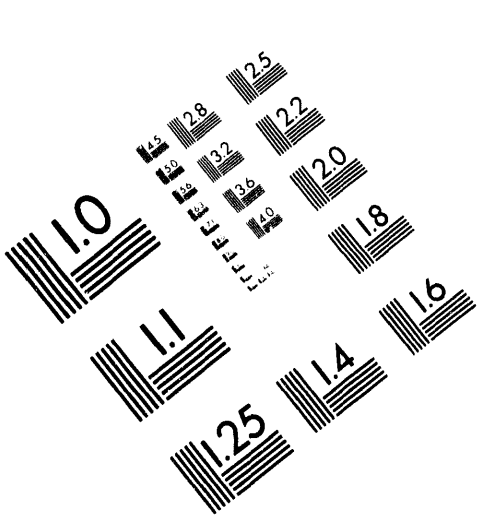

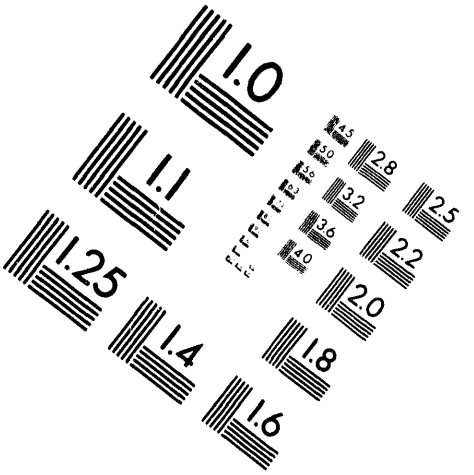

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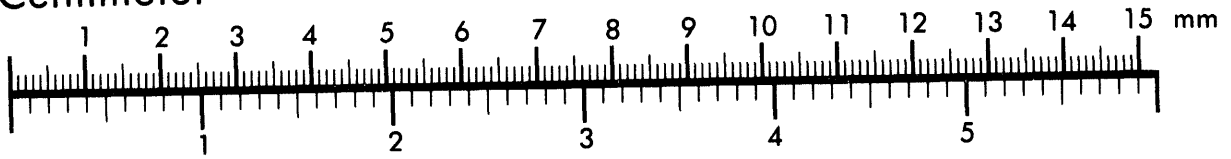

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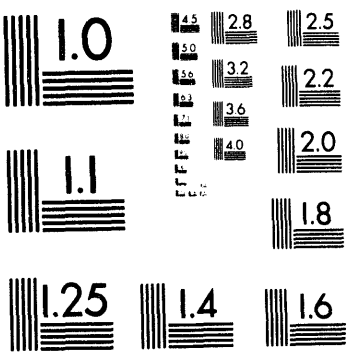

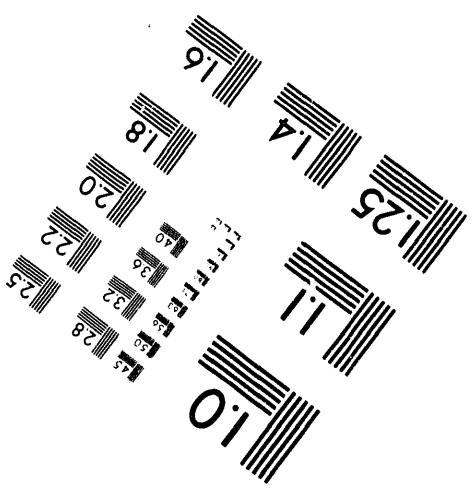

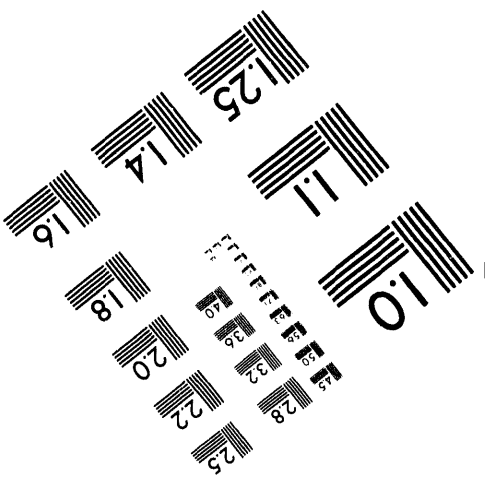

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SAND94-2117C

Title: Light Hydrocarbon Gas Conversion Using Halogenated Porphyrin Catalysts

Authors: Margaret C. Showalter and John A. Shelnutt

Institution/ Organization: Fuel Science Department, Sandia National Laboratories

Contract Number: FEW-4262

Period of Performance: October 1993 - September 1994

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

Objective:

