**Catalytic Conversion of Light Alkanes
Phase I**

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**Topical Report
January 1990 - January 1993**

Work Performed Under Contract No.: DE-FC21-90MC26029

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ACKNOWLEDGEMENTS

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ABSTRACT

The Topical Report on Phase I of the project entitled, Catalytic Conversion of Light Alkanes reviews the work done between January 1, 1990 and September 30, 1992 on the Cooperative Agreement. The mission of this work is to devise a new catalyst which can be used in a simple economic process to convert the light alkanes in natural gas to oxygenate products which can either be used as clean-burning, high octane liquid fuels, as fuel components or as precursors to liquid hydrocarbon transportation fuel.

This Topical Report documents our efforts to design, prepare, characterize and test novel catalysts for the mild selective reaction of light hydrocarbons with air or oxygen to produce alcohols directly. These catalysts are designed to form active metal oxo (MO) species and to be uniquely active for the homolytic cleavage of the carbon-hydrogen bonds in light alkanes producing intermediates which can form alcohols. Research on the Cooperative Agreement is divided into three Phases relating to three molecular environments for the active catalytic species that we are trying to generate. In this report we present our work on catalysts which have oxidation-active metals in electron-deficient porphyrinic macrocycles (PHASE I).

SUMMARY OF PHASE I - RESULTS TO DATE AND STATUS

We have conceived and reduced to practice new catalytic principles which have encouraged us to design and to synthesize a new family of catalysts that are effective in the conversion of light alkanes to alcohols or other oxygenates. Until now, the chemical reactions needed to produce the desired oxygenates from alkanes could only be accomplished selectively by specialized enzymatic systems operating *in vivo*. These systems are impractical for commercial fuel production. Aided by computer-assisted molecular design techniques we have created a family of synthetic catalysts which may operate based on fundamental principles similar to those employed by the biological systems. Our new catalysts, however, can be synthesized in the laboratory from inexpensive raw materials.

In each of the first two years of the Cooperative Agreement we synthesized, tested, patented and examined a new electron-deficient porphyrinic macrocycle in detail and many others in a less comprehensive manner. From considering both the electronic and the molecular structure together with the chemical and catalytic activity of metal complexes of the series $M(TPPF_{20})X$, $M(TPPF_{20}\beta-Cl_8)X$ and $M(TPPF_{20}\beta-Br_8)X$; $M = Fe, Mn, Cr, Co, Cu, Ru$; $X = F, Cl, Br, N_3, O, OH$ we have established a structure-activity correlation which has enabled us to design and begin the synthesis of superior macrocyclic ligand systems. As we have pointed out in past reports, the iron complexes were far and away the best catalysts for light alkane oxidations using molecular oxygen as oxidant. Although these complexes are by far the most active low-temperature liquid phase alkane oxidation catalysts known, we have determined that an increase in activity is still needed to meet the criteria which we have determined for commercial applications. Increased rate can be obtained in many ways including: more electron withdrawal from the macrocycle, better design of molecular (steric) structure; and smaller substituent groups which confer lower molecular weight and a lower per pound cost. Thus, in the third year of the Cooperative Agreement we have embarked on a catalyst synthesis program directed toward complexes which are more active, lower molecular weight and cheaper to make. Included in the new series of complexes which are being constructed are those in which the bulky perhalophenyl groups are being replaced by the even more electron-withdrawing cyano, fluoro, trifluoromethyl, nitro, chloro groups and others. Testing of the first members of this new set of complexes has begun and is showing significant progress. Active catalysts have been synthesized that have nitro groups in the four meso-positions of an iron porphine complex. We expect the new generation of Phase I catalysts to arise from this class of metal complexes.

Large numbers of metal complexes were prepared during the course of this work. Recitation of all of the synthetic details of these preparations would make this report unwieldy. For this reason the reader is referred to the original quarterly reports for this information.

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1.0 INTRODUCTION

We have found a family of new catalytic materials which, if successfully developed, will be effective in the conversion of light alkanes to alcohols or other oxygenates. Catalysts of this type have the potential to convert natural gas to clean-burning high octane liquid fuels directly without requiring the energy-intensive steam reforming step. In addition they also have the potential to upgrade light hydrocarbons found in natural gas to a variety of high value fuel and chemical products. In order for commercially useful processes to be developed, increases in catalytic life, reaction rate and selectivity are required. Recent progress in the experimental program geared to the further improvement of these catalysts is outlined in Sections 5 and 6.

2.0 PURPOSE

The mission of the work presented in this quarterly report is to generate novel catalytic technology which will permit the development of a simple, efficient and economical process for the direct conversion of natural gas to liquid transportation fuels. This process should be simple enough to liquify natural gas economically even at a remote reservoir site. It is a further mission of this work to find new routes from natural gas or its components to high value oxygenates by direct air-oxidation using these new catalysts.

The technical objective of the research is to design the first effective molecular catalyst for the direct air-oxidation of the hydrocarbons found in natural gas to an alcohol-rich oxidate which can either be used directly or converted into gasoline via known technology. The development of an efficient catalyst for the smooth and selective oxidation of light alkanes to alcohols will not only provide a solution to the problem of liquifying natural gas, but will create new opportunities to utilize the relatively inexpensive and abundant light alkanes for the production of a variety of valuable fuel and chemical products. Processes for converting natural gas or its components (methane, ethane, propane, and the butanes) to alcohols for use as motor fuels, fuel additives or fuel precursors will not only add a valuable alternative to crude oil but will produce a clean-burning, high octane alternative to conventional gasoline.

3.0 BACKGROUND

As petroleum reserves dwindle, all hydrocarbon raw materials which could be converted to usable liquid fuels become more dear. Often the search for oil yields extensive gas reservoirs. Gas availability on a worldwide scale rivals that of crude oil but problems of transportation and differences in end use application often limit its' utility. Most natural gas is found in areas remote to its ultimate use. Currently much of this remote gas is associated with petroleum production. Because it cannot be used at the location where it is produced, it is often flared on a large scale, representing not only a wasted energy resource but also contributing to global warming as a result of carbon dioxide production. Because of its low energy density, methane is relatively costly to transport. Figure 3-1 shows the relative differences between the costs of transporting various liquid and gaseous fuels(1). It is readily seen that the conversion of methane to a liquid fuel such as methanol or a hydrocarbon liquid would both drastically cut the cost of transport over long distances, and provide an alternative fuel liquid from an abundant, under-utilized resource.

Catalytic alkane conversion science is maturing to the point that one can envision the economically attractive conversion of natural gas to liquid fuels on a commercial scale by the turn of the century. This situation has many international and national implications. Remote accumulations of low value gas such as exist on the North slope of Alaska and various off-shore sites could be exploited. Value could be maximized for domestic gas reserves in high value-added products. The National interests would be well served if the U.S. held the technological lead in gas conversion technology and could influence the course of gas conversion abroad. One of the most costly steps in the current technology for converting natural gas to liquid fuels is the energy-intensive steam reforming step. The products of steam reforming are catalytically converted to methanol which has value as an alternative liquid fuel product or which could be converted to gasoline via existing technology.

FIGURE 3-1

Fig. 3.1 Relative cost of transport of liquid and gaseous fuels
(LNG = Liquefied Natural Gas)

We have uncovered a new catalytic approach to the direct production of a methanol-rich oxidate from natural gas which avoids costly steam reforming completely. Work conducted in Sun laboratories under the joint sponsorship of the Department of Energy (METC), the Gas Research Institute, and the Sun Company, Inc., has produced a family of new catalytic materials which, if successfully developed, will be effective in the conversion of light alkanes to alcohols or other oxygenates. We have found that it is possible to catalytically convert methane, and the C_2 - C_4 hydrocarbons that are present in smaller but significant amounts in natural gas, to alcohols by direct reaction with air or oxygen. In particular, we have found that the C_4 component of natural gas can be catalytically converted to fuel oxygenates in excellent yield, and significant progress has been made in converting the C_3 component to an oxygenate product without combusting the hydrocarbon substantially. The C_1 and C_2 components can also be converted to alcohol-rich oxygenates but more progress is still required before a practical catalytic route becomes possible.

At the outset of this work we envisioned converting natural gas to an alcohol-rich oxidate which could subsequently be converted to hydrocarbon gasoline via MTG technology. During the period of this research, however, the benefits of oxygenates as clean-burning, high octane, liquid fuel materials has become apparent. Alcohols and the ethers that can be made from them are the oxygenates that are used to replace aromatics, reduce toxicity and reduce ozone and carbon monoxide in the reformulated gasolines of the 90's. As a result it is more reasonable to consider the direct air-oxidation of light alkanes to produce alcohol-rich oxidates for use as components of reformulated gasoline or as liquid fuel alternatives to gasoline in areas where there is non-attainment of CO or ozone limits set forward by the Clean Air Act. Alcohols of the type that can be formed directly from natural gas components: methanol, ethanol and tert-butyl alcohol, TBA, are not only useful as liquid fuel components themselves but are used in the manufacture of ether oxygenates such as MTBE, TAME, and ETBE as well. Table 3-1 shows some of the fuel-related properties of the C_1 - C_4 alcohols and the ethers that can be made from them. It can be seen that these materials have desirable fuel properties in addition to meeting the fuel oxygen-content requirements of the Clean Air Act.

- 5 -
TABLE 3-1

PROPERTIES OF ETHERS AND ALCOHOLS

<u>PROPERTY</u>	<u>MTBE</u>	<u>ETBE</u>	<u>GTBA</u>	<u>IPA</u>	<u>ETOH</u>	<u>MeOH</u>
Oxygen, wt %	18.2	15.7	21.6	26.6	34	49.9
Sp. Gravity	0.74	0.74	0.791	0.789	0.79	0.796
Boiling Point, °F	131	163	181	180	172	149
RVP (lbs/in ²)	7.8	2.5	1.8	1.8	2.3	4.6
Blending RVP	9	5	12	14	23	75
RON BV	110-122	117-121	~103	113-119	~122	126
MON BV	98-102	100-105	~91	95-101	~96	104
(R+M)/2 BV	103-110	~110	~97	104-110	~100	115

As desirable as it is to convert light alkanes directly to alcohols, doing this in an efficient manner using existing technology is a major problem. The light alkanes: methane, ethane, propane and the butanes, are among the most unreactive of organic substrates. They are also among the most abundant and inexpensive raw materials. They are found not only in natural gas, but in light petroleum fractions, and are being generated in ever-increasing quantities in petroleum refineries due to the increasing severity of catalytic cracking of heavier crudes. There exist few commercial processes for the efficient upgrading of these substrates to high value products and no DIRECT catalytic functionalization of these substrates to produce chemical or fuel alcohols.

During a six-year period in which Sun has invested over six million dollars in research support, coupled with an ongoing program sponsored jointly by Sun, the DOE and GRI, we have formulated and demonstrated a novel catalyst concept which allows the low temperature liquid or vapor phase catalytic conversion of light alkanes, (C_1-C_4), to their respective alcohols or ketones. This concept grew out of an understanding of biomimetic systems, together with new inorganic and catalytic chemistry. It is known that high oxidation state metal oxo ($M=O$) complexes will react with alkanes to give alcohols under mild conditions. Iron oxo ($Fe=O$) intermediates are, no doubt, involved in the enzymatic hydroxylation of C-H bonds in vivo (Cytochrome P-450). To date no one has been able to satisfactorily synthesize these $Fe=O$ species under mild conditions using ONLY molecular oxygen as oxidant. Even nature requires the stoichiometric consumption of a co-reductant which donates the electrons and protons needed for closing the catalytic oxidation cycle. Nature's co-reductant is NADH which is converted to NAD while donating electrons and proton. Synthetic biomimetic systems add stoichiometric reagents for providing two protons and two electrons for every hydrocarbon molecule which is oxidized. These reagents are regenerated in vivo but, in vitro processes require sacrificial consumption of valuable raw materials in the regeneration process. This stoichiometric requirement imposes severe and usually prohibitive economic constraints on commercial applications of such a catalytic process.

In our laboratories we have learned how to tune the redox potential of metals in macrocyclic ligand environments to make them active for the selective air-oxidation of alkanes using ONLY molecular oxygen. As we mentioned above, nature uses electrons and protons together with iron to split the oxygen molecule and generate $\text{Fe}=\text{O}$. In so doing half of the oxygen molecule is converted to water while the other half is useful in oxidizing a substrate. We have asked the question whether oxygen can be split between two $\text{Fe}(\text{II})$ centers to make two $\text{Fe}=\text{O}$ species using all of the oxygen as effective oxidant. While Cytochrome P-450 and MMO act as monooxygenases, we are making complexes which may act as synthetic dioxygenases. We have incorporated a number of oxidation-active metal centers into our synthetic catalysts in addition to iron and have found that we are able to convert methane, ethane, propane and the butanes either to the corresponding alcohol or carbonyl compound depending on the nature of the metal center in the macrocyclic ligand system.

The ease of oxidation of the substrates that we have studied are in the order: isobutane > butane > propane > ethane > methane, which is also the order of increasing C-H bond dissociation energy, Figure 3-2. Isobutane is the easiest of the light hydrocarbons to oxidize. As a result we are close to having achieved a practical catalytic process for isobutane oxidation. High rates, yields and selectivities have been observed. We believe that we are within a factor of three or four of the rate necessary for a practical process. For this reason, it is likely that at the end of the current Cooperative Agreement we should proceed to the proof-of-concept phase for a process that converts isobutane to tert-butyl alcohol. There are many reasons why such a process is of interest. First, sales of butanes from the gas industry to refiners is down due to the vapor pressure restrictions on automotive transportation fuels. Conversion of C_4 's to TBA would be a way to put unwanted butanes back into gasoline. TBA is both a commercially tested high octane, clean burning motor fuel component and in addition is the precursor to MTBE, a rapidly growing commodity fuel material which is being used to meet oxygen mandates of the Clean Air Act.

FIGURE 3-2

HYDROCARBON REACTIVITY SERIES

4.0 EXISTING APPROACHES TO THE PROBLEM

4.1 Approaches Not Involving Oxygen

The direct low temperature condensation of methane into higher hydrocarbons with the liberation of hydrogen is a highly endoergic reaction (5), Table 4-1. A hydrocarbon condensation process must, therefore, provide a thermodynamic driving force in order for it to proceed. Oxidation of the hydrocarbon is a chemical solution to this problem, Table 4-1. For example, oxidative reaction of the hydrocarbon with a halogen such as chlorine or bromine will provide an exothermic process for producing higher molecular weight hydrocarbons (6). Direct reaction with the halogen to form alkyl halides which can be converted in a second step to higher alkanes is also thermodynamically allowed (7). While these and other similar schemes are interesting and may ultimately be useful, they consume costly raw materials and often produce corrosive by-products. It seemed to us, therefore, that the most straightforward and inexpensive oxidant to be used in liquifying a light alkane is air or oxygen.

TABLE 2-1

Thermodynamic Driving Force for
Oxidative Conversion of Methane

<u>Reaction</u>		<u>G_R^a</u>
2CH ₄	→ CH ₃ -CH ₃ + H ₂	+31.4
2CH ₄ + 1/2 O ₂	→ CH ₃ -CH ₃ + H ₂ O	-24.0
CH ₄ + 1/2 O ₂	→ CH ₃ OH	-37.6

^a In Kcal/mole @ 227°C

4.2 Oxidative Approaches

Two ways in which oxygen can react with methane are: a) to oxidize it to methanol, or b) to oxidatively dimerize it to give ethylene and water, Figure 4-1. Either product - ethylene or methanol - can be converted to gasoline by reaction over zeolitic catalysts (8,9). Our approach is to develop a catalyst which will oxidize natural gas (largely methane) to methanol, and then to convert the methanol to gasoline. It may be possible to implant an oxidation catalyst into a zeolitic structure capable of converting methanol to gasoline, or the methanol may be converted to gasoline in a separate step.

4.3. Natural Gas To Liquid Fuels Via Alcohols

There are at the present time no effective catalysts for the efficient conversion of the light alkanes - methane, ethane and propane - to alcohols using air or oxygen as the sole reagent. Recent reports (21,22) indicate that substantial amounts of methanol are produced from vapor phase non-catalytic reactions of methane but conversions and rates are low. Kinetic analysis (23) suggests to us that without the use of catalytic agents, the free radical oxidation of methane will not produce methanol in sufficiently high yield to be useful in a commercial gasoline process.

Currently available heterogeneous catalysts which are able to oxidize alkanes promote far deeper oxidation than is desired (24). Carboxylic acids or anhydrides, not alcohols, are the products which are generally produced (25). Currently available homogeneous catalysts have to date proven to be ineffective for catalyzing the air-oxidation of methane, ethane or propane in the liquid phase. The only catalysts which selectively transform alkanes to alcohols under mild conditions are the enzymatic systems. For this reason, there has been a large amount of effort over the past twenty years aimed at elucidating the mechanism of the enzymatic systems, applying enzyme catalysis to hydrocarbon oxidation in vitro, and modeling the enzyme's activity using synthetic biomimetic systems.

FIGURE 4-1

SOME POSSIBLE PATHWAYS FOR CONVERTING NATURAL GAS TO LIQUID FUEL

A large amount of excellent work has been done on processes for converting methane to ethylene (10-20). We would prefer the route through methanol as an intermediate for several reasons. Firstly, alcohols are liquids and can be readily transported to a terminal or a refinery site. Secondly, the catalyst for converting methanol to gasoline is proven in commercial operation. Thirdly, alcohols have value as fuels, fuel additives and commodities. Methanol may be mandated as a whole fuel in the future in areas of low environmental compliance. Finally, on-site conversion of methane to gasoline could be accomplished in an integrated reactor train under a single set of conditions, if desired. The conditions for oxidizing methane to methanol are similar to those for converting methanol to gasoline allowing process efficiencies which will improve economics.

4.4 The Biomimetic Approach

A number of biological systems including cytochrome P-450 and methane monooxygenase have been found to convert alkanes to alcohols in vitro (27-33). Both heme and non-heme iron centers have been implicated in the oxygen atom transfer step. Growing understanding of the biological systems together with the need for catalysts which can activate aliphatic C-H bonds for selective hydroxylation has stimulated intense activity in attempting to mimic biological systems with synthetic analogs (33-40). Much important knowledge has been gained which is highly relevant to the design of catalytic systems for selective air-oxidation of alkanes to alcohols. In addition, this work has brought into focus the problems with the biological systems for operation in an abiotic medium. An acceptable catalyst will be one which effectively applies relevant aspects of the biological systems while circumventing or solving the problems.

