

BIOMIMETIC CATALYST DEVELOPMENT FOR NATURAL GAS CONVERSION

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INTRODUCTION

Enzymes such as cytochrome P₄₅₀ are known to catalyze difficult reactions including the partial oxidation of unactivated alkanes to alcohols. We are using computer aided molecular design (CAMD) in conjunction with activity testing to develop biomimetic catalysts for the oxidation of light alkanes. Our stepwise approach to catalyst development involves first using CAMD to design and model potential metalloporphyrin catalysts, followed by synthesis and characterization of promising catalysts, and finally utilizing our catalysts in bench scale oxidation reactions. The information gained in laboratory testing enables us to evaluate and refine our models, and thus continue to design catalysts which are incrementally better. We anticipate that this iterative approach will lead to the development of biomimetic catalysts which are active enough to use air for the conversion of natural gas to oxygenated products.

Metalloporphyrins have been shown to catalyze the oxidation of light alkanes with air or oxygen as the oxidant under mild conditions with no added co-reductant.¹ Prior work has indicated three beneficial properties of the metalloporphyrin catalysts. These activity-enhancing features are: (1) the presence of strongly electron-withdrawing substituent groups at the periphery of the porphyrin ring, (2) an axial ligand complex favoring the most negative Fe(III)/Fe(II) redox potential, and (3) steric restraints on close bimolecular face-to-face approach of catalyst molecules.^{1,2} We have designed and synthesized, and are currently testing a series of catalysts, the fluorinated iron dodecaphenylporphyrins (FeF_xDPP where x=0,20,28,36), with enhanced features (1) and (3), and with an additional feature -- a rigid cavity that promotes the binding of the substrate alkane molecule. Figure 1 shows the dodecaphenylporphyrin catalysts which are the subject of the current investigation.

EXPERIMENTAL

Molecular mechanics calculations were carried out on Silicon Graphics workstations using POLYGRAF software and a metalloporphyrin forcefield developed previously.³ The forcefield has been extensively validated for predicting metalloporphyrin structures and relative energies.^{3,4} Iron(III) parameters were the same as those used previously⁴, and fluorine and oxygen parameters were taken from the DREIDING force field.⁵

Catalysts were tested for activity in the oxidation of isopentane with both iodobenzene (PhIO) and oxygen as the oxidants. Catalyst concentration is 1-100µM. In the PhIO reactions, substrate, catalyst, and oxidant are mixed in an organic solvent, usually benzene, at room temperature. In a typical experiment, substrate concentration is 2M and PhIO concentration is 50mM. For the oxygen reactions, a solution of substrate and catalyst in solvent is sealed into a bomb reactor in which all internal surfaces are coated in teflon. The bomb is then pressurized with oxygen and heated while stirring. In a typical experiment, substrate concentration is

2M, oxygen pressure is 100-200psi, and temperature is 100°C. Reaction products were analyzed by gas chromatography after 2-15 hours.

RESULTS AND DISCUSSION

Catalyst Design. Electron withdrawing substituents at the periphery of an iron porphyrin oxidation catalyst have at least two beneficial effects.² First, such substituents may activate the high oxidation state metal-oxo intermediate thus increasing catalyst reactivity. Second, by removing electron density from the porphyrin ring, the substituents make the porphyrin macrocycle less susceptible to self-destruction by electrophilic attack by the oxo intermediate of the catalyst. Iron dodecaphenylporphyrin can be systematically fluorinated to give the catalyst series shown in Figure 1. An interesting feature of this catalyst series is that it allows us to study the effect of electron withdrawing groups in the absence of significant structural changes of the macrocycle. Computer modelling and spectroscopic characterization indicate that the series of FeF_xDPP catalysts, where x=0,20,28,36, have essentially the same structure, thus any difference in activity should be due to electronic factors alone.

Molecular modeling studies show that the FeDPP catalysts have a rigid cavity formed by the porphyrin ring and the quasi-axial CH's and CF's of the phenyl substituents. The cavity is of the size and shape of small linear alkanes. Figure 2 shows the shape of FeF₂₀DPP. This rigid cavity is predicted to improve catalyst activity and selectivity by providing a "microreactor" environment for the oxidation reaction. In addition, these bulky catalysts should be more stable than typical planar porphyrin catalysts.

Energy minimization and molecular dynamics calculations show that methane will bind to the cavity and remain for significant times even in a vacuum at temperatures up to and above room temperature. Substrate binding is partly a consequence of the rigidity of the binding cavity and the favorable electrostatic interaction between the light hydrocarbon and the fluorocarbon groups of the cavity. The presence of this light hydrocarbon binding cavity should enhance catalytic activity by increasing the residence time of the substrate at the active metal site. Radical trapping of the intermediates R· and ·OH in the cavity may also promote recombination to form the alcohol product, thus enhancing selectivity. Finally, ejection of the product upon formation is expected as a result of the repulsion of the alcohol oxygen atom by the fluorine atoms lining the pocket. This repulsive interaction between the product and the substrate binding cavity serves two purposes. First, it clears the cavity after the reaction has occurred for the next alkane molecule to enter; and second, it prevents further oxidation of the alcohol molecule. The former effect is expected to improve catalytic rates; the latter is expected to improve selectivity for alcohol versus other oxidation products (ketones, aldehydes).