The objective of this project is to develop novel catalysts for the direct conversion of gaseous hydrocarbons to liquid fuels. The current work investigates the use of biomimetic metalloporphyrins as catalysts for the partial oxidation of light alkanes to alcohols.

Accomplishments and Conclusions:

Background. Enzymes such as the cytochromes P450 are known to catalyze the partial oxidation of unactivated alkanes to alcohols. Analysis of these natural systems indicates structural features needed to create a biomimetic catalyst which will mimic the enzyme's high catalytic activity and selectivity. Metalloporphyrins have been reported to catalyze the oxidation of light alkanes to alcohols under mild conditions using molecular oxygen as the oxidant without the need for added co-reductant (Ellis, Jr., P.E., Lyons, J.E., Symp. Oxygen Activation in Catalysis, ACS, April 22-27, 1990. European Patent Appl. No. 88304455.4, 1988). We are attempting to develop more active catalysts for this process, toward the goal of obtaining a catalyst which is active enough to convert methane to methanol.

We are using computer-aided molecular design (CAMD) in conjunction with activity testing to develop improved metalloporphyrin catalysts. Our stepwise approach to catalyst development involves first using CAMD techniques to design potential porphyrin catalysts, followed by the synthesis and characterization of promising catalysts, and finally subjecting these catalysts to bench scale activity testing. Catalyst testing experiments give insights into important structure-activity relationships which are used to evaluate and refine our modeling tools so that better catalysts can be developed.

Analysis of biological systems and prior work with metalloporphyrin catalysts has led to the identification of structural features needed for an optimum oxidation catalyst. Two such desirable features are the presence of electron-withdrawing substituent groups at the periphery of the porphyrin ring which increases catalyst activity, and steric restraints on close bimolecular face-to-face approach of catalyst molecules which enhances catalyst stability (Nappa, M.J., Tolman,

C.A., *Inorg. Chem.* **1985**, *24*, 4711). Our catalyst design work has focused on porphyrins which incorporate these features, and which have an additional feature -- a rigid binding cavity adjacent to the porphyrinic metal center which mimics the cavity created by the protein moiety in enzymatic systems.

We have found that placing large numbers of bulky substituent groups, such as phenyl groups, around the periphery of a porphyrin macrocycle causes a nonplanar distortion of the macrocycle which creates a rigid cavity adjacent to the metal center. We have designed a series of dodecaphenyl substituted iron porphyrin catalysts which have this built-in cavity. Figure 1 shows the shape of iron dodecaphenylporphyrin, our designed catalyst with a rigid cavity; and for comparison, iron tetraphenylporphyrin, a commercial planar catalyst. It is thought that this cavity will promote substrate binding and trap reactive intermediates adjacent to the metal center. This "micro-reactor" environment should improve catalyst activity and might also influence selectivity. Highly substituted porphyrins such as our iron dodecaphenylporphyrin catalysts should also have improved stability relative to traditional planar porphyrin catalysts because there is considerable steric hindrance to bifacial approach of two porphyrin molecules, thus inhibiting bimolecular catalyst destruction.

Electron withdrawing groups can be substituted on the phenyl rings of iron dodecaphenylporphyrin to create a series of catalysts with a range of overall electron depletion at the metal center. Currently, we are studying a series of fluorinated dodecaphenyl substituted iron porphyrins FeF_xDPP where x = 0, 20, 28, 36. These catalysts have a range of overall electron depletion which can be estimated by the sum of the Hammett substituent constants ($\Sigma\sigma$), as tabulated in Figure 2. This catalyst series is unique because the bulky phenyl substituents create a nonplanar distortion leading to the formation of a cavity, as discussed above. In addition, these catalysts maintain this same shape across the series, even with the addition of fluorine substituents. In most other investigations of the effect of electron withdrawing substituents on metalloporphyrin catalyst activity, the addition of electron withdrawing groups to the porphyin macrocycle has been accompanied by a change in the degree of porphyrin nonplanarity. Our unique catalyst series allows us to study the effect of increased electron depletion of the metal center isolated from a structural change.