5.0 TECHNICAL BACKGROUND

5.1 ENZYMATIC CATALYSIS OF HYDROXYLATION

5.1.1 Cytochrome P-450

The monooxygenase, cytochrome P-450, contains an iron center in a porphyrinic environment which, in the presence of reduced nicotinamide adenine dinucleotide (NADH), can activate molecular oxygen to form a high-oxidation state iron oxo ($\text{Fe}=\text{O}$) species which is capable of hydroxylating the C-H bond of an alkane (27-30). In vitro experiments have shown that hydrocarbons such as norbornane (41) octane (42-43), and hexane (44), can be catalytically hydroxylated using this system. Conditions are mild (20°C , 1 ATM. air) and reaction rates are moderately high (> 40 moles alcohol/mole enzyme/min.) (45). The function of NADH in this system is to furnish the necessary electrons and protons to the iron center to generate the active species, Eq. 1.

5.1.2 Methane Monooxygenase (MMO)

Less is known about MMO, a non-heme iron containing methanotroph which slowly converts methane to methanol at room temperature (33). The active site is believed to contain two iron centers bridged by either an oxo or a hydroxo bridging unit (46). Again, nature's co-reductant, NADH, is essential for producing the catalytically active species in some systems.

5.2 BIOMIMETIC OXIDATION

5.2.1 Useful Concepts for Catalysis

Among the most useful concepts emanating from the many attempts to mimic enzymatic systems is the idea that high oxidation state iron intermediates are the active sites for alkane oxidation (34). In the case of the heme-iron system of cytochrome P-450, an iron oxo intermediate has been implicated (30a). Porphyrinato iron(III) complexes have been used to model this biocatalyst. Single oxygen atom transfer reagents such as iodosylbenzene or organic peroxide have been used to mimic NADH/O_2 in forming the active intermediate (33-36), Figure 5-1. The presumed high oxidation state metal oxo apparently converts aliphatic hydrocarbon substrates to the alcohol. It appears, therefore, that if one can generate these species in situ, alkanes will be converted to alcohols.

Another useful concept arising from the studies of biological oxidations carried out to date is the utility of a rigid hydrophobic pocket around the iron which attracts the alkane from an aqueous medium. The shape and size of the pocket orients the hydrocarbon molecule for hydroxylation. It's rigidity also helps to prevent self-oxidation which can result in destruction of the complex. Thus a catalyst which could generate high oxidation state iron oxo units in a hydrophobic pocket could exhibit high oxidation activity without ligand destruction.

FIGURE 5-1

BIOLOGICAL AND BIOMIMETIC ALKANE OXIDATION

FIGURE 5-2

A HYPOTHETICAL SYNTHETIC DIOXYGENASE

5.2.2 Problems for Commercial Catalysis

The major problem with either biological or biomimetic systems investigated to date is the stoichiometric consumption of expensive coreductants or oxygen atom transfer reagents. Biological systems use NADH stoichiometrically in the production of the active iron ($\text{Fe}=\text{O}$) centers. The NAD which is formed in this process must be reduced by some reagent which is sacrificed in order to return the NAD to NADH. The simplest means which has been found to date to furnish the required two electrons and two protons to a biomimetic catalyst systems is to split the hydrogen molecule over a group VIII metal catalyst in situ, Figure 5-2 (47).

FIGURE 5-2

HYDROGEN AS A CO-REDUCTANT IN A BIOMIMETIC OXIDATION

Although it has been successful only for conversion of very reactive hydrocarbons, such an approach could provide the possible pathway shown in Eq. 2 for the direct conversion of alkanes such as methane into alcohols. But even this relatively straightforward approach would be too costly to convert natural gas to alcohols for fuel use since it requires stoichiometric consumption of one mole of hydrogen per mole of alkane converted.

Another major problem with these biomimetic systems is deactivation of the catalyst by oxidative destruction. Two ways in which this comes about are by a) μ -oxo dimer formation and b) oxidative degradation of the ligand system. As mentioned above, nature uses a hydrophobic pocket to deter these deactivation processes. By rigidly holding the iron porphyrin in place the hydrophobic pocket prevents two iron atoms from getting close enough to form an inactive μ -oxo dimer. It also keeps weak C-H bonds away from the active center so that the organic system stays intact. Nature has regeneration mechanisms to combat destruction of portions of the enzyme system - a synthetic abiotic system would not have such possibilities. Any major destruction of the ligand system in a synthetic catalyst would result in loss of both selectivity and activity.

5.2.3 The Suprabioc Approach

An abiotic catalyst which employs an active metal oxo intermediate must have several features that are above and beyond the capability of biological systems. First it must be able to generate the metal oxo species directly from molecular oxygen without the costly requirement of a stoichiometric added coreductant. Secondly, since no repair mechanisms are possible, it must be resistant to processes of catalytic deactivation both at the metal center and at the ligand system. In this proposal we will describe a rationale for creating just such a suprabioc system, we will provide initial results which indicate that a good measure of success has already been achieved, and we will propose additional work for further development of new suprabioc catalyst systems in order to produce efficient processes for converting light alkanes to valuable fuels and chemicals.

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6.0 SUPRABIOTIC CATALYSTS

6.1. CRITERIA FOR A SUPRABIOTIC CATALYST

As was discussed above, a practical catalyst which operates via metal oxo intermediates for converting alkanes to alcohols must be more than biomimetic. In some ways it must be suprabiotic. When we consider how the biological systems work, we can learn some important lessons which indicate possible ways in which to activate alkanes and oxygen. One thing that we learn is that in order to activate oxygen it is necessary to bind both ends of the dioxygen molecule before cleaving and transferring it to a substrate. The enzymes use iron(II) to reductively bind one side of the dioxygen molecule and an electron and a proton to bind the other side, giving Fe-O-O-H. It is possible to do this conceptually with two Fe(II) centers instead. If two Fe(II) sites cooperate to reductively bind dioxygen, a peroxidic intermediate, Fe(III)-O-O-Fe(III), would result which could cleave to form two moles of a ferryl complex, Fe(IV)=O, which might be capable of converting an alkane to an alcohol. In this system, both oxygen atoms of O₂ would be utilized, as opposed to only one when monooxygenase enzymes are used. Water would not be formed. We have envisioned a new type of catalyst which could meet the following criteria:

- a. It could generate metal oxo (M=O) from reaction of the metal center (M) with molecular oxygen ONLY. No co-reductant or external source of protons or electrons would be required.
- b. The metal oxo center must 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.
- c. After converting the alkane to alcohol the center must expel the product from the coordination sphere and regenerate the metal center (M) for starting another catalytic cycle.

The proposed catalytic cycle shown below in Figure 6-1 indicates how these criteria could be met. Since nature uses a porphyrinic macrocycle as the ligand system this seemed to be a reasonable starting point for this research. The cycle shown below, Figure 6-1, uses elementary steps which all have precedent in inorganic chemistry.

FIGURE 6-1
ALKANE HYDROXYLATION WITH O_2 USING A SUPRABIOTIC CATALYST

Oxygen reacts with the metal center to form a superoxo complex which combines with another center to form a μ -peroxo complex. Cleavage of the O-O bond in the peroxo complex leads to the metal oxo complex which oxidizes the alkane. One of the reasons why this doesn't happen readily under normal circumstances is that the highly reactive metal oxo complex combines rapidly with a metal center to form a catalytically inactive μ -oxo complex, Eq. 3.

It is the goal of the catalyst design portion of this project to adjust the electronic characteristics of the ligand system about the metal center in such a way as to encourage O-O bond cleavage, and to stabilize the monomeric metal oxo relative to inactive μ -oxo intermediates.

6.2 CATALYST DESIGN CONCEPT

At the conclusion of the first three years work on the Cooperative Agreement it is instructive to re-visit the suprabiotic concept and evaluate catalyst performance relative to this idea. As we first envisioned a suprabiotic catalyst, it was one which could operate in the absence of costly stoichiometric co-reductants using only air to oxidize an alkane to an alcohol but in some respects mimic biology in that the active intermediates would be similar. It appears as though the active intermediate which oxidizes alkanes in both Cytochrome P-450 and methane monooxygenase is a ferryl species, Fe=O . We devised a possible conceptual route to active ferryl using only iron, air and substrate, Figure 6-1.

Prior to our work no success had been achieved in attempting to oxidize alkanes to alcohols with only air or oxygen in this manner. Many attempts had been made using porphyrinato complexes both with and without bulky groups which would prevent μ -oxo dimer formation, Figure 6-1f. The only successful alkane oxidations using porphyrinato complexes were achieved using costly single atom donor oxidants such as iodosylbenzene, hypochlorites, or hydroperoxides.

The problems associated with this system for air-oxidations of alkanes to alcohols were many. First, although formation of μ -oxo dimer from the iron(II) precursor is detrimental, μ -peroxo dimer formation is crucial. Secondly, access of the alkane to the active center must be good. Thirdly, the alkyl radical formed by C-H bond homolysis should remain in the coordination sphere until rebound to the alcohol occurs. Fourth, the alcohol should be expelled as quickly from the coordination sphere as possible to prevent over-oxidation. Next, μ -oxo dimer formation must be reversed or prevented. Finally, the iron(III)/(II) reduction potential must be high enough to continuously regenerate active Fe(II) from the pool of Fe(III) even in the presence of molecular oxygen. In addition, the ligand system must be robust to oxygenation, and must not have electrons readily available to reduce the high oxidation state ferryl before it can oxidize the alkane. The kind of porphyrin complexes available prior to our work did none of these things and consequently were inactive catalysts.

Using perhaloporphyrin complexes we: a) stabilized active iron-oxygen centers to both of the kinds of decay referred to above, b) provided a lipophilic environment to attract the alkane to the active site, c) provided a hydrophilic environment to expel alcohol from the coordination sphere, d) tuned the redox potential of the metal center so that μ -oxo dimer was no longer inactive and so that iron(II) species could be continually regenerated in an oxidizing environment. Figure 6-1a suggests how our perhaloporphyrins may act as a suprabiotic catalyst for converting alkanes to alcohols.

FIGURE 6-1a

PROPERTIES OF A SUPRABIOTIC CATALYST

- COOPERATIVE IRON (II) SITES

- LIPOPHILIC ENVIRONMENT *

- HIGH $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ REDUCTION POTENTIAL^I

• HYDROPHOBIC ENVIRONMENT

- SUPPRESSED μ -OXO FORMATION

- STABILITY TO OXIDATION

We have discussed how the electronic and steric environment about the oxidation-active metal center affects the rate and selectivity of alkane oxidation in homogeneous liquid phase oxidations. Reaction rate seems to be highly dependent on proper tuning of redox potentials. In the liquid phase we have achieved unprecedented reaction rates and have electrochemical evidence that much higher rates can still be achieved.

While steric effects influence rate as well, we are finding that their prime importance is in reaction selectivity. Ejecting formed alcohol from the coordination sphere is of great importance as we have seen in both homogeneous and heterogeneous alkane oxidation. Although our greatest gains to date are in tuning the redox potential for high activity, and although there is still room for significant improvement here, we will be concentrating in the future on those aspects of catalyst structure that will effect selectivity to alcohol. Of all of these structural factors, the most important is hydrophobicity of the ligand environment. Our current designs address these points and we are confident that we will continue to make significant gains in both reaction rate and selectivity until all of the light alkanes can be smoothly converted to alcohols by direct, practical, air-oxidations.

It should be noted at this point that we are proposing a completely novel solution to the 'μ-oxo dimer problem'. Most efforts in the past have sought to prevent formation of this unreactive species by steric hindrance which prevents the iron centers from getting close to one another (48-49). Our approach is an electronic rather than a steric one. An implication of our approach is that even a μ-oxo complex which has been properly tuned electronically will provide a good standing concentration of active metal oxo.

An important aspect of catalyst design employed in this work is the utilization of a non-oxidizable ligand. Firstly the ligand cannot be oxidized by the very high oxidation states generated at the metal center. For example, if one attempts to form an iron(V) oxo species by treatment of tetraphenylporphyrinatoiron(III)chloride with iodosylbenzene, one forms instead the iron(IV) radical cation by electron transfer from the porphyrin ligand (50). The ligands used in this work must be resistant to this kind of electron transfer and provide a stable coordination sphere even for metals in very high oxidation states. It goes without saying that the ligands employed must be inert to autoxidation and other potentially destructive processes.

Finally, the alkane must be brought into the coordination sphere of the metal. Biology uses the strategy of the hydrophobic pocket. It should be realized, however, that biological systems operate in an aqueous medium. The complexes used for liquid phase oxidation in our work are hydrocarbon soluble. Although affinity of the substrate for the catalyst is a desirable kinetic factor, this component will be built into the catalyst only if inadequate rates are achieved with our early prototypes. Our vapor phase catalysts will be capable of chemisorption of the hydrocarbon in order to achieve C-H bond activation at active centers.

6.3 INITIAL PERFORMANCE OF POTENTIALLY SUPRABIOTIC SYSTEMS

6.3.1 Effects of Axial Ligation

Our initial studies used tetraphenylporphyrinato metal(III) complexes of first row transition metals including chromium, manganese and iron as catalysts for the reaction of a series of light alkanes with molecular oxygen, Table 6.1 This series was comprised of four hydrocarbons having medium to strong carbon-hydrogen bonds: isobutane (94 kcal/mole), propane (96 kcal/mole), ethane (98 kcal/mole), and methane (104 kcal/mol). Isobutane oxidations were carried out at 80°C, propane was oxidized at 150°C, ethane at 200°C, and methane at 300°C. When the axial ligand, X, was chloride or acetate, no activity was observed for any of these hydrocarbons under these conditions. When the axial ligands were azide or nitride, isobutane and propane were oxidized at an appreciable rate. The macrocyclic ligand system, however, was not oxidatively stable and was rapidly destroyed during the reaction resulting in catalyst deactivation.

6.3.2 Electron Withdrawal from the Macrocycle

In order to make the macrocycle more oxidatively stable, all of the C-H bonds of the phenyl groups in the tetraphenylporphyrinato ligand were replaced with C-F bonds. This had the effect of reducing the oxidizability of the ligand both by molecular oxygen and by the metal itself. Although modest gains in activity were observed for manganese and chromium centered reactions, tetrakis(pentafluorophenyl)porphyrinato iron complexes were more active by an order of magnitude than their unfluorinated counterparts, Table 6-1. In all cases the half life of the catalysts improved as well. It should be mentioned here that unusually high selectivity from the alkane to the alcohol is observed with iron complexes of the fluorinated porphyrins. During the course of the Cooperative Agreement we have generated perhaloporphyrin complexes that are nearly four times more active for isobutane oxidation than $\text{Fe}(\text{TPPF}_{20})\text{N}_3$, Table 6-1. About half of this activity increase is due to halogenation at the pyrrole positions and half is due to superior process conditions.

TABLE 6-1
LIQUID PHASE OXIDATION OF ALKANES
USING SOLUBLE SUPRABIOTIC SYSTEMS

- CATALYST ACTIVITY^a -

SUPRABIOTIC	<u>ISOBUTANE</u>	<u>PROPANE</u>	<u>ETHANE</u>	<u>METHANE</u>
P-450 MODELS:	<u>AT 80°C^b</u>	<u>AT 150°C</u>	<u>AT 200°C^c</u>	<u>AT 300°C</u>

Fe(TPP)N₃

130

70

0

0

Fe(TPPF₂₀)N₃

1600

600

20

0

Fe(FPc)N₃

600

150

70

^a Moles product/mole catalyst/hr. (first-hour results)

^b Alkane oxidized at 5 bars O₂ pressure in benzene.

^c Alkane oxidized at ~ 70 bars air pressure in benzene.

It is believed that the superior results observed for the iron complex were due to the high activity of an iron oxo intermediate which was stabilized by a ligand with strong electron withdrawing groups which prevented ligand oxidation and concomitant reduction of the iron. The results for manganese and chromium may not have been as dramatic because Mn and Cr oxo complexes are more accessible and thus not as active as oxidants toward alkanes. Initial electrochemical investigations of these materials at the California Institute of Technology indicate that iron can achieve extraordinarily high oxidation states in the fluorinated macrocyclic environment without ligand decomposition and evidence for iron(V) in a porphyrinic ligand has been found for the first time (51). In addition, the extraordinary high Fe(III)/Fe(II) reduction potential that these complexes exhibit allows the generation of oxygen binding sites even under oxidizing conditions.

6.3.3 Benefits of Removing C-H Bonds on Catalyst Life

Although we had provided significant oxidative stabilization of the ligand in these systems by replacing twenty hydrogens with fluorine atoms, there are still eight more hydrogens attached to the pyrrole rings in the porphyrin. These present additional sites of oxidative instability which must be dealt with. One approach has been to replace these eight hydrogens by halogenation (52). As mentioned above, the perhaloporphyrin complexes are more robust and more active than the partially halogenated catalysts.

Another approach to achieving catalyst stability is to go from the porphyrinic systems to the similar phthalocyanines. We have been successful in preparing perfluorophthalocyanato metal azides which have somewhat lower activity than that of the porphyrins but longer life. Long life is attributable both to the total lack of C-H bonds and to the presence of nitrogens in the bridge positions of the macrocycle. These catalysts do not produce alcohols in as high selectivity as do their porphyrin analogs.

6.3.4 Summary of Initial Studies

A large amount of fundamental work has been done at Sun to lay the groundwork for the development of a superior catalyst for the oxidative conversion of light alkanes to liquid fuels through alcohols as intermediates. New catalyst concepts have been envisioned, new catalysts prepared and tested and results superior to those generated by any known catalyst system have been obtained. We have activated the light alkanes (C_1 - C_4) toward selective catalytic air-oxidation in the liquid phase for the first time. We are now well positioned to go forward with this work and develop truly superior practical catalysts for converting natural gas and other light alkanes into valuable fuel and chemical products. In particular, we are now able to enter the proof-of-concept stage of a process aimed at producing TBA from isobutane and expect that with continual catalyst development future processes for IPA from propane, and methanol from methane or natural gas will be ready to enter the proof-of-concept stage.

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7.0 CATALYSIS BY ELECTRON DEFICIENT METALLOPORPHYRINS

During the course of the Cooperative Agreement we have determined that by increasing the amount of electron withdrawal from either the meso- or the beta-(pyrrolic) positions of the porphyrinato macrocycle surrounding an oxidation active first row metal center, we are able to greatly increase the M(III)/M(II) reduction potential of the complex. This results in an enormous increase in light alkane oxidation activity and provides us for the first time with a family of metal complexes capable of catalyzing the direct selective air-oxidation of these refractory materials. In a study encompassing porphyrin complexes of the metals: iron, manganese, chromium, cobalt, ruthenium and copper, we have shown that although copper complexes are not active, the activity of all the other metals responds positively to electron withdrawal in both the meso- and the beta-positions. We have further shown that the light alkane air-oxidation activity of the iron complexes of electron deficient porphyrins are in all cases far superior to that of the other metals.