Past work has shown that bulky substituents attached to the porphyrin which prevent close face-to-face approach of two porphyrin molecules increase the resistance of the porphyrin to bimolecular destruction.² In our highly substituted FeDPP catalysts, there is considerable steric hinderance to the face-to-face approach of two porphyrin macrocycles. The steric constraints on face-to-face interactions of the porphyrin molecules may also play a beneficial role in the reaction mechanism proposed by researchers at Sun Marketing and Refining Company.¹ In the proposed mechanism, adventitious impurity or the alkane itself reduces Fe to start the catalytic cycle. A peroxo-bridged dimer is formed and splits to give the reactive Fe(IV)=O intermediate. This ferryl intermediate subsequently reacts with the alkane (RH) to form the alcohol (ROH). A competing reaction of the ferryl intermediate is the formation of μ -oxo porphyrin dimer, Fe(III)-O-Fe(III), which is less reactive with the alkane. Thus, steric hinderance of the formation of face-to-face μ -oxo dimer is desirable, but formation of the peroxo dimer must still be favorable. Molecular modeling indicates that this is the case for the FeDPP catalysts as shown in Figure 3. The peroxo dimer, which should be able to form with the DPP catalysts, may however, be strained which could aid in the formation of the active ferryl (oxo) intermediate thus further enhancing catalytic activity.

Catalyst Testing. Initial experiments for testing our catalysts have been performed using either oxygen or iodossylbenzene (PhIO) as the oxidant and isopentane as the substrate. We have observed the predicted trend that as the number of fluorine substituents increases, so does the catalyst activity for the FeF_xDPP series.

Figure 4 shows the correlation between catalyst activity and overall electron depletion of the porphyrin measured by $\Sigma\sigma$, the sum of the Hammett substituent constants. However, all of the designed catalysts were significantly less active than the commercial planar catalyst $\text{FeF}_{20}\text{TPP}$ (TPP = tetraphenylporphyrin), despite the built in cavity or "microreactor" of the FeDPP catalysts. We are trying to develop a better understanding of this apparent low activity on the part of our designed catalysts.

We have observed that the number of catalyst turnovers in our partial oxidation test reactions is dependent upon a number of experimental parameters, including initial catalyst concentration, solvent, and temperature. We are currently determining optimum experimental conditions so that more meaningful catalyst activity comparisons can be made. In a related experiment, solutions of substrate and solvent with no catalyst, $\text{FeF}_{20}\text{TPP}$, or $\text{FeF}_{20}\text{DPP}$, were prepared and allowed to stand in the laboratory with air in the headspace. After 4 months, GC analysis showed that essentially no reaction had occurred in the control and $\text{FeF}_{20}\text{TPP}$ vials. However, the $\text{FeF}_{20}\text{DPP}$ had catalyzed the oxidation of isopentane to alcohols. This experiment indicates that under certain conditions, the $\text{FeF}_{20}\text{DPP}$ catalyst may be more reactive than its planar $\text{FeF}_{20}\text{TPP}$ counterpart. Work is in progress to further our understanding of these results.

Because the ultimate goal of this research is to develop catalysts for natural gas conversion, we have begun testing our catalysts with gaseous substrates. We have attempted the oxidation of isobutane by both oxygen and PhIO using our catalysts. Results indicate the same trends observed with isopentane. That is, as the number of fluorines in the DPP series increases so does the catalytic activity. Again $\text{FeF}_{20}\text{TPP}$ is more active than all of the FeDPP 's toward the production of alcohols under the reaction conditions employed. However, unlike the isopentane experiments which were "clean" (the only significant products were alcohols), additional products were produced in the isobutane experiments. We are currently working to identify and quantitate these additional reaction products so that we can more accurately evaluate and compare our catalysts. We are also working on modified reactor configurations and sample handling techniques so that we may also test our catalysts with the $\text{C}_1\text{-C}_3$ hydrocarbons.