Catalyst Activity Testing. Previously, we studied this FeF_xDPPCl catalyst series in the oxidation of isopentane by molecular oxygen. For comparison, we also tested the commercial planar catalyst $FeF_{20}TPPCl$. This reaction was very selective for the production of alcohols. Figure 3 is a plot of catalyst activity as a function of the sum of the Hammett substituent constants for the tested DPP catalysts. We observed the predicted trend -- catalytic activity increased with the overall electron depletion of the metal center for the FeF_xDPPCl series. However, the overall activity of the FeF_xDPP catalysts was much lower than that of the planar catalyst, $FeF_{20}TPPCl$, despite the built-in cavity of the DPP catalysts. Under the reaction conditions employed in Figure 3, $FeF_{20}TPPCl$ gave 500 catalyst turnovers, which is five times more active than even the most active of the FeF_xDPPCl series. Although it is possible that the designed DPP catalysts are in fact not superior catalysts and we need to re-evaluate our design process, we are concerned that our current experimental procedures are inadequate for making valid activity comparisons. Much of our recent effort has been aimed at developing an understanding of this reaction and the apparent low activity of our designed catalysts.

We have observed that the porphyrins tested as oxidation catalysts degrade after several hours, with all catalyst being gone by the end of a 15 hour reaction. Catalyst degradation occurs in this relatively short time period even if a large amount of catalyst is used initially (1mM reaction). Such rapid catalyst deactivation is in conflict with literature reports which indicate that metalloporphyrin catalysts in this type of reaction are stable for days (Ellis, P.E., Jr., Lyons, J.E., *Catal. Lett.* **1989**, *3*, 389 and Lyons, J.E., Ellis, P.E., Jr., *Catal. Lett.* **1991**, *8*, 45). Our catalysts are stable at the temperatures and pressures used in catalyst testing. Catalyst degradation is only observed in the presence of a reactive alkane substrate. This indicates that some species formed in the course of the oxidation reaction is responsible for the catalyst degradation. The short life of our catalysts, a problem in itself, also prevents us from making adequate comparisons for our designed catalysts. Although the amount of alcohol produced by $FeF_{20}DPPCl$ is substantially less than the amount produced by $FeF_{20}TPPCl$ under identical experimental conditions, we do not know if this is an indication that the DPP catalyst is less active, less stable, or a combination of both.

Another important observation is that catalyst activity shows an inverse dependence on initial catalyst concentration, as depicted in Figure 4. Higher catalyst concentrations give substantially lower turnovers. One explanation for these data could be depletion of the available oxygen in the batch reactor. However, upon slight modification of our reactor system to replenish oxygen as it is consumed, we observed the same trend. A second possible explanation of this trend is catalyst decomposition. In high concentration experiments, there is more catalyst available for producing the desired alcohol product, but there is also more catalyst available for attack by the reactive intermediate responsible for catalyst deactivation.

In our attempts to optimize reaction conditions, we have determined that the amount of alcohol produced is affected by a number of experimental parameters including temperature, pressure, and relative amounts of reactants. However, we have not yet found a set of experimental conditions for which the oxidation reaction occurs without complete deactivation of the catalyst within 15 hours. We must first address the issue of catalyst stability before we can further optimize reaction conditions.