Figure 7-1 shows the porphyrinato macrocycle with the meso- positions labeled Z and the beta-positions labeled Y. Our work has shown that while iron complexes of the macrocyclic ligand wherein Z = phenyl(Y=H) are not catalytically active for air-oxidations of light alkanes at low temperature, those in which Z = pentafluorophenyl (Y=H) exhibit high catalytic activity. Changing the Y group from H to X, wherein X = a halogen such as chlorine or bromine causes further increase in activity. Synthesis of these complexes is diagrammed in Figure 7-2 and synthetic details can be found in quarterly reports on the Cooperative Agreement. Perhalogenated iron complexes are more active than any known metal complexes for light alkane oxidation by at least an order of magnitude and make unprecedented selective low temperature alkane oxidations possible. Alcohols are major reaction products and no expensive oxidants or co-reductants are required using these catalysts.

FIGURE 7-1
SUBSTITUTED PORPHYRIN MACROCYCLE

FIGURE 7-2

SYNTHESIS OF ELECTRON DEFICIENT PORPHYRIN COMPLEXES

FIGURE 7-2 (Contd.)

SYNTHESIS OF ELECTRON DEFICIENT PORPHYRIN COMPLEXES

M = Mn, Fe, Cr, Ru
X = N₃, Br, OH, μ -O

Table 7-1 compares the isobutane and propane oxidation activity of the series of iron porphyrin complexes described in Figure 7-1. Although these complexes are the most active known, and perhalogenation has created the most stable porphyrin complexes yet prepared, we still have further to go before we have achieved a practical catalyst which can be used in a commercial process. Proprietary economic analysis indicates that we should at least triple current activity for an economically attractive process for oxidizing isobutane to tert-butyl alcohol. Since we are so close to a practical catalyst for isobutane oxidation, we have examined the performance of $\text{Fe}(\text{TPPF}_{20\beta}\text{-Cl}_8)$ in both batch, semi-batch and continuous operation. We are conducting a kinetic study of this reaction to determine as much as possible about the characteristics of its performance. Inspection of reaction rates indicates that as much as an order of magnitude increase in activity is required before propane oxidations become practical. While rapid and selective air-oxidations of ethane and methane are still beyond the reach of currently available porphyrin complexes, advances in understanding of catalyst design principles continues to increase the likelihood of achieving this.

We are in the process of correlating electrochemical information on a large number of electron withdrawing complexes which is beginning to show how to increase oxidation activity far beyond current levels. It is becoming clear that groups Z and Y can be employed in both the meso- and beta- positions which will be far more effective than those employed to date. These include nitro groups, cyano groups, and trifluoromethyl groups. In addition to conferring higher activity on the iron center, the use of these substituents will have a number of practical benefits. They will result in catalysts of lower molecular weight and will reduce catalyst costs substantially. In some instances they will increase stability and provide greater catalyst life. Temperatures can then be raised without destroying the catalyst so that the more unreactive alkanes - ethane and methane can be oxidized. To date satisfactory synthetic routes to these new complexes are unknown and work is underway in our laboratories to prepare novel catalytic materials of this type. We have prepared the novel (bis(octaethylmeso- tetranitroporphyrinato)iron(III) μ -oxo complex $[\text{Fe}(\text{OEP}(\text{NO}_2)_4)_2\text{O}]$, and have shown that it is an active alkane oxidation catalyst. We are well on our way to synthesizing significant quantities of the tetranitro porphine $[\text{FeP}(\text{NO}_2)_4]\text{O}$ analog which will have higher activity without eight electron-donating ethyl groups. Finally, octohalotetranitro iron complexes should be even more active and stable than any catalyst now known. The synthesis of these new catalysts is underway.

TABLE 7-1

ALKANE OXIDATIONS CATALYZED BY IRON PORPHYRINS, $\text{Fe}(\text{TPPZ}_{20}\beta\text{-Y}_8)\text{X}^{\text{a,b}}$

Complex			Substrate	Time Hour	Temp °C	TON ^c	Selectivity to TBA ^d	IPA/ Acetone
Z	Y	X						
$4\text{C}_6\text{H}_5$	8H	Cl	Isobutane	6	60	0	-	
$4\text{C}_6\text{H}_5$	8Cl	Cl	Isobutane	6	60	0	-	
$4\text{C}_6\text{H}_5$	8Br	Cl	Isobutane	6	60	110	88	
$4\text{C}_6\text{F}_5$	8H	Cl	Isobutane	6	60	1160	90	
			Propane	4.5	125	390		0.8
$4\text{C}_6\text{F}_5$	8Cl	Cl	Isobutane	6	60	1800	90	
$4\text{C}_6\text{F}_5$	8Br	Cl	Isobutane	6	60	1890	91	
			Propane	4.5	125	420		1.0
$4\text{C}_6\text{F}_5$	8Br	Br	Propane	4.5	125	470		0.8
$4\text{C}_6\text{F}_5$	8Br	N_3	Propane	4.5	125	514		0.9

^a A solution of 0.013 mmoles of the catalyst in 25 ml benzene containing 6 grams of isobutane was stirred at the designated temperature under 100 psig of O_2 for the designated time.

^b Stirred solution of 0.023 mmoles of the catalyst in 60 grams of propane in 48 ml benzene at 125°C under 1000 psig air.

^c Moles tert-butylalcohol produced/mole catalyst; or Moles (isopropyl alcohol+ acetone) formed/mole catalyst used.

^d (Moles tert-butyl alcohol produced/total moles liquid product) X 100.

8.0 DESIGN OF NEW ELECTRON DEFICIENT PORPHYRIN COMPLEXES

8.1 Electronic Effects

We have shown that there is a direct correlation between Fe(III)/Fe(II) reduction potential and catalytic activity for light alkane oxidation. Figure 8-1 demonstrates this correlation for the 6 hour oxidation of isobutane at 80°C and propane at 125°C. Thus, the higher the Fe(III)/Fe(II) reduction potential, the greater is the expected catalytic air-oxidation activity of an iron porphyrin complex. Tables 8-1 and 8-2 demonstrate that cyano, nitro and trifluoromethyl groups on the periphery of a porphyrin macrocycle are expected to have greater effects than halo (Br, Cl, F) groups on the reduction potentials of metals in their coordination sphere. If the correlation between porphyrin substituent partial reduction potential values, Table 8-2, or sigma constants, Figures 8-2, 8-3, and Fe(III)/Fe(II) reduction potential holds we would expect nitroporphyrin complexes to have the highest Fe(III)/Fe(II) reduction potentials and perhaps the highest initial oxidation rates. We would predict therefore that iron porphyrins having large numbers of cyano, nitro or trifluoromethyl groups would have higher Fe(III)/(II) reduction potentials than their halo counterparts and therefore greater oxidation activity. For these reasons we have now embarked on a program geared to the synthesis of complexes of this type.

FIGURE 8-1

CATALYST ACTIVITY vs. REDOX POTENTIAL

TABLE 8-1
HALF-WAVE POTENTIALS OF IRON-PORPHYRIN COMPLEXES

<u>Complex</u>	<u>Solvent</u>	<u>Electrolyte</u>	<u>References</u>	<u>E_{1/2} Fe(III)/Fe(II)</u>
TPPFeCl	CH ₂ Cl ₂ ^a	TBAP	SCE	-0.23
	DMF ^a	TBAP	SCE	-0.19
	DMF ^b	TBAP	Ag/AgCl	-0.121
[(CN) ₄ TPP]FeCl	CH ₂ Cl ₂ ^a	TBAP	SCE	0.17
	DMF ^a	TBAP	SCE	0.17
	DMF ^b	TBAP	Ag/AgCl	0.45
[(CN) ₃ TPP]FeCl	DMF ^b	TBAP	Ag/AgCl	0.185
[Br ₄ TPP]FeCl	DMF ^b	TBAP	Ag/AgCl	0.083
[(CF ₃) ₄ TEP]FeCl	CH ₂ Cl ₂ ^c	Unk	Ag/AgCl	-0.07
[OEP]FeCl	CH ₂ Cl ₂ ^c	Unk	Ag/AgCl	-0.37

^a Kadish, et al., Inorg. Chem., 1985, 24, 2148

^b Bocian, et al., J. Am. Chem. Soc., 1987, 109, 5593

^c Ogoshi, et al., Chemistry Letters, 1991, 1547

TABLE 8-2

**PORPHYRIN SUBSTITUENT PARTIAL
REDUCTION POTENTIAL VALUES^a**

<u>Substituent</u>	<u>Position</u>	<u>Partial Potential (mV)^b</u>
Porphin Core		-1660.0
-CH ₃	Meso	-15.0
-CH ₃	Beta	-23.7
-C ₂ H ₅	Beta	-23.7
-(CH ₂) ₂ CO(OCH ₃)	Beta	-7.5
-H	Beta	0.0
-H	Meso	0.0
-CH ₂ CO(OCH ₃)	Beta	+7.5
-C ₆ H ₅	Meso	+25.0
Vinyl	Beta	+30.0
4-Pyridyl-	Meso	+70.0
-Cl	Beta	+93.0
-Br	Beta	+100.0
-CO(CO ₂ H ₅)	Beta	+130.0
-CO(CH ₃)	Beta	+145.0
-CO(H)	Beta	+200.0
-CN	Beta	+240.0
-NO ₂	Beta	+370.0

^a Worthington, *et al.*, J. Inorg. Biochem., **12**, 1980, 287.

^b The sum of the partial reduction potential values for the porphyrin will be vs Ag/AgNO₃ (0.10M) in DMF.

FIGURE 8-2

Plot of the first free base porphyrin reduction potential $E_{1/2}$ for substituted mesophenyl type porphyrins vs. the sum of the Hammett substituent constants, $\Sigma\sigma_p$. (Worthington, *et al.*, J. Inorg. Biochem., 12, 1980, 281)

FIGURE 8-3

RELATIONSHIP BETWEEN REDUCTION POTENTIAL
AND RESONANCE EFFECT OF SUBSTITUENTS
ON THE PORPHYRIN RING

8.1.1. Electrochemistry of a Series of Electron-Deficient Iron Porphyrin Complexes

In the past the very critical determinations of Fe(III)/Fe(II) reduction potential had been done in three different laboratories and not always under identical conditions. Because of the apparent direct relationship between reduction potential and catalytic activity of iron porphyrin complexes we reinvestigated this area again. The Fe(III)/Fe(II) redox potentials vs. SCE for the series of iron porphyrins have been determined under a set of consistent conditions. The CV's were all obtained in CH₂Cl₂ and tetrabutylammonium chloride (TBACl) was used as supporting electrolyte. A glassy carbon electrode was used. Figure 8-4 shows the CV's and Table 8-3 lists the half-wave potentials determined for each compound in the series.

8.2 STRUCTURAL EFFECTS

Structural features of electron deficient porphyrin complexes also appear to play an important role in catalytic air-oxidation reactions. In particular, steric interactions which could limit or prevent μ -oxo dimer formation, Figure 6-1f, may be important for high catalytic activity. We have identified two different types of steric interactions which may be important. One way in which μ -oxo dimer formation could be suppressed is through severe buckling of the porphyrin macrocycle due to steric bulk in the beta-positions. It can be seen that as the bulk of the β -substituent increases from H to Cl to Br, the extent of buckling increases. It does not seem possible to make the μ -oxo species when the beta-positions bear eight bulky bromines.

FIGURE 8-4

CVs of a Set of
Fe(II) Porphyrins

TABLE 8-3

Fe(III)/Fe(II) REDOX POTENTIALS FOR A SERIES OF
IRON PORPHYRINS^a

Compound	Fe(II)/(III) $E_{1/2}$ (eV)	Source
FeTPP(Cl)	-0.22	Aldrich
FeT(2,6-dichloro)PP(Cl)	-0.22	MidCentury
FeTF ₂₀ PP(Cl)	+0.07	Aldrich
FeTF ₂₀ PPBr ₈ (Cl)	+0.19	WAL #976483
FeTF ₂₀ PPCl ₈ (Cl)	+0.28	Wagner #984757

^a The CV's were all obtained in CH₂Cl₂ and tetrabutylammonium chloride (TBACl) as supporting electrolyte. A glassy carbon electrode was used.

Secondly, large electron withdrawing groups such as chloro-in the ortho-position of the phenyl rings of tetraphenylporphyrinato complexes make μ -oxo dimer formation impossible. For this reason we have prepared the perhaloporphyrinato complex, $\text{Fe}(\text{TPPCl}_{28})\text{Cl}$. Wijesekera, et. al., Angewandte Chemie, 1990, and have shown that the $\text{Fe}(\text{III})/(\text{II})$ reduction potential of this complex is nearly as high (0.27v) as that of $(\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl})$. It is possible that $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$ could form a μ -oxo dimer. On the other hand $\text{Fe}(\text{TPPCl}_{28})\text{Cl}$ could not form a μ -oxo dimer because of the huge non-bonded interactions resulting from the eight ortho-chloro substituents on each macrocycle, cause significant buckling of the macrocycle, Figures 8-5, 8-6.

8.2.1 Oxidation of Alkanes Using $\text{Fe}(\text{TPPCl}_{28})\text{Cl}$ as Catalyst

We attempted the oxidation of isobutane (20%) in benzene under standard test conditions (100 psig O_2 , 6 hours) at 40, 60, and 80°C using $\text{Fe}(\text{TPPCl}_{28})\text{Cl}$ as the catalyst. No reaction occurred. Under these conditions nearly 2,000 turnovers would have been observed at 60°C using $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$ as the catalyst. One interpretation of these results is that not only is the μ -oxo dimer, $[\text{Fe}(\text{TPPCl}_{28})]_2\text{O}$, unable to form, but even the μ -peroxo dimer, $[\text{Fe}(\text{TPPCl}_{28})]_2\text{O}_2$ cannot be made. Inspection of the molecular model of the monomeric $\text{Fe}(\text{II})$ complex, Figure 8-5 shows that the iron is surrounded by a nearly symmetrical barrier of chlorine atoms. Thus, it is possible that steric hindrance about the iron centers is so great that this complex may not be able to reductively bind dioxygen, Figure 5-2(b).

If this explanation is correct then small single oxygen atom transfer reagents should still be able to oxidize the iron center to a ferryl which will oxidize hydrocarbons. It has been found that $\text{Fe}(\text{TPPCl}_{28})\text{Cl}$ oxidizes cyclohexane to the alcohol and the ketone and oxidizes cyclohexene to the epoxide when iodosyl benzene is the oxidant.

FIGURE 8-5

Fe(TPPCl₂₈)

FIGURE 8-6

Thus, when a small oxygen donor having oxygen in the reductively bound state is used, oxidations presumably occurring through an active ferryl intermediate are possible. When it is necessary to reductively bind a dioxygen molecule in order to get the active catalytic intermediate, steric bulk prevents this reaction from occurring.

Thus, we may now have spanned the range of steric requirements for both μ -oxo and μ -peroxo complex formation. It would appear that a properly tuned iron complex which can readily form a μ -peroxo dimer but which cannot form μ -oxo dimer should give the greatest concentration of active ferryl, and thus should be the best catalyst. We are currently studying other complexes with varying steric requirements to test this hypothesis.

8.3 SUMMARY - ELECTRON DEFICIENT PORPHYRIN COMPLEXES

8.3.1 Active Catalysts from Metals in Electron Deficient Porphyrins

We have shown that the catalytic activity of tetraphenylporphyrinato complexes of oxidation-active first row transition metals is increased by halogenation of the tetraphenylporphyrin ring system (1-3). As the degree of halogenation is increased, the catalytic activity increases. Iron(III) complexes were shown to be more active than those of chromium, manganese or cobalt in all cases. The iron perhaloporphyrin complex: tetrakis(pentafluorophenyl) β -octachloroporphyrinatoiron(III)chloride, $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$, has unprecedented light alkane air-oxidation activity. Using this catalyst, isobutane can be oxidized in neat solution at temperatures ranging from room temperature to 80°C in from 85 to 95% selectivity at isobutane conversion levels over 20%. Over 150,000 moles of tert-butyl alcohol can be produced per mole of iron using this catalyst. Propane can be converted to a mixture of isopropyl alcohol and acetone in a selective manner.

8.3.2 Electron Withdrawal, Reduction Potential and Catalytic Activity

As the C-H bonds around the periphery of the tetraphenylporphyrinato ligand system are changed to C-X bonds ($X = F, Cl, Br$), the Fe(III)/(II) reduction potential increases. Table 8-4 shows that the catalytically inactive parent iron porphyrin, Fe(TPP)Cl, exhibits an Fe(III)/(II) half-wave potential at -0.22V whereas the $E_{1/2}$ exhibited by the highly active perhaloporphyrin complex, Fe(TPPF₂₀ β -Cl₈)Cl, is fully 0.5V higher. It appears that there is a direct relationship between the extent of electron withdrawal from the porphyrin ring, which causes an increase in the Fe(III)/(II) reduction potential, and the catalytic activity of the iron complex.

8.3.3 Porphyrin Ring Buckling, Steric Hindrance and Catalytic Activity

What was surprising about Table 8-4, however, was that the catalytic activity of Fe(TPPF₂₀ β -Br₈)Cl was not lower than that of Fe(TPPF₂₀ β -Cl₈)Cl. Structural information currently being gathered indicates that the steric bulk of the β -bromo substituents may prevent access of large molecules to the central iron atom. This has two possible consequences which could affect reaction rate. Firstly, a sterically hindered porphyrin might bind dioxygen to give a μ -peroxo complex which could cleave to form an active ferryl oxo species. It would be unlikely that a diiron μ -oxo complex, however, would be very stable if it is formed at all. To the extent that ferryl oxo complexes are active intermediates and that diiron μ -oxo species are not, a steric environment which prevents μ -oxo formation could cause an oxidation rate enhancement.

TABLE 8-4

RELATIONSHIP BETWEEN CATALYST REDUCTION POTENTIAL AND ACTIVITY

<u>CATALYST</u>	$\frac{\text{Fe(III)}/\text{(II)}}{E_{1/2} \text{ (V)}}^a$	<u>T.O.</u> ^b
Fe(TPP)Cl	-0.221	0
Fe(TPPF ₂₀)Cl	+0.07	1160
Fe(TPPF ₂₀ β -Br ₈)Cl	+0.19	1890
Fe(TPPF ₂₀ β -Cl ₈)Cl	+0.28	1800

^a Cyclic voltammetry in CH₂Cl₂, vs. SCE, TBAC- supporting electrolyte, glassy carbon electrode

^b Catalyst turnovers for 60°C isobutane oxidations in benzene.