Future Work. In addition to continuing our catalyst testing to more adequately characterize and understand the current series of FeDPP catalysts, we are designing and synthesizing other highly substituted porphyrin catalysts. Synthesis of the fully fluorinated $\text{FeF}_{20}\text{DPP}$ is in progress. This catalyst will complete the fluorinated DPP series and is expected to be more active than all those tested so far. In addition, we are developing other dodecaphenyl substituted porphyrin catalysts in which groups such as Cl or NO_2 are substituted on the phenyl rings. We are also developing a new class of catalysts, the substituted octaphenylporphyrins (FeOPP). These catalysts will allow us to substitute electron withdrawing groups directly on the porphyrin macrocycle at the meso positions. An example of this type of catalyst is iron octaphenyl *meso*-tetranitro porphyrin. However, while some of the substituted OPP catalysts are nonplanar, they do not have the deep, rigid binding cavity of the DPP catalysts.

CONCLUSIONS

CAMD has been used to design a novel series of alkane oxidation catalysts, the fluorinated iron dodecaphenylporphyrins. Designed features in these catalysts include the systematic variation of the number of fluorine substituent across the series and a rigid binding cavity common to all catalysts in the series. Catalyst activity testing is underway for this series of catalysts. Results thus far indicate that catalytic activity does increase as the degree of fluorination increases. However, under the experimental conditions utilized, the overall activity of the catalysts is lower than expected. Further work is in progress to more adequately characterize the activity of this novel series of catalysts.

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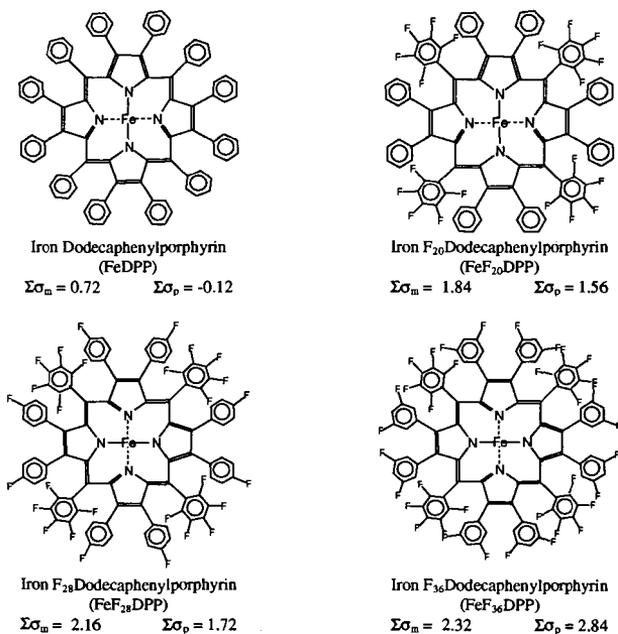


Figure 1. Structures of the catalysts in the fluorinated iron dodecaphenylporphyrin series. $\Sigma\sigma$ is the sum of the Hammett substituent constants (shown for both meta and para), which is used as a measure of the overall electron depletion of the metal center.

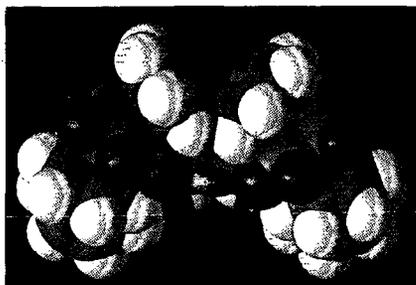


Figure 2. Energy minimized structure of FeF₂₀DPP showing the rigid binding cavity.

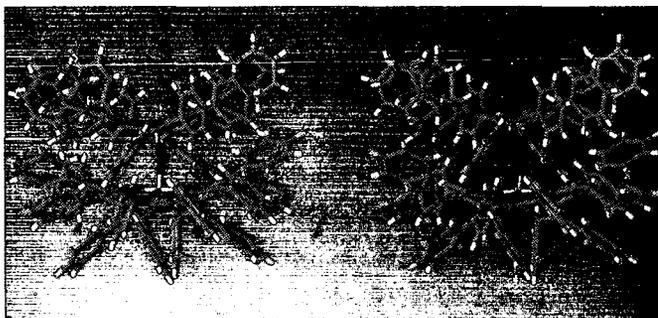


Figure 3. Calculated structures of the μ -oxo (left) and peroxy- (right) dimers of a fluorinated dodecaphenylporphyrin. Calculated energies predict that the active peroxy-dimer is energetically favored, but the inactive μ -oxo-dimer is unfavored by greater than 50kcal/mol.

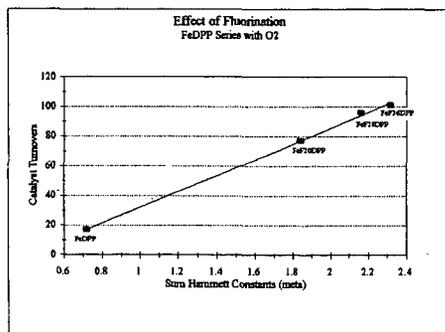


Figure 4. Plot showing the correlation between catalyst activity and electron depletion of the metal center, measured by $\Sigma\sigma$, for the FeDPP catalyst series.