The oxidation of methane to methanol was attempted using molecular oxygen as the oxidant in a homogenous batch process similar to that used previously for isopentane oxidation. For these experiments, a solution of 10μM catalyst in bezene was sealed into the teflon reactor with a liner volume of 75ml, the reactor was pressurized with 50psi of methane and then oxygen was added. Replicate experiments were performed with 100psi of oxygen and 300psi of oxygen. The reactor was heated to 100°C and stirred for 22 hours. GC/FID was used to analyze the gaseous headspace and benzene solution for methanol. We tested both $FeF_{20}TPPCl$ and $FeF_{20}DPPCl$ in this reaction, as well as performing the reaction in the absence of catalyst. Although a very small amount of methanol and some other products were produced in this reaction, it was not catalytic. There were no differences in the $FeF_{20}DPP$ catalyzed, $FeF_{20}TPP$ catalyzed, and uncatalyzed experiments under the reaction conditions employed. The porphyrin catalysts did not degrade in these experiments, which is consistent with our previous observation that the catalyst only deactivated when the desired isopentane oxidation reaction occurred. It is not surprising that these initial experiments with methane were unsuccessful. We need to develop

a better understanding of this chemistry and develop more active and stable catalysts before we will be successful at converting methane.

Catalyst Synthesis. We have also continued our efforts to synthesize catalysts with a greater overall electron depletion of the metal center. Some of the catalysts for which the synthesis is in progress are shown in Figure 5. These catalysts have the potential to be very active based on the sum of the Hammett substituent constants. Although we have had some difficulty with the synthesis of some of these highly substituted catalysts, this effort is continuing. We are encouraged by the recently successful synthesis of some key intermediates. Iron octa(isopropylphenyl)porphyrin, a parent compound to some of the current synthesis targets, has been synthesized. Preliminary activity testing indicates that this is not a very effective oxidation catalyst. However, this compound was not expected to be a good catalyst. Some of the halogenated and nitrated octaphenyl porphyrins in this series are expected to be much more active. Efforts in synthesis are continuing so that once some of the experimental issues are addressed, we will have a variety of catalysts available for testing.

Plans:

Our primary concern at present is catalyst deactivation. Degradation of the porphyrin catalysts in our alkane oxidation experiments not only limits the usefulness of the process in general, but also prevents us from making adequate comparisons of our designed catalysts. We are currently obtaining the hardware needed for performing *in-situ* UV/VIS spectroscopy in our batch reactor. This will give us information on the rate of catalyst decomposition, and may help to identify any intermediate species formed. We are also setting up necessary hardware for sampling both the gas and liquid phases in the reactor throughout the course of the reaction. Hopefully, this close monitoring of the reaction will give us mechanistic information and direct us to ways to prevent rapid catalyst decomposition. Once we understand the chemical reaction in more depth, we may be able to modify catalyst structural features and experimental conditions to improve catalyst lifetime.

In addition to a more in-depth investigation of the present homogeneous reaction, we plan to experiment with metalloporphyrin catalysts supported on various media (i.e. carbon, silica gel, polymers). Supported porphyrin catalysts offer several advantages over the current homogeneous process. First, supporting the catalysts may increase stability under oxidizing conditions. Second, the catalyst can be more easily recovered if it is on a solid support. Finally, supported catalysts may be more practical for the oxidation of gaseous substrates such as methane. The current homogeneous process when applied to methane involves dissolving significant quantities of two gases, oxygen and methane, in a solvent containing catalyst. Application of the catalyst to a porous support through which the gases can diffuse could improve contact of the gases with each other and the catalyst. However, investigating supported porphyrins as alkane oxidation catalysts does have an associated risk. Most literature reports of supported porphyrins being utilized as alkane oxidation catalysts use iodosylbenzene or some other single oxygen atom transfer agent as the oxidant. It is unclear whether or not an isolated porphyrin molecule on a support can activate dioxygen, the oxidant used in our studies. Two mechanisms have been proposed for the metalloporphyrin catalyzed homogenous oxidation of

alkanes by dioxygen without a co-reductant. The mechanism proposed by workers at Sun Marketing and Refining Company requires the cooperation of two porphyrinic molecules to form a μ-peroxo-porphyrin dimer which then splits to give a reactive iron-oxo complex (Ellis, Jr., P.E., Lyons, J.E., Symp. Oxygen Activation in Catalysis, ACS, April 22-27, 1990.) If this step of the mechanism is correct, a supported porphyrin which could not interact with other catalyst molecules should not be able to catalyze the oxidation of alkanes to alcohols by O_2. However, it has also been proposed that this reaction proceeds via a classical radical-chain autoxidation mechanism (Paulson, D.R., Ullman, R., Sloane, R.B., Closs, G.L., *J. Chem. Soc., Chem. Comm.* **1974**, 186; and Grinstaff, M.W., Hill, M.G., Labinger, J.A., Gray, H.B., *Science* **1994**, *264*, 1311). If such is the case, isolated metalloporphyrin molecules on a support could serve as catalytic centers for the desired oxidation reaction.