8.4 REFERENCES

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9.0 CHARACTERIZATION OF ELECTRON DEFICIENT PORPHYRIN COMPLEXES

9.1 SPECTROSCOPIC STRUCTURE DETERMINATION OF THE PERHALOPORPHYRIN MACROCYCLES - RESONANCE RAMAN SPECTROSCOPY

Recent work (7) has determined that the greater the steric bulk of hydrocarbon substituents in the β -(pyrrolic) positions of a nickel tetraphenylporphyrin complex, $\text{Ni}(\text{TPP}\beta\text{-R}_8)$, the greater is the degree of buckling of the porphyrin. This distortion is reflected in the shift of the structure-sensitive resonance Raman bands, ν_2 and ν_4 , to lower frequency. We have found a very similar pattern of behavior for nickel tetrakis(pentafluorophenyl)porphyrin complexes, $\text{Ni}(\text{TPPF}_{20}\beta\text{-Y}_8)$, $\text{Y} = \text{H}, \text{Cl}, \text{Br}$ (7). Table 9-1 indicates that as the β -group becomes bulkier the TPPF_{20} macrocycle goes from a planar geometry when $\text{Y} = \text{H}$, to a highly buckled saddle shape when $\text{Y} = \text{Br}$, with the octachloro substituent being intermediate in geometry.

We have shown in fact that the structure-sensitive marker bands near 1500 cm^{-1} and 1300 cm^{-1} in the series of electron-deficient metalloporphyrin complexes: $\text{M}(\text{TPPF}_{20}\beta\text{-Y}_8)$, $\text{M} = \text{Cu}, \text{Co}, \text{Ni}, \text{Zn}, \text{Pd}$; $\text{Y} = \text{H}, \text{Cl}, \text{Br}$, systematically move to lower frequency as the group in the β -position becomes more bulky. This trend indicates that the greater the bulk of the β -substituent, the more buckled is the porphyrin ring and the more pronounced the saddle shape. The three crystal structures determined to date confirm this general trend. The molecular motions designated ν_4 and ν_2 are shown in Figure 9-1. It can be seen that our $\text{Ni}(\text{TPPF}_{20})$ complex is structurally similar to nickel TPP complexes in which the $\beta\text{-Y}$ groups are hydrogen or methyl, our $\text{Ni}(\text{TPPF}_{20}\beta\text{-Cl}_8)$ is structurally similar to nickel TPP complexes in which the $\beta\text{-Y}$ groups are ethyl or propyl and our $\text{Ni}(\text{TPPF}_{20}\beta\text{-Br}_8)$ complex is structurally similar to a very buckled nickel TPP complex in which the $\beta\text{-Y}$ groups are phenyl substituents.

We have recently obtained the resonance raman spectra of the iron complexes $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$ where $\text{Y} = \text{H}, \text{Cl}, \text{Br}$. These bands are much broader than in the case of the metal(II) complexes discussed above. In addition the spectra are more complex. On the other hand when pyridine is added the spectra become simple and look very similar to those $\text{M}(\text{II})$ spectra referred to above, Figure 8-2. As in the case of the NMR studies discussed in section 5.1.2.2, the pyridine treatment may have caused reductive elimination of Cl and we may be seeing the $\text{Fe}(\text{II})$ complex with expected ν_4 at 1350 and ν_2 at 1553 cm^{-1} .

TABLE 9-1

EFFECT OF β -STERIC BULK IN THE NICKEL $\text{TPP}-\beta\text{R}_8^{15}$ AND $\text{TPPF}_{20}-\beta\text{Y}_8$ COMPLEXES ON STRUCTURE-SENSITIVE RR MARKER BANDS. ^a

Compound	Soret (nm)	$\nu_4 (\text{cm}^{-1})$	$\nu_2 (\text{cm}^{-1})$
$\text{Ni}(\text{TPPF}_{20})$	406	1375	1586
$\text{Ni}(\text{TPP})$	414	1374	1572
$\text{Ni}(\text{TPP } \beta\text{-Me}_8)$	429	1362	1574
$\text{Ni}(\text{TPPF}_{20}\beta\text{-Cl}_8)$	428	1363	1557
$\text{Ni}(\text{TPP } \beta\text{-Et}_8)$	433	1350	1562
$\text{Ni}(\text{TPP } \beta\text{-Pr}_8)$	434	1360	1560
$\text{Ni}(\text{TPPF}_{20}\beta\text{-Br}_8)$	438	1354	1542
$\text{Ni}(\text{TPP } \beta\text{-Ph}_8)$	449	1353	1545

^a $\text{CH}_2\text{Cl}_2(442\text{nm excitation})$

**FIGURE 9-1 SCHEMATIC REPRESENTATIONS OF THE SKELETAL VIBRATIONS
CORRESPONDING TO THE BREATHING MODES OF THE PORPHYRIN
MACROCYCLE**

FIGURE 9-2

THE EFFECT OF PYRIDINE ON THE RESONANCE

RAMAN SPECTRUM OF $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$

Although we have not as yet generated crystals of the iron $\text{TPPF}_{20\beta}\text{-Y}_8$ complexes ($\text{Y} = \text{Cl}, \text{Br}$) of sufficient quality to obtain a crystal structure, we have obtained resonance Raman data which show that ν_2 and ν_4 have both shifted to lower frequency. The paramagnetic $\text{Fe}(\text{TPPF}_{20\beta}\text{-Cl}_8)$ complex is converted to a diamagnetic species, probably $\text{Fe}(\text{II})$, by treatment with excess pyridine. When a methylene chloride solution of $\text{Fe}(\text{TPPF}_{20\beta}\text{-Cl}_8)$ is treated with pyridine, and its resonance Raman spectrum obtained, the structure-sensitive marker bands ν_4 and ν_2 , respectively, appear at 1353 and 1554 cm^{-1} , in good agreement with the positions of these bands in $\text{Ni}(\text{TPPF}_{20\beta}\text{-Cl}_8)$.

9.2 X-RAY CRYSTAL STRUCTURES

Figure 9-3 shows the structures of $\text{Cu}(\text{TPPF}_{20\beta}\text{-Cl}_8)(16)$. It is clear that the extent of buckling is far more severe in the octabromo complex than in the octachloro compound. Inspection of the structure of the $(\text{TPPF}_{20\beta}\text{-Br}_8)$ macrocycle in Figure 9-3 shows a deep saddle created by severe buckling of the porphyrin ring system. One could imagine the difficulty of making a diiron μ -oxo bridged species from such a severely buckled complex.

FIGURE 9-3

STRUCTURES OF PERHALOPORPHYRIN COMPLEXES

The X-ray crystals structures of CuLBr and ZnLBr, $L = (\text{TPPF}_{20}\beta\text{-Br}_8)$, have also been completed. The ORTEP diagrams (Figure 9-4 and 9-5 respectively). The CuLBr structure is isostructural with the previously solved NiLBr structure. The structure of ZnLBr is different. There is a mirror plane through opposite nitrogen atoms, and four different solvent molecules in the crystal. Several solvents (o-dichlorobenzene, water, carbon tetrachloride and acetone/methanol (50%:50%)) were resolved in the unit cell. The unit cell including all these solvents is illustrated in Figures 9-5 (b) and (c). Note that in this structure, there is an oxygen atom coordinated to the Zinc atom pulling it slightly out of the porphyrin plane. This is the first of the halogenated metalloporphyrin crystal structures where the metal atom is not co-planar with the 4-nitrogen atom plane.

We have not determined the structures of a number of peralogenated porphyrins and metalloporphyrins. Several of these structures have been shown in previous quarterly reports. The buckling of these complexes has been noted and the effect of buckling on catalytic activity discussed. Table 9-6 summarizes the crystal structure data gathered which indicate the degree of distortion from planarity of the atoms in the porphyrin ring.

FIGURE 9-4

Cu(TPPF₂₀Br₈)

FIGURE 9-5(a)
Zn(TPPF₂₀β-Br₈)

FIGURE 9-5(b)
Zn(TPPE₂₀-Br₈) Unit Cell

FIGURE 9-5(c)
ZnBr Unit Cell

FIGURE 9-6
CRYSTAL STRUCTURE DATA:

Distortion (Å from plane of porphyrin)	CuCl ₈	NiBr ₈	CuBr ₈	H ₂ Br ₈	ZnBr ₈
<i>C_{meso}</i>	±0.128	±0.211	±0.177	±0.091	±0.021
<i>C_β</i>	±0.797	±1.326	±1.247	±0.903	±0.971
N	±0.12	±0.19	±0.15	±0.076	±0.082
Cl or Br	±1.19	±2.05	±1.99	±1.72	±1.68
'Core Size' Ct---N	2.007	1.902	1.969		2.042

9.3 ELECTRONIC STRUCTURES OF HALOGENATED METALLOPORPHYRINS

The absorption bands of a series of halogenated porphyrins shift to lower energies as the size of the porphyrin substituents increases. AM1 calculations show that the red shifting in the absorption spectrum is due to a decrease in the HOMO-LUMO energy gap, which is a result of the distortion of the porphyrin ring. The electronic effect of the halogens is to lower the absolute energies of the orbitals.

Halogenated porphyrins have been shown to be unusually effective catalysts for the oxygenation of alkanes.¹⁻² It is likely that the electronic structures of these porphyrins play a role in the catalytic mechanism.

The standard model for the interpretation of porphyrin spectra is the Four Orbital Model proposed by M. Gouterman in 1961³. This model is a method of correlating the orbitals derived from simple Huckel calculations. Changes in the porphyrin absorption spectra attributable to substitution are rationalized with respect to perturbations of these four orbitals.

Porphyrin spectra feature an intense band, usually found in the ultraviolet region, known as the B band or the solet band. The second two bands at lower energy are called Q bands. Figure 9-7 shows how the one electron transitions within the four orbitals mix to give the observed transitions: Figure 9-8 shows the four orbitals.

Previous studies of brominated porphyrins have shown that each bromine at a pyrrole position caused a spectral shift of 6 nm to the red relative to the bands observed for tetraphenylporphyrin (TPP).⁴ An attempt has been made to explain these shifts in terms of a parameterized version of the standard four-orbital model⁵. Bhyrappa and Krishnan (BK) only considered electronic effects of the bromine substituents in their analysis of the absorption spectra⁵. Recent crystal structures⁶ of these halogenated compounds have shown that significant bending of the porphyrin ring occurs, so it is likely that the BK explanation will require some revision.

9.3.1 Calculation Details

In order to assess the changes in spectra with halogenation of the porphyrin, AM1⁷ calculations have been performed using MOPAC⁸. These calculations include full CI within Gouterman's four orbitals.

The calculations have been performed upon two series of halogenated porphyrins. The first series includes TF₂₀PP, TF₂₀PPCl₈, and TF₂₀PPBr₈. The second series includes the same porphyrins with Zn in the core rather than two hydrogens.

Crystal structures have been obtained for Cu-TFPPCl₈ and NiTFPPCl₈⁶. The calculations on TFPPCl₈ used the geometry that was obtained from the crystal structure of CuTFPPCl₈⁸. Similarly, the calculations on ZnTFPPBr₈ use the geometry that was obtained from the crystal structure of NiTFPPBr₈. Since these are first row transition metals, their sizes are roughly equivalent. Thus, it is not a bad approximation to replace Cu and Ni with Zn, while retaining the geometry of the original crystal structure. TFPPBr₈ and TFPPCl₈ have been optimized using the MOPAC geometry optimization routine⁹. The geometries used for TFPP and ZnTFPP are also Biograf minimized structures using Dreiding force fields. The initial guess for the optimization of TFPPBr₈ and TFPPCl₈ was based upon the crystallographic data, with the metal replaced by two hydrogens.

FIGURE 9-7

CONFIGURATION INTERACTION IN THE FOUR ORBITAL MODEL

The transitions are defined as:

$$\begin{matrix} Q_x \\ B_x \end{matrix} = [(b1c2) \pm (b2c1)]$$

$$\begin{matrix} Q_y \\ B_y \end{matrix} = [(b1c1) \pm (b2c2)]$$

The symmetries of the orbitals are as follows:

$$b1=b_{1u}, \quad b2=a_u, \quad c1=b_{3g}, \quad c2=b_{2g}$$

see Figure 2 for pictures of the orbitals

FIGURE 9-8
THE FOUR ORBITALS

B_{2g}

unoccupied

B_{3g}

B_{1u}

occupied

A_u

9.3.2 Experimental Section

TFPP obtained from Aldrich was purified using techniques described earlier¹⁰. TFPPCl_8 ¹¹ and TFPPBr_8 ¹ were prepared according to literature procedures. All zinc-metallated species were prepared by refluxing the appropriate porphyrin with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in methanol. The zinc acetate was purchased from Aldrich Chemicals. All porphyrins were purified on a silica gel column (150 A pore size and 75-150 μ particle size).

Absorption spectra were measured using a Cary 14 spectrophotometer. The porphyrin solutions were prepared by dissolving approximately 1.25 mg of porphyrin in 50 ml of methylcyclohexane and a subsequent 20:1 solvent: solution dilution. Spectra were obtained at 25°C.

9.3.3 Results

The experimental data are given in Table 9-7; corresponding calculational data are set out in Table 9-8.

TABLE 9-7
ABSORPTION DATA

Compound	Q _x	Q _y	Soret
ZnTFPP	544 nm		412 nm
ZnTFPPCl ₈	575 nm		442 nm
ZnTFPPBr ₈	596 nm		464 nm
TFPP	584 nm	506 nm	412 nm
TFPPCl ₈	624 nm	536 nm	436 nm
TFPPBr ₈	640 nm	553 nm	452 nm

TABLE 9-8
CALCULATED BAND POSITIONS

Compound	Q _x	Q _y	Soret _x	Soret _y
ZnTFPP	508 nm	508 nm	319 nm	317 nm
ZnTFPPCl ₈	535 nm	533 nm	329 nm	328 nm
ZnTFPPBr ₈	545 nm	543 nm	339 nm	338 nm
TFPP	585 nm	515 nm	332 nm	330 nm
TFPPCl ₈	626 nm	611 nm	384 nm	382 nm
TFPPBr ₈	652 nm	636 nm	401 nm	399 nm

9.3.4 Discussion

Examination of Tables 9-7 and 9-8 shows that the calculations reproduce the experimental trends. As the size of the substituents increases, the red shift in the absorption spectrum increases. Thus, porphyrins with hydrogen at the beta (pyrrolic) positions exhibit the highest energy transitions, whereas those compounds with bromine in the pyrrolic positions have the lowest energy transitions. In order to ascertain the source of this red shifting, the four-orbital transition energies were examined. The data are displayed in Figure 9-9. The orbital energies are given in Table 9-9. It seems clear that the red shifting is caused by sterically induced distortion; if electronegativity of the ligands were the key factor, chlorine would red shift more than bromine. Figure 9-9 shows that as the ligands get bulkier, the four-orbital transition energies decrease. This decrease in transition energies causes the red shifting of the bands. Table 9-9 shows that the energies of the filled orbitals decrease with increasing electronegativity of substituents. However, the unfilled orbitals are stabilized to a greater extent than filled orbitals. Thus, the energy gap between the occupied and the unoccupied orbitals decreases, thereby shifting the absorption bands to lower energy.

In order to unambiguously determine the effect of bending of the porphyrin ring, the following calculation was performed; the bromines of TFPPBr₈ were removed and replaced with hydrogens, while the geometry of TFPPBr₈ was retained. Since steric factors were not changed, the only variable examined is the electronegativity of the ring substituent. The results of this calculation are given in Table 9-10.

It is clear that if the electronic effects of bromine caused the red shifting then replacement of the bromines with hydrogens should have reduced the red shifting of the bands by a significant amount. However, the bands of the bent TFPP are still significantly red shifted compared with the transition energies of the planar TFPP. The data in Table 9-10 also show that the absolute energies of the orbitals are much lower when bromine is the ring substituent rather than hydrogen. Thus, the electronic effect of bromine is to lower the overall orbital energies.

FIGURE 9-9
FOUR ORBITAL TRENDS

ZnTFPP

$$b_1 \longrightarrow c_2 \quad E = 5.78 \text{ eV}$$

$$b_2 \longrightarrow c_1 \quad E = 5.33 \text{ eV}$$

$$b_1 \longrightarrow c_1 \quad E = 5.63 \text{ eV}$$

$$b_2 \longrightarrow c_2 \quad E = 5.47 \text{ eV}$$

ZnTFPPCl₈

$$b_1 \longrightarrow c_2 \quad E = 5.57 \text{ eV}$$

$$b_2 \longrightarrow c_1 \quad E = 5.33 \text{ eV}$$

$$b_1 \longrightarrow c_1 \quad E = 5.53 \text{ eV}$$

$$b_2 \longrightarrow c_2 \quad E = 5.37 \text{ eV}$$

ZnTFPPBr₈

$$b_1 \longrightarrow c_2 \quad E = 5.62 \text{ eV}$$

$$b_2 \longrightarrow c_1 \quad E = 5.21 \text{ eV}$$

$$b_1 \longrightarrow c_1 \quad E = 5.51 \text{ eV}$$

$$b_2 \longrightarrow c_2 \quad E = 5.33 \text{ eV}$$

TABLE 9-9
ORBITAL ENERGIES

Compound	b ₁	b ₂	c ₁	c ₂
TFPP	-8.66 eV	-8.43 eV	-2.27 eV	-2.15 eV
TFPPCl ₆	-9.73 eV	-9.65 eV	-3.56 eV	-2.99 eV
TFPPBr ₆	-9.13 eV	-9.02 eV	-2.91 eV	-2.69 eV
ZnTFPP	-8.60 eV	-8.29 eV	-2.97 eV	-2.82 eV
ZnTFPPCl ₆	-8.87 eV	-8.67 eV	-3.34 eV	-3.30 eV
ZnTFPPBr ₆	-8.88 eV	-8.60 eV	-3.38 eV	-3.26 eV

TABLE 9-10
TEST OF STERIC EFFECTS

Compound	Q _x	Q _y	Soret _x	Soret _y
TFPP no bending	585 nm	515 nm	332 nm	330 nm
TFPPBr ₆	652 nm	636 nm	401 nm	399 nm
TFPP bent structure	643 nm	624 nm	391 nm	389 nm
Orbital Energies	b ₁	b ₂	c ₁	c ₂
TFPP bent structure	-8.63 eV	-8.57 eV	-2.34 eV	-2.08 eV
TFPPBr ₆	-9.13 eV	-9.02 eV	-2.91 eV	-2.69 eV

The red shift in spectra with increased bending of the porphyrin ring can be attributed to a loss in orbital overlap within the porphyrin ring. As the porphyrin ring buckles, the p_z type molecular orbitals cannot overlap as efficiently. Thus, the antibonding interactions decrease, lowering the energy of the orbitals. Upon examination of Figure 2, it is clear that the antibonding interactions are much more significant in the unoccupied orbitals; hence the energy reduction is much greater in these orbitals compared with the filled orbitals, decreasing the overall transition energy.

