. Electrochemical studies which will be reported elsewhere [31] have shown that halogenation of the porphyrin greatly increases the reduction potential of the $Fe^{+3/+2}$ couple [Fe(III) + e^- → Fe(II)].

In-situ absorption spectroscopy has enabled us to examine metalloporphyrin catalyzed hydroxylation under reaction conditions. Figure 3 shows the spectra from a $Fe(TPPF_{20})Cl$-catalyzed reaction of isobutane with air producing t-butyl alcohol. When 500 psig of air is pressed on 20 g. of isobutane in 80 g. of benzene containing 0.01 mmole of $Fe(TPPF_{20})Cl$ at room temperature, the 415 nm absorption normal for the hemin diminishes and new peaks at 396 and 443 nm arise. The 443 nm peak, which persists throughout the entire 3 hours of reaction, is similar to the Fe(II) spectrum reported by Suslick, et. al. [32] during the photoreduction of Fe(III)(TPP)Cl. The 396 and 559 nm bands are those that are expected for the μ-oxo di-iron species. After the experiment intact μ-oxo di-iron complex, $Fe(TPPF_{20})_2O$, can be recovered from solution.

CONCLUSIONS

Halogenation of porphyrinato iron(III) complexes produces highly active catalysts for the air-oxidation of light alkanes under mild conditions in a selective manner without the need for costly co-reductants or oxygen-atom transfer agents. The greater the extent of porphyrin halogenation the greater is both the catalyst life and activity. Similarities between the behavior of these halogenated porphyrin

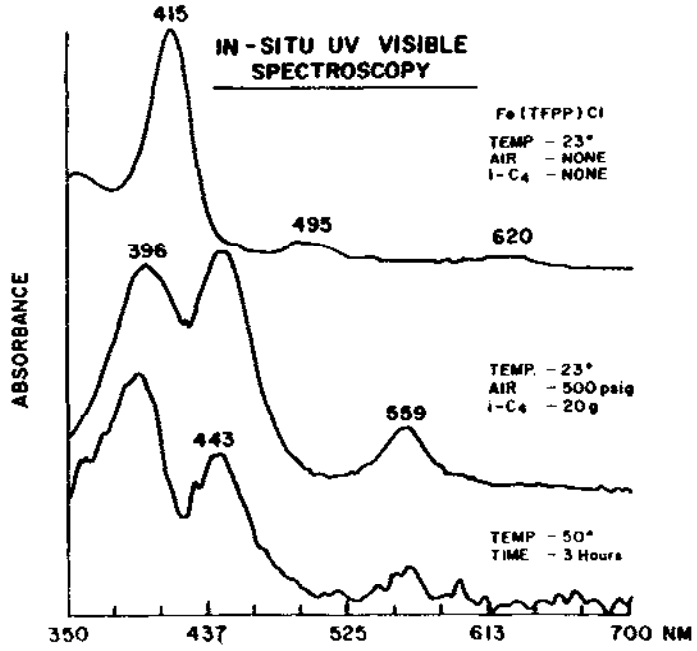


Fig. 3. In-situ absorption spectra under oxidation conditions.

complexes and known biomimetic catalyst systems suggest that they may have some mechanistic features in common. Spectroscopic and electrochemical studies are consistent with a reaction pathway which involves activation of dioxygen by formation of oxo- and peroxo- bridged iron porphyrin binuclear species.

Future work will include the preparation of more active iron centers in increasingly more stable macrocyclic ligand environments for use as catalysts for the low temperature selective air-oxidation of alkanes.

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