Our initial supported catalyst studies will be performed with catalysts on hand and simple, readily available supports. A method for anchoring halogenated metalloporphyrins such as $FeF_{20}TPPCl$ to aminopropyl modified silica has been reported in the literature (Battioni, P., Bartoli, J.F., Mansuy, D., Byun, Y.S., and Traylor, T.G., *J. Chem. Soc., Chem. Comm.* **1992**, 1051). We will first attempt the preparation of this catalyst, and will also try to attach some of our fluorinated dodecaphenyl iron porphyrins to aminopropyl modified silica by the same procedure. Oxidation experiments using these types of supported catalysts will determine the directions of further research in this area. If early results indicate that supported metalloporphyrin catalysis of the oxidation of light alkanes by oxygen is feasible, we will explore other porphyrin/support combinations. If cooperativity between metalloporphyrin centers is required for the activation of dioxygen, as in the Sun mechanism, we may need to design and synthesize covalently linked porphyrin dimers for anchoring on a support.

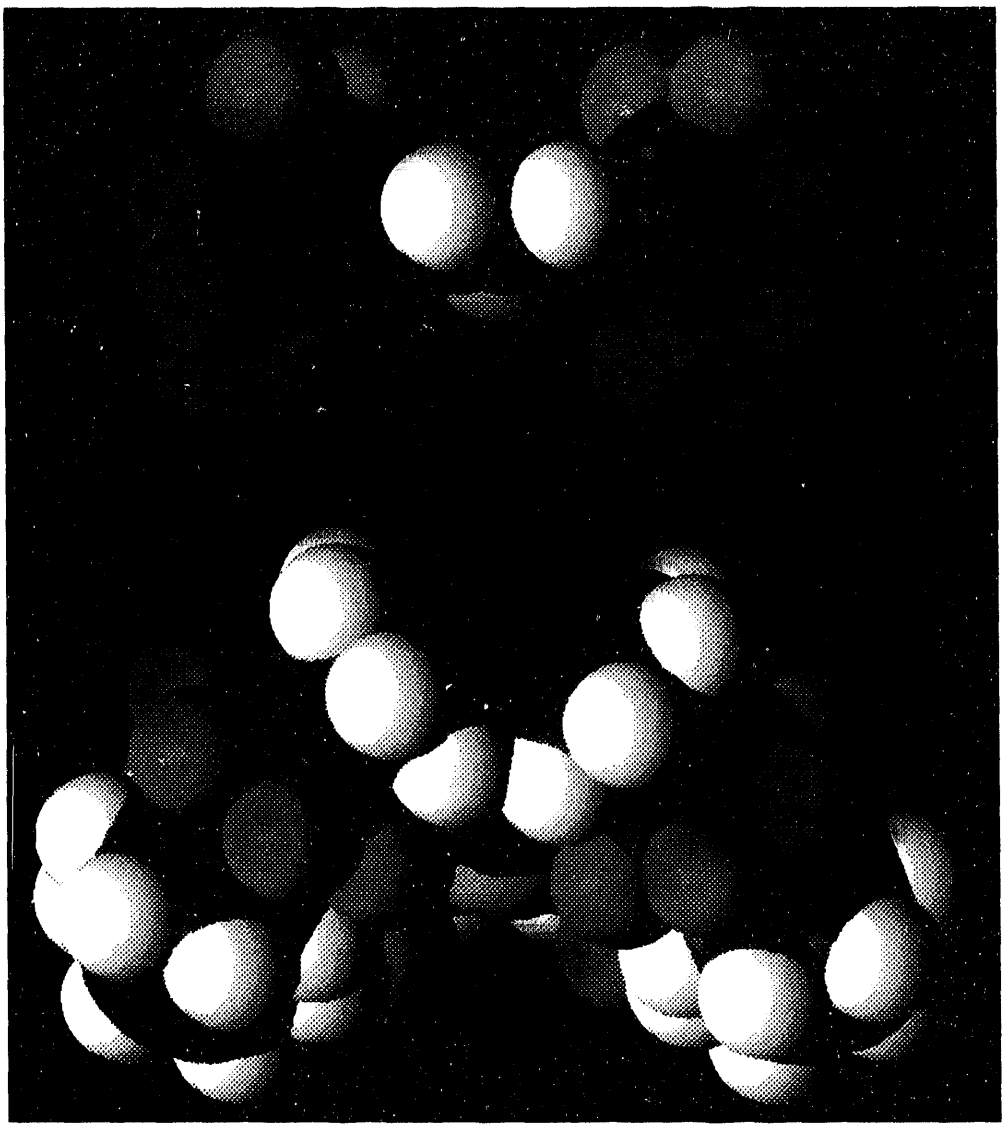
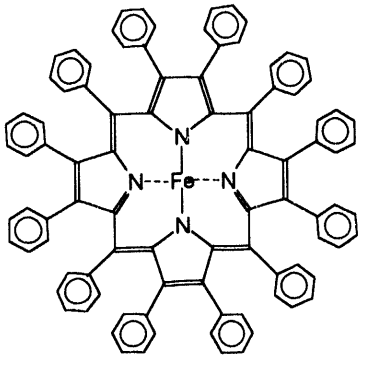
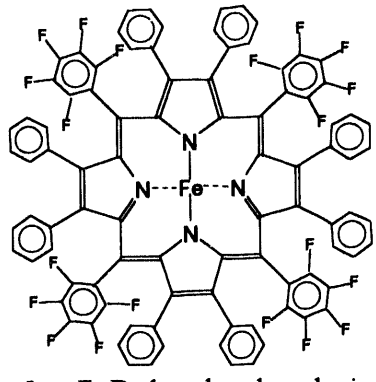