9.3.5 Conclusions

1. The red shifting in the absorption spectrum is due to the contractions of the energy gap between the HOMOs and LUMOs, which is a result of the distortion of the porphyrin ring.
2. The electronic effect of the halogens is to lower the absolute energies of the orbitals, thereby explaining the increased stability of the porphyrin to ring oxidation.

9.3.6 References

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9.4 ELECTRON AFFINITY STUDIES OF IRON HALOPORPHYRIN COMPLEXES

In past quarterly reports we have described the method used to determine the electron affinity of metalloporphyrin complexes. This serves as a gas phase check on the ease of reduction of iron(III) to iron(II) and is expected to relate to both solution phase reduction potential and to catalytic activity.

Table 9-11 shows the relationships between electron affinity, reduction potential and catalytic activity for a series of iron haloporphyrin complexes. Indeed there is correspondence between electron affinity and reduction potential, and therefore to catalytic activity. We have also determined gas phase electron affinity for the complexes $\text{Fe}(\text{TPP}\beta\text{-Cl}_8)\text{Cl}$ (0.2.10ev), $\text{Fe}(\text{TPP}\alpha\text{-Cl}_8\beta\text{-Cl}_8)\text{Cl}$ (2.93ev), and $\text{Fe}(\text{TPPCl}_{28})\text{Cl}$ (2.93ev), although these results are preliminary and must be refined. These numbers correspond qualitatively with reduction potentials determined by cyclic voltammetry.

9.4.1 Results and Discussion

Another means of determining the ease of reduction of an iron(III) center is to determine its' gas phase electron affinity. This should vary in the same way with electron withdrawal from the porphyrin ring as does reduction potential. This measurement is, however, free from solvent effects and will be confirmatory of the ease of adding an electron to the metal center.

TABLE 9-11

**RELATIONSHIPS BETWEEN ELECTRON AFFINITY,
REDUCTION POTENTIAL AND CATALYTIC ACTIVITY**

<u>COMPOUND</u>	<u>EA (ev)E</u>	<u>E_{1/2}(ev)^a</u>	<u>ACTIVITY^b</u>
Fe(TPP)Cl	2.15	-0.221	0
Fe(TPPF ₂₀)Cl	3.15	+0.007	1160
Fe(TPPF ₂₀ ^β -Cl ₈)Cl	c	+0.28	1800

a Cyclic voltammetry in CH₂Cl₂ vs. SCE, TBAC-supporting electrolyte, glassy carbon electrode

b Catalyst turnovers for 60°C isobutane oxidations in benzene.

c This complex thermally autoreduced at 300°C during vaporization producing Fe(II)(TPPF₂₀^β-Cl₈) and Cl.

The method used to determine the electron affinity of a metalloporphyrin involves the Fourier transform ion cyclotron resonance mass spectrometry (FTMS) technique (Buchanan, M.V., et al., Fourier Transform Mass Spectroscopy, American Chemical Society, Washington, DC., 1987, p. 1-20.) The experiment is done under high vacuum where ions are formed by electron impact or electron attachment and trapped using a combination of electric and magnetic fields. After pulsing the electron gun to form the ions they are stored for a variable reaction time during which they react with neutral molecules present. After the reaction time the concentrations of the various ionic species in the trap are determined. This analysis is done by exciting the ions at their cyclotron frequencies and detecting currents induced in antenna electrodes as a result of this cyclotron motion of the charged particles. The signal thus obtained which consists of a mixture of signals at the cyclotron frequencies of all the ions is digitized and Fourier transformed to obtain a mass spectrum. The particular instrument used is an FTMS-1000 (EXTREL FIMS, Madison, WI) located in the Chemistry Department of the University of Delaware.

A schematic diagram of the equipment is shown in Figure 9-10. Volatile samples are introduced to the vacuum system through a standard batch inlet system. Involatile samples such as the metalloporphyrins are introduced with a heated solid sample probe. In a typical experiment the metalloporphyrin is introduced on the probe. On heating the sample a low pressure of the metalloporphyrin is generated in the vacuum system. A reference electrophile of known electron affinity is admitted through the batch inlet. The electron beam is pulsed on for 10 msec. at an energy of 4 eV. The anions of both the metalloporphyrin and the electrophile are formed and charge transfer between the two species occurs. The ionic contents of the trap are examined as a function of time until it is clear that the charge transfer has come to equilibrium. From the ratio of ion concentrations at equilibrium and the ratio of neutral pressures the equilibrium concentration for the charge transfer reaction can be established. Hence the free energy change can be established. This procedure has successfully given electron affinities for several nickel porphyrins (Chen, H.L., Pan, Y.H., Groh, S., Hagan, T.E. and Ridge, D.P., J. Am. Chem. Soc., 1991, **113**, 2766-2767). Ionization potentials can be determined in an analogous way by monitoring charge transfer between a metalloporphyrin cation and an electron donating species of known ionization potential (e.g. ferrocene).

To date the electron affinities of three iron porphyrin complexes have been determined. Table 9-12 shows the increase in electron affinities in the order: $\text{Fe}(\text{TPP}) < \text{Fe}(\text{TPPF}_{20}) < \text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)$.

We are also using this technology to study the reactions of metalloporphyrins with oxygen atom donors to attempt to gain insight into the formation and stability of ferryl and other metal oxo complexes. To identify reaction intermediates, iron porphyrin anions are introduced into the ion trap as described above. A neutral O atom donor such as NO_2 is introduced through the batch inlet system. Any oxo species generated is then further examined. The Oxo metalloporphyrins can be transferred to a second trap where their chemistry with alkanes is examined. We have found that cations of $\text{Fe}(\text{TPP})$ and $\text{Fe}(\text{TPPF}_{20})$ react with NO_2 in the presence of isobutane to form $\text{M}(\text{OH})^+$ and $\text{M}(\text{NO})^+$. $\text{Fe}(\text{TPPF}_{20}\text{Cl}_8)^+$ reacts very slowly with NO_2 and gives only $\text{M}(\text{OH})^+$.

The interpretation of these results is that a) the following reaction occurs:

just as is postulated in biological systems and that b) the MO bond strength for the TPP complex is >73.4 kcal/mole while that of the $\text{TPPF}_{20}\text{Cl}_8$ complex is less than this. Perhaps, therefore the O-atom donor properties of the metalloporphyrin complexes are important in hydrocarbon oxidation and ferryl complexes formed in electron deficient systems are more active than those formed in TPP complexes.

FIGURE 9-10

FTMS DETERMINATION OF ELECTRONM AFFINITY

Involatile compounds were introduced into ICR cell by heating them in a probe mounted capillary tube. The pressure is controlled by controlling the temperature of the probe.

TABLE 9-12

ELECTRON AFFINITY OF IRON PORPHYRINS

<u>COMPOUND</u>	<u>EA(eV)</u>
Fe(TPP)Cl	1.87
Fe(TPPF ₂₀)Cl	1.98
Fe(TPPF ₂₀ β -Cl ₈)Cl	> 2.28

9.5 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) STUDIES OF IRON HALOPORPHYRIN COMPLEXES

The electronic structure of nitrogen in a porphyrin affects the binding ability and therefore the redox potential of the central metal in a metalloporphyrin. The electronic structure of the nitrogen can be modified by functional groups attached to the porphyrin. When tetraphenylporphyrin is modified by halogen groups, the corresponding Fe(III) porphyrins show a great improvement in light alkane oxidation activity. X-ray Photoelectron Spectroscopy (XPS) is an effective tool to differentiate the change in the electronic structure of nitrogen and/or the central metal by measuring XPS core level binding energies of nitrogen and the central metal ion (1-4). The present XPS study examines some porphyrins and iron porphyrins recently developed for the oxidation of light alkanes.

9.5.1 X-ray Photoelectron Spectroscopy (XPS or ESCA)

XPS studies were carried out using a Kratos Xsami surface analysis system. The system is equipped with a dual anode X-ray source (Mg and Al anode) and hemispheric analyzer. This study used only Al Ka=1486.6 eV radiation operated at 180 W (12 mA, 15 kV). The X-ray gun was set 15mm away from the sample to reduce possible damage to porphyrin samples by heat generated in the X-ray source. The base pressure in the main chamber was below 5×10^{-9} torr. Porphyrin samples were prepared on a gold foil in a way similar to that reported by Karweik and Winograd (5). The gold foil was then mounted on a stainless sample holder. The sample holder was then attached to a direct insertion probe which can be heated to 300°C or cooled under a liquid nitrogen flow and transferred to the main chamber for analysis. In this study the experiments were conducted at room temperature.

XPS spectra were acquired using the Kratos Vision software. Binding energy (BE) measurement was referenced to Au 4f7/2 = 84.1 eV. For N1s the BE measurements were reproducible within +/- 0.2 eV. For Fe_{2p}3/2 the BE measurements were reproducible within +/- 0.2 eV. When F is present, a strong energy loss peak of the F1s line overlaps with the Fe_{2p}3/2 line and affects the accuracy of the Fe_{2p}3/2 BE measurements. In this case the measurements are reproducible within +/- 0.5 eV. The BE results reported were an average of 2-3 measurements. We are currently negotiating with Kratos to modify the data reduction software so that the F1s energy loss line can be subtracted and hence an improvement in the accuracy of Fe_{2p}3/2 BE measurements can be obtained. Curve fitting of the N1s spectrum was achieved using the curve fitting routine in the Kratos Vision software. The N1s spectra were resolved assuming a peak shape of 50-50 Gaussian-Lorentian combination and an equal full-width-half-maximum (FWHM) for both aza and pyrrole nitrogens in the free base porphyrins.

9.5.2 Materials

Tetraphenylporphyrin (H₂TPP), tetrakis(pentafluorophenyl)-porphyrin (H₂TPPF₂₀), Fe(III)TPP₂Cl and Fe(III)TPPF₂₀Cl were purchased from Aldrich Chemical Co. μ -oxo-(Fe(III)TPP)₂O was obtained from Strem Chemicals Inc. All the above chemicals were used as received. Tetrakis(pentafluorophenyl) β -octabromoporphyrin (H₂TPPF₂₀Br₈) was synthesized by Sun.

9.5.3 Free Base Porphyrins

Three free base porphyrins: tetraphenylporphyrin (H₂TPP), tetrakis(pentafluorophenyl)porphyrin (H₂TPPF₂₀) and tetrakis-(pentafluorophenyl) β -octabromo-porphyrin (H₂TPPF₂₀Br₈) were examined.

The XPS N1s spectrum of H₂TPP is shown in Figure 9-11a. The spectrum can be curve fitted into two sets of N1s lines. Each set contains a main peak and a satellite line 2.9 eV away from the main peak. The lower binding energy set (main peak=398.0 eV) is assigned to the aza nitrogen (N:) and the higher binding energy set is assigned to the pyrrole nitrogen (N:H) in the porphyrinato ring. The binding energy (BE) difference between the two main N1s peaks is 2.1 eV. The XPS N1s spectra of H₂TPPF₂₀ and H₂TPPF₂₀Br₈ also show two sets of N peaks. The results of binding energy measurements are summarized in Table 9-13.

From Table 9-13, it is clear that modification of the porphyrinato ring with halogen groups results in an increase in the XPS N1s BE. Replacing phenyl group with pentafluorophenyl group, increases N1s BE by 0.8 eV for aza and pyrrole nitrogens. Introduction of the bromo group to the beta position of H₂TPPF₂₀ results a further increase of 0.4 eV in the N1s BE. The increase in the N1s BE suggests a lower electron density of nitrogen in the halogen modified porphyrins than H₂TPP. The lower electron density can be attributed to the strong electron withdrawing properties of F and Br.

Hollander and Shirley(6) have compared the correlation of N1s BEs with atomic charges calculated by (a) CNDO (b) an extended Huckel method and (c) Pauling valence bond method. They concluded that the range of CNDO charges were the most plausible and resulted in the following equation:

$$\Delta E / \Delta Q = 10 \text{ eV}$$

Where ΔE is the BE shift in eV and ΔQ is the change in the electron density. Fadley *et. al.* (7) and Siegbahn *et. al.* (8) have shown that the relation between core level BE shift and the valence electron density change can be extended to all elements. Based on the above equation suggested by Hollander and Shirley, the results of N1s BE measurements indicate that the addition of a H⁺ to N reduced electronic charge by 0.21 electron. Modification of the porphyrin by replacing the 20 phenyl H's by 20 F atoms in the four phenyl rings reduces electronic charge of N by 0.08 electron. Further modification of H₂TPPF₂₀ with 8 bromo groups in the beta position reduces 0.04 electron from each N.

TABLE 9-13

RESULTS OF XPS BINDING ENERGY MEASUREMENTS

Sample	<u>BINDING ENERGY (eV)</u>			
	N1s		Fe _{2p} 3/2	
	Aza N	pyrrole N	Metallo N	
H ₂ TPP	398.0	400.1		
H ₂ TPPF ₂₀	398.8	400.9		
H ₂ TPPF ₂₀ Br	399.2	401.3		
Fe(III)TPPCI	-		399.0	711.6
FeTPPF ₂₀ -		399.4	713.2	
(Fe(III)TPP) ₂ O	-		398.2	710.4

FIGURE 9-11a XPS SPECTRUM OF H_2TPP

FIGURE 9-11b XPS SPECTRUM OF $Fe(TPP)Cl$

Kadish *et. al* have also correlated XPS $\text{Fe}_{2p3/2}$ BEs with half-wave potentials for reduction of Fe(III) to Fe(II) for a series of Fe(III)TPPX and FeOEP(III)X where X = ClO_4 , Cl, Br or N_3 (1). They found a linear relationship between $\text{Fe}_{2p3/2}$ BEs and the half-wave potentials. Their results are reproduced in Figure 9-14 (open circles). When our data for Fe(III)TPPCl and Fe(III)TPPF₂₀Cl are included in Figure 9-14 (filled circles), the trend remains. Thus the relationship between $\text{Fe}_{2p3/2}$ BE and half-wave potential for reduction of Fe(III) to Fe(II) seems also to apply to Fe(III)TPPCl and Fe(III)TPPF₂₀.

9.5.4 Iron Porphyrins

Three iron porphyrins were examined; Fe(III)TPPCl, μ -oxo-(Fe(III)TPP)₂O and Fe(III)TPPF₂₀.

Figure 9-11b shows the XPS N1s spectrum of Fe(III)TPPCl. Only one set of N1s main peak (BE = 399.0 eV) with a shake satellite was observed. Similar N1s spectrum was observed for the other two iron porphyrins. The observation of only one set of N 1s peaks indicates that Fe(III) bonds equally to four nitrogens in the porphyrin. The N1s BEs of those iron porphyrins are summarized in Table 9-13.

The N1s BEs of Fe(III)TPPCl and μ -oxo-(FeTPP)₂O are 0.9 and 0.2 eV higher than the aza N of H₂TPP respectively. The N 1s BE of Fe(III)TPPF₂₀ is 0.7 eV higher than that of the aza N of H₂TPPF₂₀. The results indicate that although the Fe of μ -oxo-(FeTPP)₂O is in the 3+ state, it does not modify the electron density of N as extensively as the Fe^{3+} in FeTPP or FeTPPF₂₀. The results also indicate that the effect of Fe^{3+} ions on the N1s electron density is stronger for FeTPP than FeTPPF₂₀ (1.0 vs 0.6 eV).

FIGURE 9-12

XPX Fe_{2p} SPECTRA OF Fe(III)TPPCI(a),Fe(III)

TPPF₂₀Cl(b), AND OXO-(FeTPP)₂O(c)

Figure 9-12 shows the XPS Fe_{2p} spectra of Fe(III)TPPCl (2a), $\text{Fe(III)TPPF}_{20}\text{Cl}$ (2b) and $\mu\text{-oxo-(FeTPP)}_2\text{O}$ (2c). The $\text{Fe}_{2p3/2}$ BEs of the iron porphyrins, measured from peak maximum, are also listed in Table 9-13. $\text{FeTPPF}_{20}\text{Cl}$ shows the highest $\text{Fe}_{2p3/2}$ BE and $(\text{FeTPP})_2\text{O}$ shows the lowest $\text{Fe}_{2p3/2}$ BE. Comparing FeTPPCl with $(\text{FeTPP})_2\text{O}$, it seems that the higher the $\text{Fe}_{2p3/2}$ BE the higher is the N1s BE. However, Kadish *et. al.* studied a series of Fe(III)TPPX where $\text{X} = \text{Cl, Br, ClO}_4$ or $\text{N}_3(1)$. They observed that $\text{Fe}_{2p3/2}$ binding energies have little effect on N 1s BE. Their $\text{Fe}_{2p3/2}$ BEs for FeTPPCl and $(\text{FeTPP})_2\text{O}$ are similar to our results. They, however, only observed a 0.2 eV (vs 0.8 eV in this study) difference in N1s BEs between FeTPPCl and $(\text{FeTPP})_2\text{O}$. The reason for this inconsistency between their and our results is not clear at this moment.

FIGURE 9-14

XPS Fe_{2p}3/2 BE vs. Fe(III)/Fe(II)

REDUCTION POTENTIAL

9.5.5 References

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9.6 ELECTRONIC SPECTROSCOPY OF HALOPORPHYRIN COMPLEXES

9.6.1 UV/Visible Spectroscopy of $M(II)(TPPF_{20\beta}-Y_8)$

We have proposed that constant regeneration of Fe(II) during oxidation due to high Fe(III)/Fe(II) reduction potentials is the key to active alkane oxidation catalysts. Although Fe(II) complexes may not be air stable and therefore inconvenient to analyze spectroscopically, many stable metal(II) porphyrin complexes exist and their UV/Visible spectra have now been recorded. Table 9-14 lists the positions of the Soret bands for the complexes $M(II)(TPPF_{20\beta}-Cl_8)Cl$ and $M(II)(TPPF_{20\beta}-Br_8)Cl$. For first row group VIII transition metals, Soret absorptions between 428 and 439 nm are observed.

9.6.2 Electronic Structure of Halogenated Metalloporphyrins

The absorption bands of a series of halogenated porphyrins shift to lower energies as the size of the porphyrin substituents increases. AM1 calculations show that the red shifting in the absorption spectrum is due to a decrease in the HOMO-LUMO energy gap, which is a result of the distortion of the porphyrin ring. As we pointed out previously, the electronic effect of the halogens is to lower the absolute energies of the orbitals. During the past quarter geometry optimizations were improved to increase the accuracy of the calculations. As a result, the geometries became less distorted causing a decrease in the transition energies, Table 9-15. At this point, $TPPF_{20\beta}-Cl_8$ and $TPPF_{20\beta}-Br_8$ are available in their final geometries.