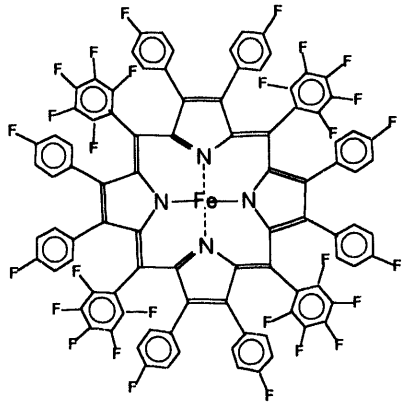
Figure 1. Structures of iron F_{20}-tetraphenylporphyrin, $FeF_{20}TPP$ (top), and iron F_{20}-dodecaphenylporphyrin, $FeF_{20}DPP$ (bottom). The highly substituted dodecaphenyl porphyrin adopts a saddle shaped structure which creates a rigid pocket adjacent to the metal center.



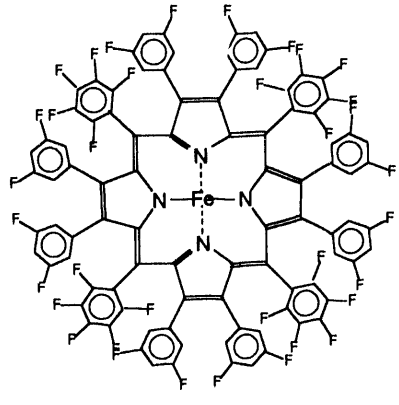
Iron Dodecaphenylporphyrin
(FeDPP)
$\Sigma\sigma_m = 0.72$ $\Sigma\sigma_p = -0.12$



Iron F_{20}Dodecaphenylporphyrin
($FeF_{20}DPP$)
$\Sigma\sigma_m = 1.84$ $\Sigma\sigma_p = 1.56$



Iron F_{28}Dodecaphenylporphyrin
($FeF_{28}DPP$)
$\Sigma\sigma_m = 2.16$ $\Sigma\sigma_p = 1.72$



Iron F_{36}Dodecaphenylporphyrin
($FeF_{36}DPP$)
$\Sigma\sigma_m = 2.32$ $\Sigma\sigma_p = 2.84$

Figure 2. Structures of the catalysts in the fluorinated iron dodecaphenylporphyrin series. $\Sigma\sigma$ is the sum of the Hammett substituent constants (shown for both meta and para), which is used as a measure of the overall electron depletion of the metal center.