TABLE 9-14
SORET POSITIONS

Chlorinated Porphyrins^a

Metal	Soret λ
Palladium	423
Cobalt	428
Copper	430
Nickel	439
Zinc	440
Silver	494

Brominated Porphyrins^b

Metal	Soret λ
Palladium	431
Copper	436
Nickel	433
Zinc	466
Silver	508

^a M(TPPF₂₀ β -Cl₈)

^b M(TPPF₂₀ β -Br₈)

TABLE 9-15
PORPHYRIN CALCULATIONS

Absorption data

Compound	Q _x	Q _y	Soret
TFPPCl ₈	624 nm	536 nm	436 nm
TFPPBr ₈	640 nm	553 nm	452 nm

Calculated data

Compound	Q _x	Q _y	Soret _x	Soret _y
TFPPCl ₈	513 nm	506 nm	342 nm	340 nm
TFPPBr ₈	558 nm	533 nm	354 nm	350 nm

Orbital Energies

	b ₁	b ₂	c ₁	c ₂
TFPPCl ₈	-9.07	-9.08	-2.77	-2.57
TFPPBr ₈	-8.97	-9.03	-2.92	-2.90

10.0 TESTING OF ELECTRON DEFICIENT PORPHYRIN COMPLEXES

10.1 OXIDATION OF ISOBUTANE

10.1.1 Oxidations in Small Tubular Reactors

Table 10-1 compares the results of the oxidations of isobutane carried out in benzene solution in the presence of either Fe(TPP)Cl or Fe(TPPF₂₀)Cl. The enormous enhancements in oxidation activity by using a TPP-type catalyst having halogenated phenyl groups is readily apparent. We then replaced the remaining eight pyrrolic H's with halogens and tested the activity of these complexes.

Table 10-2 gives the cumulative results of testing of the sixteen (TPPF₂₀β-Br₈) complexes which were synthesized and characterized. Tests were conducted at 60°C or lower in glass aerosol vessels connected to gas delivery manifolds. Stirring was accomplished with magnetic stirring bars and the solutions were heated in constant temperature silicone oil baths. It can be seen that in this ligand series, iron is far superior to either chromium or manganese as a central metal. Although many manganese and chromium complexes of the perhaloporphyrin series had been shown in earlier reports to have modest activity at or above 80°C, few of these complexes exhibited activity at 60°C or lower. Thus the lower temperature reactions clearly discriminate between iron and other metals very well with regard to catalytic activity. The copper and ruthenium complexes described above demonstrated little or no isobutane oxidation activity.

TABLE 10-1
METALLOPORPHYRIN CATALYZED OXIDATION OF ISOBUTANE AT 80°

<u>CATALYST</u>	<u>m moles CATALYST</u>	<u>CATALYST TURNOVERS</u>	<u>SELECTIVITY TO tert-BUTYL ALCOHOL%</u>
Fe(TPP)Cl	0.025	0	-
Fe(TPPF ₂₀)Cl	0.016	2040	90
Mn(TPP)OAc	0.050	0	-
Mn(TPPF ₂₀)OAc	0.016	0	-
Cr(TPP)Cl	0.025	0	-
Cr(TPPF ₂₀)Cl	0.016	0	-
Fe(TPP)N ₃	0.013	130	93
Fe(TPPF ₂₀)N ₃	0.016	2060	89
Mn(TPP)N ₃	0.013	180	88
Mn(TPPF ₂₀)N ₃	0.016	750	87
Cr(TPP)N ₃	0.025	280	89
Cr(TPPF ₂₀)N ₃	0.016	450	97
[Fe(TPP) ₂ N]	0.013	0	-
[Fe(TPPF ₂₀) ₂ N]	0.013	0	-
[Fe(TPP) ₂ O]	0.013	0	-
[Fe(TPPF ₂₀) ₂ O]	0.007	1730	92

Time = 6 hrs., Isobutane - 6-7g., Oxygen = 100 psig, Benzene - 25 ml

TABLE 10-2

ISOBUTANE OXIDATIONS CATALYZED BY (TPPF₂₀-β-Br₈) COMPLEXES

	<u>mmoles</u>	<u>T, °C</u>	<u>t, Hr.</u>	<u>T.O.^b</u>	<u>TBA Sel. %^c</u>
Fe(TPPF ₂₀)OH	0.013	60	6	1090	88
Fe(TPPF ₂₀ -β-Br ₄)OH	0.013	60	6	1220	86
Fe(TPPF ₂₀ -β-Br ₈)OH	0.013	60	6	1620	86
Fe(TPPF ₂₀ -β-Br ₈)Cl	0.013	60	6	1890	91
		40	6	690	90
		27	6	130	90
		27	124	2580	91
Fe(TPPF ₂₀ -β-Br ₈)N ₃	0.013	60	6	1550	87
		40	6	670	89
		27	6	620	na
		27	53	3180	90
Fe(TPPF ₂₀ -β-Br ₈)Br	0.013	60	6	1490	87
		40	6	470	89
		24	24	470	
<hr/>					
Mn(TPPF ₂₀)OAc	0.013	60	6	0	
Mn(TPPF ₂₀ -β-Br ₈)OH	0.013	60	6	0	
Mn(TPPF ₂₀ -β-Br ₈)Br	0.013	60	6	0	
Mn(TPPF ₂₀ -β-Br ₈)Cl	0.013	60	6	110	87
Mn(TPPF ₂₀ -β-Br ₈)N ₃	0.013	60	6	270	87
Mn(TPPF ₂₀ -β-Br ₈)F	0.013	60	6	300	98
<hr/>					
Cr(TPPF ₂₀)Cl	0.013	60	6	0	
Cr(TPPF ₂₀ -β-Br ₈)Cl	0.013	60	6	0	
Cr(TPPF ₂₀ -β-Br ₈)Br	0.013	60	6	0	
Cr(TPPF ₂₀ -β-Br ₈)F	0.013	60	6	0	
Cr(TPPF ₂₀ -β-Br ₈)N ₃	0.013	60	6	110	92
		40	6	0	
<hr/>					
Cu(TPPF ₂₀ -β-Br ₈)	0.013	60	6	45	na
Ru(TPPF ₂₀ -β-Br ₈)CO	0.013	60	6	0	
Ru(TPPF ₂₀ -β-Br ₈)(OEt ₂)O	0.013	60	6	0	

TABLE 10-2 (Contd.)

- a A solution of the catalyst in 25 ml benzene containing 6 grams of isobutane was stirred at the designated temperature under 100 psig of O₂ for the designated time.
- b Moles O₂ consumed/mole catalyst used.
- c (Moles t-butyl alcohol produced/total moles liquid product) X 100.

Table 10-3 gives the results of isobutane oxidations catalyzed by metal complexes of the perhaloporphyrins $\text{TPPF}_{20}\beta\text{-Cl}_8$. Again iron complexes were superior to those of the other metals which were examined.

10.1.2 Oxidations in a 300 ml Autoclave

10.1.2.1 Oxidations Catalyzed by $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$

10.1.2.1.1 Semicontinuous Operation

Table 10-4 shows the results of a semi-continuous oxidation of isobutane to tert-butyl alcohol in the absence of solvent. Alcohol selectivities exceeded 90% at temperatures at or below 60°C and productivities in excess of 8,000 moles product per mole catalyst were obtained in three hours. The liquid reactor effluent was analyzed immediately after being removed from the reactor, Table 10-5 and then after vacuum distillation away from the catalyst, Table 10-6. No polymeric residue was left behind, and except for some peroxidic moieties which should be destroyed, and a small amount of acetone, the product was quite suitable for use as gasoline grade TBA.

10.1.2.1.2 Conceptual Plant Design

Because the catalytic activity of $\text{Fe}[\text{TPPF}_{20}\beta\text{-Br}_8]\text{Cl}$ for isobutane oxidation is so high and reaction selectivity for t-butyl alcohol so good, we have begun to plan for a possible eventual pilot plant and commercial operation. Figure 10-1 describes a conceptual plant design. First pass economic analysis indicates that reaction rates must increase by a factor of at least four and that $\text{Fe}[\text{TPPF}_{20}\beta\text{-Br}_8]$ is as much as an order of magnitude too costly for commercial application in this way. Design of future PHASE I catalysts is being done with reduction in catalyst cost as a major consideration.

TABLE 10-3
ISOBUTANE OXIDATIONS CATALYZED BY PERHALOPORPHYRIN COMPLEXES^a

	<u>T, °C</u>	<u>T.O.^b</u>	<u>TBA SEL., %</u>
Fe(TPPF ₂₀ β-Br ₈)Cl	60	1890	91
	40	690	90
	27	130	90
Fe(TPPF ₂₀ β-Br ₈)N ₃	60	1550	87
	40	670	89
	27	620	na
Fe(TPPF ₂₀ β-Cl ₈)Cl	60	1710	89
	40	760	90
	27	220	91
Fe(TPPF ₂₀ β-Cl ₈)N ₃	60	1800	90
	40	760	92
Cr(TPPF ₂₀ β-Cl ₈)Cl	60	70	na
Cr(TPPF ₂₀ β-Cl ₈)N ₃	80	450	88
Mn(TPPF ₂₀ β-Cl ₈)Cl	80	0	-
Mn(TPPF ₂₀ β-Cl ₈)Cl(NaN ₃) ^c	80	1289	86
Mn(TPPF ₂₀ β-Cl ₈)Cl	60	0	-
Mn(TPPF ₂₀ β-Cl ₈)ClNaN ₃ ^c	60	156	88
Co(TPPF ₂₀ β-Cl ₈)	60	355	91

^a Isobutane (7g) was oxidized (6 hrs.) in 25 ml benzene at the designated temperature under 100 psig oxygen using 0.013 mmole of the designated catalyst.

^b Moles of oxygen consumed/mole catalyst used.

^c After warming the reaction mixture for 6 hrs. as indicated in footnote^a, the reaction mixture was cooled to room temperature, 10 mg of NaN₃ added and the procedure repeated according to footnote^a. The T.O. are calculated based on the second 6 hrs. period.

TABLE 10-4

IRON HALOPORPHYRIN-CATALYZED ISOBUTANE OXIDATIONS^a

Catalyst	T, C	Charge to Reactor		Reaction Products, mmoles					Conversion	Select.	TON ^c
		t, Hrs.	i-C ₄ H ₁₀	O ₂	TBA	Acetone	CO ₂	CO	i-C ₄ H ₁₀ , %	TBA, % ^b	
Fe(TPPF ₂₀ -β-Br ₈)Cl	80	3	1870	53	277	43	23	8.0	17	87	10,660
	80	3	1862	100	429	86	26	4.9	28	83	17,150
	80	3	1862	148	414	81	28	6.0	27	84	16,500
	80	3	1869	205	290	45	37	10.5	18	87	11,180
	60	3	1865	47	230	23	20	tr	14	91	8,420
	60	3	1874	139	184	18	17	tr	11	91	6,730
	25	71.5	1862	53	372	35	27	tr	22	92	13,560
Fe(TPPF ₂₀)OH	24	143	1871	53	332	17	18	0	18	95	12,150

^a Isobutane was oxidized by an oxygen-containing gas mixture (75 atm, diluent = N₂) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

^b (moles TBA/moles liquid product) X 100.

^c moles (TBA + Acetone) produced/mole catalyst used.

TABLE 10-5
LIQUID REACTOR EFFLUENT FROM ISOBUTANE OXIDATION^a

<u>PEAK</u>	<u>COMPOUND</u>	<u>WT. %</u>
1	Isobutane	3.36
2	t-Butylisopropylether	0.28
3	Methyl Formate	0.33
4	Di-t-Butyl Peroxide	1.99
5	Isopropyl-t-Butyl Peroxide	0.19
6	Acetone	3.89
7	t-Butyl Formate	0.09
8	t-Butyl Alcohol	86.66
9	Isobutyl-t-Butyl Peroxide	0.38
10	Isopropyl Alcohol	1.28
11	Isobutyl Formate	0.05
12	Isobutyl Alcohol	1.23
13	t-Butyl Hydroperoxide	0.09
14	Isobutyric Acid.	<u>0.14</u>
	TOTAL	99.96

^a Isobutane was oxidized by an oxygen-containing gas mixture (75 atm, diluent = N₂) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

TABLE 10-6

DISTILLED LIQUID PRODUCTS FROM ISOBUTANE OXIDATION^a

<u>PEAK</u>	<u>COMPOUND</u>	<u>WT. %</u>
1	Isobutane	0.06
2	t-Butyisopropylether	0.28
3	Methyl Formate	-
4	Di-t-Butyl Peroxide	2.12
5	Isopropyl-t-Butyl Peroxide	0.17
6	Acetone	3.82
7	t-Butyl Formate	0.09
8	t-Butyl Alcohol	90.60
9	Isobutyl-t-Butyl Peroxide	0.27
10	Isopropyl Alcohol	1.16
11	Isobutyl Formate	0.07
12	Isobutyl Alcohol	1.18
13	t-Butyl Hydroperoxide	-
14	Isobutyric Acid.	<u>0.15</u>
	TOTAL	99.97

^a Isobutane oxidized as shown in footnote a, Table 3. After stripping isobutane, product distilled into a chilled (-70°C) trap at 0.5 mm. (temp. = 25 to 90°C). Dry catalyst (< 40 mg.) was left behind. No detectable heavy ends remained in the pot.

FIGURE 10-1

SUN OIL COMPANY
RESEARCH & DEVELOPMENT
MARCUS HOOK, PA.

TBA FROM ISOBUTANE
PROCESS FLOW SCHEME

DESIGNED BY: ALDISA.	DATE: 9-6-90
APP. <i>Lany Intel</i>	DATE:
SCALE N/A	DWG NO.

FIGURE 10-1 (Contd.)
CONCEPTUAL DESIGN

Basis: (Hypothetical - Not Experimental)

Temperature:	75°C
Pressure:	270 psig
Residence Time:	2.5 hr.
Isobutane Conversion:	50%
Oxygen Molar Excess:	10% (based on converted i-C ₄)
Catalyst Concentration:	125 ppm (based on total isobutane feed), once-through basis

Molar Selectivity from Isobutane:

TBA, 92%
Acetone, 6.2%
Peroxides, 0.9%
Others, 0.9%

Reactor Description:

We have not committed to a particular reactor configuration. Heat transfer options call for a chemical engineering optimizing study. No extraordinary materials of construction or operating protocols are envisioned.

Ideas for consideration as design candidates include:

1. Liquid phase, continuous stirred tank, 4-7 zones with series flow through the zones. Heat removal methods for evaluation - not limited to:
 - a. Recirculating liquid cooled 20-25°F in external tubular exchangers.
 - b. Auto-refrigeration by boiling isobutane with reflux pumped back to reaction vessels.
2. Multi-stage bubble column using countercurrent vapor-liquid flow.

Catalyst:

Projected catalyst cost is \$30/lb. We expect that catalyst disposal would be accomplished by ordinary methods such as landfill and/or waste incineration.

10.1.2.2 Oxidations Catalyzed by $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$

We have also compared the activity of $\text{Fe}(\text{TPPF}_{20}\beta\text{-Br}_8)\text{Cl}$ and $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$ in neat isobutane. Again, as shown in Figures 10.2 (80°C) and 10.3 (60°C) their activity appears to be comparable, because the octachloro complex has a lower molecular weight and because chlorine gas is cheaper than bromine, the octachloro complex is a less expensive catalyst. For this reason we have examined its catalytic behavior in more detail. A series of experiments covering a temperature range of 22°C to 80°C, an oxygen partial pressure range of 63 to 210 psi, and a catalyst concentration range of 90 to 740 ppm were conducted. A summary of these runs is presented in Table 10-7.

10.1.2.2.1 Pressure Effects

Table 10-8 presents data from three experiments conducted at three oxygen partial pressures. the initial rates for the three experiments were determined by examining oxygen consumption for the first 15 minutes of reaction when less than 10% of the total conversion has occurred. When these rates are plotted against the oxygen pressure, a rough linear dependence is observed, Figure 4A (Upper).

These experiments were conducted for a 3 hour period, but oxygen consumption ceased at the times shown in the Table. The time at which no further oxygen consumption was observed is plotted against pressure, Figure 10-4B (Lower). All three reactions proceeded to approximately the same extent, and the time required for oxygen uptake diminished as the pressure increased.

TABLE 10-7

OXIDATIONS OF NEAT ISOBUTANE CATALYZED BY $\text{Fe}(\text{TPPF})_2\text{Cl}_8\text{Cl}^a$

CATALYST	REACTION	PO2	MAJOR PRODUCTS, mmoles					iC4
WEIGHT, Mg	TEMP.°C	psi	TBA	ACETONE	CO2	CO	T.O.	CONV.,%
80	60	80	300	22	26	3	5367	17.3
40	80	75	349	41	29	8	13000	21.0
40	80	142	334	38	29	6	12400	19.9
40	80	210	353	38	39	3	13033	20.9
40	60	80	371	25	11	tr	13200	21.2
40	60	142	204	13	12	tr	7233	11.7
40	22	63	366	16	na	tr	12733	20.5
20	80	75	237	24	28	4	17400	14.0
20	60	80	165	9	na	na	17606	9.3
10	80	210	100	7	na	na	14320	5.8

- a** All experiments were conducted in a glass lined batch reactor. A measured weight of catalyst was charged to a nitrogen purged reactor. The reactor pressure was brought to 500 psig and then 1865 mmols of i-C₄ was introduced. Nitrogen was added to raise the pressure to 840 psig and heating to reaction temperature commenced. Once at reaction temperature, oxygen was added to the desired partial pressure. As the reaction proceeded, the reactor pressure dropped. Once the pressure decreased by 20 psi, oxygen was added until the pressure equaled the initial pressure. In later experiments, the oxygen was added via mass flow meter and totalizer providing a measure of oxygen volume introduced.

TABLE 10-8
I-C₄ OXIDATION - INFLUENCE OF PRESSURE AT 80°C

<u>XEPT. #</u>	<u>CAT. WT.</u> <u>(mg)</u>	<u>TEMP.</u> <u>(C)</u>	<u>O₂ PRESSURE</u> <u>psi</u>	<u>INI. RATE</u> <u>mmole O₂</u> <u>per min</u>	<u>CONV. TO</u> <u>LIQ. PROD.</u> <u>(%)</u>	<u>END OF</u> <u>Rxn TON</u>	<u>END OF O₂</u> <u>UPTAKE (min)</u>
347	40	80	75	3.73	21.0%	13000	180
349	40	80	142	5.05	20.0%	12400	165
351	40	80	210	7.67	21.0%	13033	138

FIGURE 10-2
ISOBUTANE OXIDATION AT 80°C

FIGURE 10-3
ISOBUTANE OXIDATION AT 60°C

FIGURE 4A,B
i-C₄ OXIDATION
INITIAL RATES AND CATALYST LIFE

Note: All rxns went to 21% conversion to liquid products.