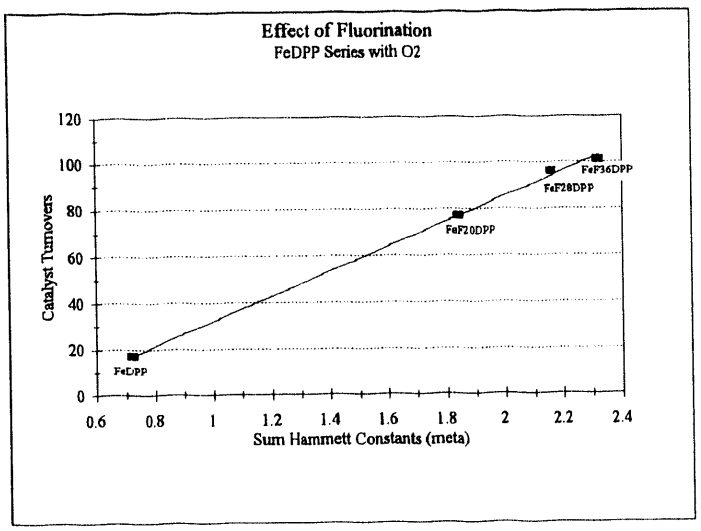


Figure 3. Catalyst activity toward the oxidation of isopentane, measured in turnovers (mol alcohol produced/ mol catalyst), as a function the sum of the Hammett substituent constants for a series of fluorinated dodecaphenyl iron porphyrins. Reaction conditions were 50μM catalyst and 2M isopentane in 10ml benzene, 300psi O_2, in a 150ml teflon lined reactor. Reaction was heated to 100°C and stirred for 15 hours. Products were analyzed by GC.

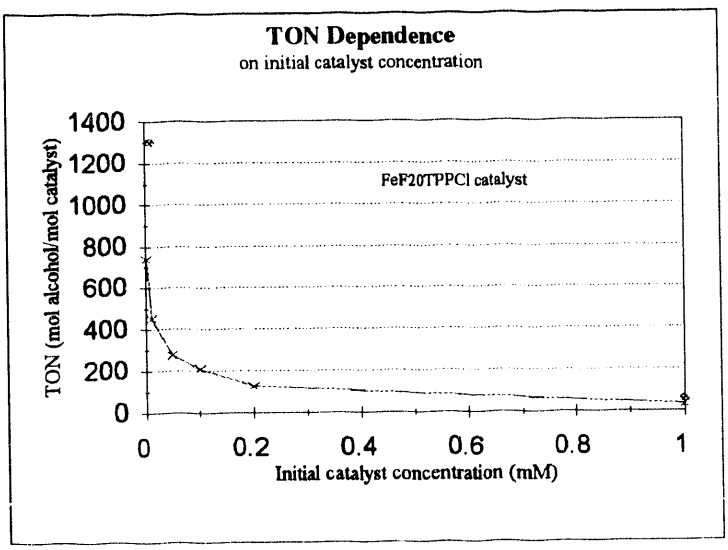
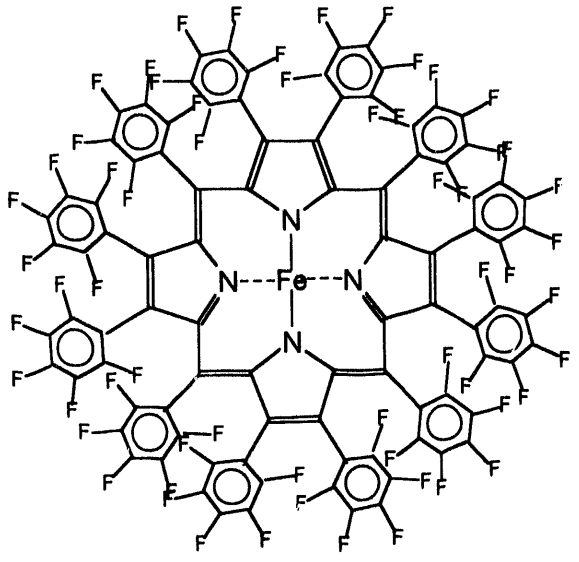
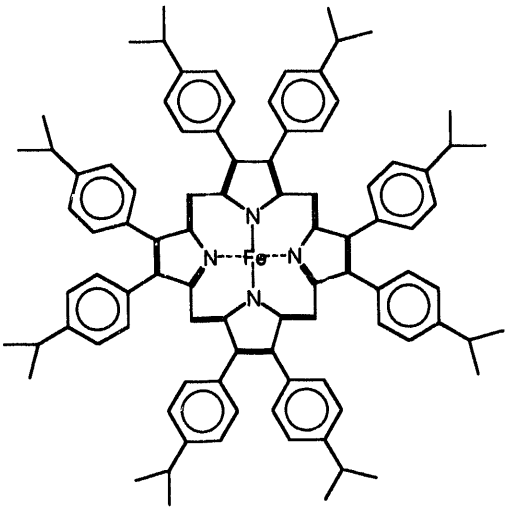


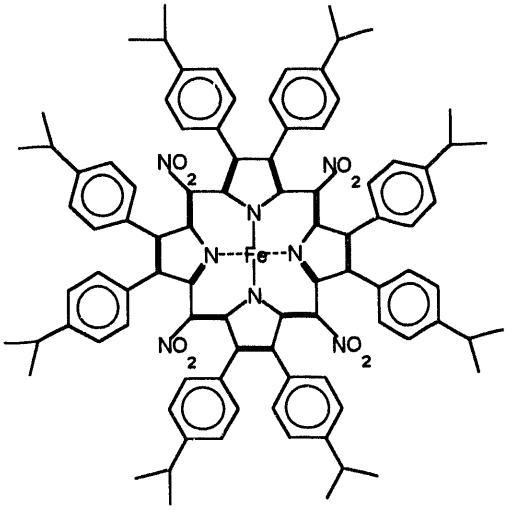
Figure 4. Plot showing the dependence of catalyst activity on initial catalyst concentration. All reactions employ catalyst at the specified concentration and 2M isopentane in 10ml benzene, in a 150ml teflon lined reactor which is heated to 100°C for 15 hours. Circles are 100psi O_2 constant pressure reactions. Crosses are 300psi O_2 sealed batch reactions where pressure drops slightly as O_2 is consumed.



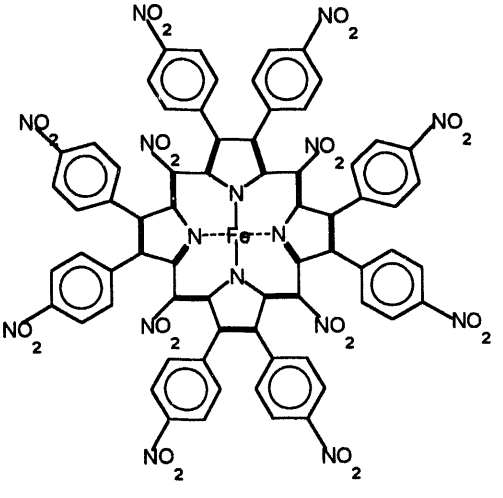
Iron F_{60}-Dodecaphenylporphyrin
$FeF_{60}DPP$
$\Sigma\sigma_p = 4.92$



Iron Octa(*p*-isopropyl)phenylporphyrin
FeOIPPP
$\Sigma\sigma_p = -0.56$



Iron Octa(*p*-isopropyl)phenyl-tetranitroporphyrin
FeOIPPTNP
$\Sigma\sigma_p = 2.56$



Iron Octa(*p*-nitro)phenyl-tetranitroporphyrin
FeONPTNP
$\Sigma\sigma_p = 4.96$

Figure 5. Some of the porphyrin catalysts currently being synthesized.

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