10.1.2.2.2 Catalyst Life

Table 10-9 presents a set of experiments in which catalyst concentration was varied. The conversion to liquid products increases with the catalyst concentration from 90 to 370 ppm. It is apparent, however, that this catalyst is only able to produce from 13,000 to 17,000 turnovers at 80°C independent of oxygen partial pressure. Similar turnover levels were observed at 60°C but since in these experiments oxygen uptake had not ceased after 3 hours, higher turnovers might ultimately be achieved at the lower temperature than at 80°C. Comparing the 60°C and 80°C experiments reveals that at a catalyst loading of 180 ppm, the higher temperature provides for a faster reaction.

10.1.2.2.3 Summary of Pressure and Catalyst
Life Studies

Initial reaction rate increases with oxygen partial pressure. Early indications are that catalyst utilization is nearly constant with oxygen pressure at 12,000 to 15,000 moles tert-butyl alcohol produced per mole of catalyst at 80°C. Catalyst utilization is at least this high at lower temperatures. These results indicate that the rate of reaction may be increased through higher oxygen pressure without impacting catalyst life.

TABLE 10-9
CATALYST CONCENTRATION EFFECTS ON I-C₄ OXIDATION

C	AT. WT.	CAT. CONC.	TEMP.	O ₂ PRESSURE	CONV. TO	TON	END OF O ₂
<u>EXPT. #</u>	<u>(mg)</u>	<u>(ppm)</u>	<u>(C)</u>	<u>psi</u>	<u>LIQ. PROD.</u>	<u>(%)</u>	<u>UPTAKE (min)</u>
					<u>per min</u>		
347	40	370	80	75	21.0%	13000	180
369	20	185	80	75	14.0%	17400	165
383	10	93	80	210	5.8%	14320	85
353	40	370	60	80	21.2%	13200	>180
367	20	185	60	80	9.3%	11606	85

10.1.2.3 KINETIC STUDIES

The liquid phase oxidation of isobutane was studied in neat isobutane, Table 10-10 using $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$ as catalyst. Kinetic results indicated that reaction appeared to be inhibited by interaction of the product alcohol with the catalyst. Mathematically this can be written, according to Langmuir's expression for reversible complexing:

$$\text{Rate} = K_1[\text{i-C}_4\text{H}_{10}]/(1+K_2[\text{TBA}])$$

The major side reaction produces acetone. In this simplified kinetic model, acetone is assumed to be the only liquid by-product and we further assume that the side-reaction to acetone is directly related to the rate of butane oxidation. the total rate expressions at constant oxygen and catalyst concentrations become:

$$d[\text{TBA}]/dt = K_1[\text{i-C}_4\text{H}_{10}]/(1+K_2[\text{TBA}])$$

$$d[\text{Acet}]/dt = K_3(d[\text{TBA}]/dt)$$

$$d[\text{i-C}_4\text{H}_{10}] = -(1+K_3)(d[\text{TBA}]/dt)$$

These equations correlate quite well with observed products, and rate constants can be estimated for K_1 , K_2 and K_3 . An activation energy of 12 kcal/mole can be estimated for the catalytic oxidation reaction, Figure 10-5.

TABLE 10-10

IRON HALOPORPHYRIN CATALYZED ISOTUTANE OXIDATIONS^a

Catalyst	T°C	t, Hrs	Reaction Products, (mmoles)					CO	CO ₂	Conversion i-C ₄ H ₁₀ (%)	Sel. TBA (%) ^b	TON ^c
			i-C ₄ H ₁₀ (mmols)	(O ₂ (psi)	TBA	Acetone						
Fe(TPPF ₂₀)OH	80	3	1869	53	310	46	7	18	17	87	11,330	
	24	143	1871	53	382	17	0	18	19	95	11,600	
Fe(TPPF ₂₀ ^β -Cl ₈)Cl	80	3	1865	142	334	38	6	29	20	88	12,400	
	21	120	1865	63	366	16	tr	na	20.5	95	12,730	
Fe(TPPF ₂₀ ^β -Br ₈)Cl	80	3	1862	148	414	81	6	28	27	84	16,500	
	80	3	1870	53	277	43	8	23	17	87	10,060	
	24	71	1862	53	372	35	tr	27	22	92	12,150	

^a Isobutane was oxidized by an oxygen-containing gas mixture (75 atm. diluent - N₂) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

^b (moles TBA/Moles liquid product) X 100.

^c Moles (TBA and acetone) produced/mole catalyst used.

TABLE 10-10

IRON HALOPORPHYRIN CATALYZED ISOTUTANE OXIDATIONS^a

Catalyst	T°C	t, Hrs	Reaction Products, (mmoles)					CO	CO ₂	Conversion i-C ₄ H ₁₀ (%)	Sel. TBA (%) ^b	TON ^c
			i-C ₄ H ₁₀ (mmols)	(O ₂ (psi)	TBA	Acetone						
Fe(TPPF ₂₀)OH	80	3	1869	53	310	46	7	18	17	87	11,330	
	24	143	1871	53	382	17	0	18	19	95	11,600	
Fe(TPPF ₂₀ β-Cl ₈)Cl	80	3	1865	142	334	38	6	29	20	88	12,400	
	21	120	1865	63	366	16	tr	na	20.5	95	12,730	
Fe(TPPF ₂₀ β-Br ₈)Cl	80	3	1862	148	414	81	6	28	27	84	16,500	
	80	3	1870	53	277	43	8	23	17	87	10,060	
	24	71	1862	53	372	35	tr	27	22	92	12,150	

Isobutane was oxidized by an oxygen-containing gas mixture (75 atm. diluent - N₂) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

(moles TBA/Moles liquid product) X 100.

Moles (TBA and acetone) produced/mole catalyst used.

FIGURE 10-5

ACTIVATION ENERGY OF K1
 WHERE $d[IB]/dt = K1 \times [PURE \text{ ISOBUTANE}]$
 40 mg. CATALYST , 75-80 psi O_2

<u>RUN</u>	<u>OC</u>	<u>RATE</u>	<u>$\frac{1}{T} \times 10^3$</u>	<u>LN RATE</u>
353	60	1.35	3.003	.3001
347	80	3.73	2.832	1.3164
391	90	5.99	2.755	1.7901

A possible mechanistic interpretation of such a kinetic postulate is shown below:

Complexation of TBA can deactivate the catalyst toward oxygen binding and could slow the rate. The more hindered the binding site the more poorly TBA will coordinate. Interestingly, $\text{Fe}(\text{TPPF}_{20}\beta\text{-Br}_8)\text{Cl}$ appears to bind the alcohol less strongly since it is more highly buckled and may suffer less inhibition of rate than the beta-chloro analog. In addition, the more electron deficient the porphyrin ring system, the more tightly an alcohol might bind. Thus K_2 may be highly dependent on the structure of the catalyst and the degree of inhibition may be influenced greatly by design of catalyst structure. Figures 10-6, 10-7, 10-8, show the hindrance to docking of TBA to an iron as a function of macrocycle structure.

10.1.2.4 MECHANISMS OF ISOBUTANE OXIDATION

In an effort to further understand the mode of operation of the perhaloporphyrin complexes in catalyzing the oxidation of isobutane to tert-butyl alcohol, TBA, we have considered that a possible pathway may involve the catalytic generation of radicals at low temperatures. Under very mild conditions radical reactions may give rise to selective oxidation processes. In this regard we have compared the thermal oxidation of isobutane with that of catalytic oxidation in an attempt to gain further insight into these reactions.

FIGURE 10-6

$\text{Fe}(\text{TPPF}_{20})(\text{TBA})$

FIGURE 10-7

$\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)(\text{TBA})$

FIGURE 10-8

10.1.2.4.1 Thermal Oxidation of Isobutane

Overall, the thermal reaction rate is independent of oxygen pressure but proportional to the square of the isobutane concentration (carbon tetrachloride solvent). The only active hydrogen is the tertiary hydrogen, so initiation gives the tert-butyl radical, t-Bu•. The following reactions form the chain:

- (1) $\text{t-Bu}\bullet + \text{O}_2 \longrightarrow \text{t-BuOO}\bullet$ A fast reaction
- (2) $\text{t-BuOO}\bullet + \text{i-BuH} \longrightarrow \text{t-BuOOH} + \text{t-Bu}\bullet$ Hydroperoxide is ~1/2 the product
- (3) $\text{t-BuOO}\bullet + \text{t-BuOO}\bullet \longrightarrow 2\text{t-BuO}\bullet + \text{O}_2$
- (4) $\text{t-BuO}\bullet + \text{i-BuH} \longrightarrow \text{t-BuOH} + \text{t-Bu}\bullet$ Alcohol is ~1/2 the product
- (5) $\text{t-BuO}\bullet \longrightarrow \text{Acetone} + \text{CH}_3\bullet$ ~ 2% of the product at 145°C

Before escaping the cage at 50-100°C, about 10% of the t-BuO• reacts with itself to form di-tert-butylperoxide which is fairly stable at this temperature.

10.1.2.4.2

Catalytic Oxidations

Thermal oxidations require elevated temperatures whereas iron perhaloporphyrin complexes catalyze reactions as low as room temperature and are highly active for isobutane oxidation at 60°C. One possible way in which these complexes may operate as catalysts is shown in Figure 5-25. If R• and HO• combine in the coordination sphere to expel ROH, this scheme can be regarded as a catalytic cycle in which the iron is a true catalyst. If, however, the bound radical product of equation (d) escapes into the medium, it would undergo radical reactions the same as those shown in the thermal pathway above. The iron complex then should be more properly regarded as a living initiator rather than as a true catalyst. If this is so, the 'catalytic' pathway should be as follows:

Termination:

Comparing pure thermal with catalyzed reactions, we see that:

- a) The initiation step in both cases makes water in addition to t-butyl radicals.
- b) Rapid decomposition of the hydroperoxide has the effect of increasing the conversion to product by increasing the free radical flux.
- c) Thus, the amount of $\text{RO}\cdot$ intermediate must also be greater, so the fraction of acetone should increase. In fact we make considerably more acetone in catalytic isobutane oxidation than in thermal oxidations.
- d) About 10% of the $\text{RO}\cdot$ should go to ROOR . Since far less ROOR than this is seen, it might either be catalytically decomposed, step (10), or the catalyst might operate to its formation.

Thus the catalyst for the hypothetical process shown above has at least three functions. It must initiate the reaction of isobutane, Figure 5-25. It must decompose tert-butyl hydroperoxide to TBA and O_2 (see next section). It may decompose di-tert-butyl peroxide under oxidation conditions, or otherwise prevent its formation.

10.1.2.4.3

Halogen Substituent Effects On The
Catalytic Activity of Iron Porphyrin
Complexes For The Decomposition Of tert-
Butyl Hydroperoxide

It has long been known that iron complexes are effective promoters of the decomposition of alkyl hydroperoxides (1). There has been considerable recent interest in the efficient catalytic conversion of tert-butyl hydroperoxide to tert-butyl alcohol (2-12), Eq. 1, but with currently available catalyst systems, elevated temperatures are often required and reaction selectivity is typically around 80%. Tetraphenylporphyrinatoiron(III)chloride was recently shown to be one of the more active catalysts for decomposition of tert-butylhydroperoxide (4), but in order to obtain relatively rapid rates it was necessary to either conduct reactions at somewhat elevated temperatures (60°C) or to add imidazole which resulted in a hydroperoxide decomposition catalyst that was active at room temperature.

In this section we report that by halogenating the porphyrin ring of iron tetraphenylporphyrinato complexes we were able to greatly enhance catalytic activity, reduce reaction temperatures and observe reaction selectivities of 90%. Perhaloporphyrinatoiron(III) complexes gave the fastest rate of hydroperoxide decomposition by any metal complex observed to date. In fact with room temperature reaction rates of well over 100 catalyst cycles per second, these are among the fastest reactions catalyzed by a synthetic homogeneous transition metal complex in solution (14). Rates are within an order of magnitude of the activity of the catalase enzyme which decomposes hydrogen peroxide to water and oxygen (15). In addition, this study may have relevance to the mechanism of some recently disclosed rapid air-oxidations of isobutane catalyzed by iron haloporphyrin catalysts (16,17).

10.1.2.4.3.1 Procedures

Materials. Metal complexes used as catalysts: tetrakis(pentafluorophenyl) β -octachloroporphyrinatoiron(III)chloride, $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$, tetrakis(pentafluorophenyl) β -octabromoporphyrinatoiron(III)chloride, $\text{Fe}(\text{TPPF}_{20}\beta\text{-Br}_8)\text{Cl}$, and tetrakis(pentafluorophenyl)porphyrinatoiron(III)chloride, $\text{Fe}(\text{TPPF}_{20})\text{Cl}$, were prepared by methods described previously (16,17). Benzene, (99.99%), Aldrich, tert-butyl alcohol, (99.6%), Aldrich, and p-xylene, (99+%), Aldrich were used as purchased. tert-Butyl hydroperoxide (90%, 5% water, 5% tert-butyl alcohol) was used as purchased from Aldrich.

Procedures. A solution of the catalyst in p-xylene (internal standard) was quickly added to a rapidly stirring solution of tert-butyl hydroperoxide in the solvent at room temperature. Oxygen evolution was measured manometrically and liquid products were analyzed periodically by standardized gas chromatography.

10.1.2.4.3.2 Results:

Figure 10-9 compares the activity of a number of iron complexes for the decomposition of tert-butyl hydroperoxide, TBH, in benzene. It is clear that porphyrinato iron(III) complexes are quite active for catalyzing this transformation and that the extent of porphyrin ring halogenation has a dramatic effect on the catalytic activity of the porphyrinato iron(III) complex used. Very low concentrations of the perhaloporphyrin complexes $\text{Fe}(\text{TPPF}_{20}\beta\text{-Y}_8)\text{Cl}$, $\text{Y}=\text{Cl}, \text{Br}$ were extremely effective in catalyzing room temperature TBH decomposition. Table 10-11 compares the product profile and extent of conversion of TBH in benzene after two or three hours. Selectivity to tert-butyl alcohol, TBA, was found to be 90% in all instances in which perhaloporphyrinato complexes were used as catalysts. Selectivity was lower when partially halogenated or unhalogenated porphyrins were used.

FIGURE 10-9

Formation of tert-butyl alcohol, TBA, from tert-butyl hydroperoxide (10 ml) in benzene (48 ml)-p-xylene (2.4 ml) using 2×10^{-4} mmoles of catalyst:

TABLE 10-11

CONVERSION OF tert-BUTYL HYDROPEROXIDE TO tert-BUTYL ALCOHOL

<u>CATALYST</u>	<u>TIME HOURS</u>	<u>t-BuO₂H CONV.,%</u>	<u>— PRODUCTS, MOLAR SEL.,% —</u>		
			<u>t-BuOH</u>	<u>(t-BuO)₂</u>	<u>(CH₃)CO</u>
Fe(acac) ₃	2.3	< 5	67	tr	32
Fe(TPP)Cl	1.9	27	82	7	11
Fe(TPPF ₂₀)Cl	3.3	72	87	10	3
Fe(TPPF ₂₀ β Br ₈)Cl	1.9	95	90	8	2
Fe(TPPF ₂₀ β Cl ₈)Cl	3.3	100	90	8	2

^a The catalyst, 2×10^{-4} mmoles, in 2.4 ml p-xylene was rapidly added to a stirred solution of 10 ml t-BuO₂ h (90%) in 48 mls benzene. O₂ evolved was measured monometrically and liquid samples taken periodically and analyzed by standardized gc.

Kropf and Ivanov recently observed second order dependence on hydroperoxide concentration during some copper phthalocyanine complex-catalyzed decompositions of tert-butyl hydroperoxide (12) carried out at 60°C in chlorobenzene. Interestingly, these workers found that electron donation to the phthalocyanine macrocycle enhanced catalytic activity whereas electron withdrawal retarded it. Figure 10-10 shows the apparent second order dependence on hydroperoxide concentration exhibited by decompositions catalyzed by both halogenated and unhalogenated tetraphenylporphyrinatoiron(III)chloro complexes in benzene as a solvent. Incremental addition of the radical inhibitor, 2,4-di-tert-butyl-p-cresol, prolonged an induction period which grew longer by a time that was proportional to the concentration of inhibitor used, Figure 10-11. At inhibitor concentrations 10,000 fold greater than that of the iron porphyrin complex, the induction period was still less than one hour long.

10.1.2.4.3.3 Discussion

There has been much discussion in the recent literature (9,13,18) surrounding the issue of heterolytic vs. homolytic O-O bond cleavage in hydroperoxides during metalloporphyrin catalyzed hydroperoxide decomposition. It has been shown that tert-butyl hydroperoxide undergoes homolytic O-O bond cleavage in the presence of porphyrinato iron complexes (18, 19, 20). Peracidic compounds undergo heterolytic cleavage under the same conditions (18). A recent report (13) indicates that electron "push" from electron donating substituent groups on the macrocycle coupled with electron "pull" from the peroxide bound to an iron in the macrocycle result in enhanced rate of heterolytic O-O bond cleavage, Eq. 2. Electron pull from the bound peroxide is generated by electron withdrawing groups in the p-position on the aromatic peracids used in the study. These observations are reasonable since by pushing electron density from the macrocyclic ligand toward the iron center one might stabilize a high-oxidation state ferryl and by removing electron density from the aromatic peracid portion of the complex one would stabilize developing negative charge.

FIGURE 10-10

Second order plots for the catalytic decomposition of tert-butyl hydroperoxide in benzene. $\diamond$ $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$, $\triangle$ $\text{Fe}(\text{TPPF}_{20})\text{Cl}$, $\circ$ $\text{Fe}(\text{TPP})\text{Cl}$.

FIGURE 10-11

Effect of BHT on the decomposition of tert-butyl hydroperoxide (10 ml)
catalyzed by $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$, 2×10^{-4} , mmoles, in benzene (48 ml)-
p-xylene (2.4 ml).

The studies reported in this communication demonstrate the effects of electron "pull" from the porphyrin macrocycle and electron "push" from the alkyl-hydroperoxide that is decomposed. Surprisingly, the result is that of greatly enhanced decomposition rates. These observations could be rationalized by a mechanism shift to homolytic O-O bond cleavage, Eq. 3, which is enhanced by electron withdrawal from the macrocyclic ligand and thus from the metal center which it surrounds. Electron withdrawal would be expected to raise the Fe(III)/Fe(II) reduction potential (16,17) and favor the homolytic O-O bond dissociation step resulting in the production of iron(II) from the iron(III) peroxy complex with release of alkylperoxy radicals. The resulting tert-butylperoxy radical could react further to produce oxygen and the tert-butoxy radical, Eq. 4, which ultimately gives TBA (9,12,18).

A catalytic reaction which is consistent with the observations presented above can be envisioned as proceeding via the pathway shown in Scheme 10-12, below. Early studies of metal complex catalyzed hydroperoxide decomposition were rationalized based on M(III)/M(II) catalysis via the well known Haber-Weiss cycle shown in Figure 10-12.

More recent studies, however, have indicated that metal oxo species may be involved (18-21) in metalloporphyrin-catalyzed alkylhydroperoxide decomposition.

FIGURE 10-12

HABER WEISS DECOMPOSITION OF HYDROPEROXIDES USING METALLOPORPHYRINS AS CATALYSTS (PORPHYRIN RING OMITTED)

Balch and his co-workers have found (19) that $\text{Fe}(\text{TPP})\text{OH}$ reacts stoichiometrically with tert-butylhydroperoxide to form the alkylperoxy iron(III) complex suggested in Figure 10-12. In the presence of a suitable base (19) this complex homolyzes to form not $\text{Fe}(\text{II})$, but the ferryl complex, Eq.5. Figure 10-13 shows the possible generation of alkoxy and alkylperoxy radicals by a mechanism in which no iron(II) species take part, but rather the catalysis occurs via a one-electron homolytic $\text{Fe}(\text{III})/\text{Fe}(\text{IV})=\text{O}$ couple. At this time it is not possible to assess the relative contributions from pathways shown in Figures 10-12 and 10-13.

The similarity between the effects of reduction potential on catalytic activity for both the decomposition of tert-butyl hydroperoxide to tert-butyl alcohol and the air-oxidation of isobutane (16, 17) to tert-butyl alcohol raises the possibility that these reactions have pathways in common. We continue to pursue the synthetic potential of this reaction, extend the trends in catalytic activity with increasing reduction potential, and consider possible implications of this work for air oxidations using perhaloporphyrin catalysts.

FIGURE 10-13

POSSIBLE METAL OXO PATHWAYS FOR DECOMPOSITION OF HYDROPEROXIDES
USING METALLOPORPHYRIN CATALYSTS (PORPHYRIN RING OMITTED)

10.1.2.4.3.4 REFERENCES

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10.2 OXIDATION OF PROPANE

Propane is a more difficult alkane to oxidize than is isobutane. This is probably related to the greater bond dissociation energy of the secondary C-H bonds in propane which is over 4 kcal/mole greater than the bond dissociation energy of the tertiary C-H bond in isobutane. Thus it is expected that converting isobutane to TBA would be easier than converting propane to isopropyl alcohol, IPA.

10.2.1 Oxidation-Catalyzed by $\text{Fe}(\text{TPPF}_{20}\beta\text{-Br}_8)\text{Cl}$

Table 10-9 compares the propane oxidation activity of the more active iron, manganese and chromium complexes having the perhaloporphyrin ligand system: $\text{TPPF}_{20}\beta\text{-Br}_8$, with that of the same metals in the partially halogenated ligand system: TPPF_{20} . The iron manganese and chromium TPPF_{20} azides were used for comparison with the perhalo complexes since they were the most active of this group. Replacing the eight remaining hydrogens in TPPF_{20} with bromines increases the oxidation activity of the complexes but much higher activity is needed for a commercially practical process for making oxygenates from propane. Nonetheless, the results shown in Table 10-12 represent the best low-temperature catalytic oxidations of propane known to us. All of the perhaloporphyrin complexes used were tested at 125°C. No 100°C testing was done on the perhaloporphyrin complexes even though it is likely that slow oxidation would occur at this temperature. We felt that it would be a better expenditure of time to forego 100°C testing until better catalysts were available and spend the time in trying to synthesize a superior second generation catalyst.

The first generation perhaloporphyrin complex is not active enough to catalyze oxidation of the primary C-H bonds of ethane or methane. These are the toughest C-H bonds to cleave and more active catalysts are needed here as well. We also did not use the first generation perhaloporphyrin complex on methane and ethane at very elevated temperatures since results with propane oxidation showed that even at 125°C some catalyst decomposition occurred over time.

TABLE 10-12

PROPANE OXIDATIONS USING FIRST ROW METAL COMPLEXES
OF $\text{TPPF}_{20}\text{-}\beta\text{-Br}_8$ AS CATALYSTS^a

	<u>Time</u> <u>Hours</u>	<u>T, °C</u>	<u>T, O.^b</u>	<u>IPA</u> <u>Acetone^c</u>
$\text{Fe}(\text{TPPF}_{20})\text{N}_3$	3	125	330	0.8
	6	125	410	0.7
$\text{Fe}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{Cl}$	4.5	125	420	1.0
$\text{Fe}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{Br}$	4.5	125	470	0.8
$\text{Fe}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{N}_3$	4.5	125	514	0.9
$\text{Cr}(\text{TPPF}_{20})\text{N}_3$	4.5	125	41	<0.1
$\text{Cr}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{Cl}$	4.5	125	111	0.3
$\text{Cr}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{N}_3$	4.5	125	87	0.6
$\text{Mn}(\text{TPPF}_{20})\text{N}_3$	3	125	0	--
$\text{Mn}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{Cl}$	4.5	125	0	--
$\text{Mn}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{N}_3$	4.5	125	87	1.0
$\text{Mn}(\text{TPPF}_{20}\text{-}\beta\text{-Br}_8)\text{F}$	4.5	125	370	0.9

^a Propane (1.36 mol) was added to benzene (48 ml) containing the catalyst (0.013 mmol). The solution was stirred for 3 hours at 125°C under 1000 psig of air in a glass lined autoclave. Liquids and gases were analyzed by GC. Production of carbon oxides never amounted to 10% of total products. Isopropyl alcohol and acetone exceeded 90 mole % of carbon containing reaction products in all cases.

^b Moles of acetone plus isopropyl alcohol formed per mole of catalyst used.

^c Molar ratio isopropyl alcohol to acetone formed.

10.2.2 Oxidations of n-Butane and Propane Catalyzed by Complexes
of $\text{TPPF}_{20}\beta\text{-Cl}_8$

We have examined the oxidations of n-butane and propane using the complexes $\text{M}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{X}$ where $\text{M} = \text{Fe}, \text{Cr}$, and $\text{X} = \text{Cl}, \text{N}_3$. Table 10-13 shows the results of this study. It can be seen that Both the iron and chromium complexes are more active in acetonitrile than in benzene. Very rapid rates of $\text{Cr}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{N}_3$ -catalyzed butane oxidation are observed after a one hour induction period, Figure 10-14. It is of further interest that the iron complex gives greater yields of alcohol and lower yields of ketone and C_2 oxidative cleavage products than does the Cr complex. MEK is formed in 50-60% selectivity using the Cr complex.

The complex: $\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$ catalyzes a very selective oxidation of propane to isopropyl alcohol, IPA, at 125°C . In acetonitrile the IPA selectivity is nearly 80%. This reaction also occurs more rapidly in acetonitrile than in benzene. Despite the fact that IPA is formed more selectively in the presence of this catalyst than with any other known system, the rates of reactions using this catalyst are slow.

TABLE 10-13

ALKANE OXIDATIONS CATALYZED BY $\text{TPPF}_{20}\beta\text{-Cl}_8$ COMPLEXES OF IRON AND CHROMIUM^aOXIDATION PRODUCT MOLAR SELECTIVITY, %

<u>SUB-STRATE</u>	<u>CATALYST</u>	<u>SOLVENT</u>	<u>REAC. TIME HR.</u>	<u>SBA ($2\text{-C}_4\text{H}_9\text{OH}$)</u>	<u>MEK ($2\text{-C}_4\text{H}_9\text{OH}$)</u>	<u>ACETAL-DEHYDE (CH_3CHO)</u>	<u>ACETIC ACID ($\text{CH}_3\text{CO}_2\text{H}$)</u>	<u>IPA ($2\text{-C}_3\text{H}_7\text{OH}$)</u>	<u>ACETONE ($\text{CH}_3)_2\text{CO}$)</u>	<u>TO</u>
n-Butane	$\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$	Benzene	4.5	28	56	(tr)	15			243
	$\text{Cu}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$	Benzene	5.5	40	60	-	-			9
		Benzene	23.0	10	60	3	27			711
		Acetonitrile	23.0	7	48	5	40			1518
	$\text{Cr}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{N}_3$	Benzene	2.2	7	64	4	25			659
		Acetonitrile	3.5	12	51	3	34			1508
Propane	$\text{Fe}(\text{TPPF}_{20}\beta\text{-Cl}_8)\text{Cl}$	Benzene	4.5					57	31	88
		Acetonitrile	6.0					79	20	185
		Acetonitrile	6.0					80	19	247

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^a The alkane, 60g. in 48 ml. of the solvent containing 0.023 mmole catalyst was oxidized at 125°C under 1500 psig of air.

FIGURE 10-14

OXIDATION OF n-BUTANE IN ACETRONITRILE AT 125°C

CATALYZED BY $\text{Cr}(\text{TPPF}_{20\beta}\text{-Cl}_8)\text{N}_3$

(TABLE 10-13)

10.3 AZIDO AND PERHALO PHTHALOCYANINE COMPLEXES AS AIR- OXIDATION CATALYSTS

Transition metal porphyrin complexes do not have good oxidative stability at temperatures of 100°C or more. Phthalocyanine complexes are known to be more robust materials and cobalt phthalocyanine catalysts are used for mercaptan oxidations in the petroleum industry (17). Phthalocyanine complexes, however, are not very hydrocarbon soluble nor very active for low temperature alkane oxidation.

We have found, Tables 10-14, 10-15 that chromium and manganese phthalocyanine azides catalyze selective oxidation of isobutane to tert-butyl alcohol and that ironperfluorophthalocyanine azides are robust, soluble, active catalysts for the selective oxidation of isobutane and propane under mild conditions of temperature and pressure. Propane is oxidized selectively to C₃ oxygenates with low yields of carbon oxides. Even refractory hydrocarbons such as methane and ethane can be oxidized in the presence of Fe(FPc)N₃ but rates, yields and selectivity to alcohols are very low. Methane is oxidized at 285°C and 2000 psig of a 3/1 mixture of methane and air in 1/1 benzene/water to give methanol in 11% selectivity at 60% oxygen conversion using this catalyst. By-products are largely carbon oxides.

TABLE 10-14
OXIDATION OF ISOBUTANE^a CATALYZED BY METAL PHTHALOCYANINE AZIDES

<u>COMPLEX</u>	<u>mmoles</u>	<u>T, °C</u>	<u>t, hrs.</u>	<u>TON^b</u>	<u>SEL.^c</u>
Mn(Pc)	0.013	80	6	0	-
Mn(Pc)N ₃	0.013	80	6	400	88
Cr(Pc)	0.013	80	6	0	-
Cr(Pc)N ₃	0.013	80	7.5	220	91
Fe(Pc)	0.030	80	6	0	-
[Fe(Pc)] ₂ N	0.016	80	6	0	-
Fe(FPc)	0.023	80	6	0	-
Fe(FPc)N ₃	0.013	80	6	990	82
Fe(FPc)N ₃	0.013	60	6	156	92

^a The catalyst was stirred in 25 ml benzene containing 6 grams isobutane under 100 psig of O₂ at the designated temperature for the time indicated.

^b Moles O₂ consumed/mole catalyst used.

^c Moles t-butyl alcohol produced/total moles liquid product) X 100.

TABLE 10-15

**OXIDATION OF PROPANE^a CATALYZED BY AN IRON
PERFLUOROPHTHALOCYANINE AZIDE**

<u>COMPLEX</u>	<u>mmoles</u>	<u>SOLVENT</u>	<u>T, °C</u>	<u>T, hrs.</u>	<u>TON^b</u>	<u>IPA/ ACETONE^c</u>
Fe(<u>FPc</u>)	0.023	Benzene	125	3	0	-
Fe(<u>FPc</u>)N ₃	0.028	Benzene	125	6	48	0.7
Fe(<u>FPc</u>)	0.023	CH ₃ CN	125	3	57	0.7
Fe(<u>FPc</u>)	0.028	CH ₃ CN	150	3	460	0.3
Fe(<u>FPc</u>)N ₃	0.028	CH ₃ CN	150	3	754	0.7
Fe(<u>FPc</u>)Cl	0.028	CH ₃ CN	150	3	606	0.7
Fe(<u>FPc</u>)N ₃	0.028	C ₆ H ₅ CN	150	3	1210	0.6

^a Propane (1.36 mol) was added to the solvent (48 ml) containing the catalyst. The reaction mixture was stirred at the designated temperature under 1000 psig of air in a glass-lined autoclave. Liquids and gases were analyzed by g.c. Production of carbon oxides never exceeded 10% of total products. Isopropyl alcohol and acetone exceeded 85 mole % of carbon-containing reaction products in all cases.

^b Moles of acetone plus isopropyl alcohol formed per mole of catalyst used.

^c Molar ratio of isopropyl alcohol to acetone formed.

10.4 SYNTHESIS CHARACTERIZATION AND TESTING OF A NEW TETRANITROPORPHINATOIRON COMPLEX

We have recently demonstrated for the first time that a simple porphinic macrocyclic iron complex having only nitro substituents in the meso-position is an active catalyst for light alkane oxidation. The importance of this finding is threefold. First, the catalyst can be made by a simple nitration of the iron porphine precursor with N_2O_4 . Secondly, the first demonstration of activation of the macrocycle by meso-substitution with a group other than perfluorophenyl both substantiates the theory on which this line of research is predicated and opens the door to the use of a variety of potentially more electron deficient substituents. Finally, use of the electron withdrawing nitro group instead of the heavy and costly perfluorophenyl group greatly lessens catalyst cost while potentially enhancing per pound activity of the iron catalyst. This work is of particular importance preliminary to entering the proof-of-concept phase. Thus, we have prepared an iron complex of the octaethyltetranitroporphinato ligand system, $Fe(OEP)X$ and compared its activity with that of the octaethylporphinato parent complex, $Fe(OEP)X$. The tetranitro complex showed high activity despite the negative effect of eight electron donating ethyl groups in the β -positions.

10.4.1 Nitration of $Fe(OEP)Cl$

$Fe(OEP)Cl$ [Aldrich] is dissolved in 150 ml CH_2Cl_2 and stirred under N_2 . To this solution 1.0 g of an anion-exchange resin IRA-904 [Rohm and Haas] is added to neutralize and nitrous acid formed by reaction of NO_2 gas with H_2O . A solution NO_2 [Matheson], 0.35g, in 10 ml of CH_2Cl_2 is added dropwise over 30 minutes at room temperature. The solution material is filtered and evaporated to dryness using a rotary evaporator. The solid material is purified by chromatography on silica gel two major bands are obtained: the first a reddish-green material, UV/Vis ($CHCl_3$); 410 and 577 nm, and a second reddish-brown band with absorbances at 305 and 577 nm. The mass spectrum (Oneida) of the first band shows a parent peak at 767.5 which corresponds to the $Fe(OEP)NO_2)_4^+$ ion (Figure 10-15). The NMR shows that the meso-protons have disappeared completely. At this point the axial ligand is unknown. The second band appears to be a tetranitro-

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Start : 18:33:51

10

Comm: SAMPLE IN NOBA 8KV FAB KRYPTON

Mode: FAB +Q1MS LMR UP LR

Oper: RKI

Inlet :

Base: 307.3

Inten : 1486230

Masses: 100 > 1000

Norm: 307.3

RIC : 14350335

peaks: 501

Peak: 1000.00 mAU

Data: + 38 > 46 - 9 > 21

1000993-A, PEE, KBR,cj15.ras Tue Sep 29 09:45:11:94 1992

1: cj15: 1000993-A, PEE, KBR,cj15.ras Tue Sep 29 09:45:11:94 1992

FIGURE 10-16

IR SPECTRUM OF AN $\text{FeP}[\text{meso}-(\text{NO}_2)_4]$
COMPLEX - FIRST BAND

1000993-A, PEE, KBR,cj15.ras Tue Sep 29 09:45:11:94 1992

FIGURE 10-17

1: cj15: 1000993-A, PEE, KBR,cj15.ras Tue Sep 29 09:45:11:94 1992

porphine also. Perhaps the two materials have different axial ligands. The IR spectra of these two materials are very similar. The first band from the column 1000993-A has N-O stretches at 1368 and 1537 cm^{-1} (Figures 10-16, 10-17) and the second band having similar stretches at 1365 and 1539 cm^{-1} (Figures 10-18, 10-19).

10.4.2 Testing of a Tetranitroporphine Complex

The $\text{Fe}[\text{OEPmeso}-(\text{NO}_2)_4]$ complex referred to in the previous section, 0.013 mmole, was dissolved in 25 ml benzene and 7.0 grams of isobutane was added. Oxygen, 100 psig, was continuously applied as the mixture was stirred at 60°C. After six hours 8.6 mmole of O_2 was taken up (T.O. = 660) and t-butyl alcohol produced in 85% overall selectivity. A duplicate run reproduced this finding closely. A similar run at room temperature over a 72 hour period gave nearly 1000 turnovers and produced TBA in 90% selectivity. Similar runs at 60 and 80°C using $\text{Fe}[\text{OEP}]\text{Cl}$ as a standard showed no activity and produced no oxidation products after six hours. Thus, replacing the meso-hydrogens in OEP with nitro groups changed an inactive complex into a highly active one. Electrochemical studies are underway and will be discussed in future reports.

11.0 CONCLUSIONS

Now that we have established structure-reactivity relationships which correlate both the Fe(III)/Fe(II) reduction potential and the steric environment about the metal center with catalytic activity we are beginning to design ligand systems which have electronic and steric properties that will produce superior catalysts. Paramount among the considerations now being employed in addition to chemical characteristics are economic characteristics as well. For instance, the cost of raw materials and the molecular weight of the macrocycle are two factors which will be critical in the design of inexpensive catalysts for commercial production of fuels. We are indeed fortunate that iron provides the most active catalyst rather than a costly noble metal.

Clearly the replacement of four perfluorophenyl groups ($-C_6F_5$, M.W. = 77) with four nitro groups ($-NO_2$, M.W. = 46) substantially lowers the molecular weight and therefore the cost of catalytic equivalents. The nitro group can be introduced as N_2O_4 , an inexpensive reagent, whereas the C_6F_5 group requires the very costly perfluorobenzaldehyde as a starting material. Other small but potent electron withdrawing groups will be introduced in the future to achieve desired activity while lowering catalyst cost. This research program has provided the knowledge base for developing active, low-cost catalytic materials that will provide the light alkane conversion processes of the future. As we complete the first three-year segment we are ready to begin the proof-of-concept stages for a catalytic process to convert isobutane to tert-butyl alcohol. We are also able to convert propane to isopropyl alcohol and expect that future research will enable us to develop liquid phase catalysts for converting methane and ethane into fuel oxygenates as well.