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TITLE: Light-Hydrocarbon Gas Conversion

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OBJECTIVE: Use computer-aided molecular design (CAMD) methods to design a new generation of catalysts for light hydrocarbon-oxidation reactions. Synthesize and test promising engineered catalysts for activity, stability and selectivity. The research program is to explore the development of novel catalysts for the direct conversion of natural gas (C_1-C_4 components) to oxygenate additives for clean fuels and/or other valuable intermediates. The work will focus, initially, on homogeneous transition metal catalysts that are being developed at Sandia for conversion of methane and CO_2 using porphyrin metal complexes. Our activities will also include pillared clays, modified zeolites, carbonized foams, and other designed, shape-selective microporous materials. We will make extensive use of computer-aided molecular design (CAMD) techniques to guide the synthesis of new catalysts. Molecular mechanics and molecular orbital calculations will be used to evaluate possible molecular catalyst designs. Promising computer-designed catalysts will then be synthesized and extensively characterized. The tailored catalysts will be tested for catalytic activity and selectively using batch microreactors. Elements of the research are: (1) CAMD of selective substrate binding cavities attached to the catalytic metal center, (2) molecular modelling of catalysts and catalyst-substrate/product/solvent interactions, (3) synthesis of promising catalyst designs, (4) activity testing of designed catalysts in a Sandia patented photochemical alkane-oxidation process using O_2 as oxidant, and (5) testing of catalysts in alkane-oxidation systems not requiring co-reductant.

TECHNICAL APPROACH: Computer-aided molecular design methods are being used to design a new generation of metal-tetrapyrrole catalysts for light hydrocarbon gas oxidation. The goal is to enhance the activity, stability and selectivity of these catalysts. Analysis of naturally occurring enzymes that catalyze alkane oxidation (cytochrome P_{450}) and gaseous molecule reactions (carbonic anhydrase) has identified several structural features that are requisite in a synthetic analog that is to mimic the high activity and selectivity of the enzymatic reactions. These include (1) a metal center with the suitable coordinated molecular groups and promoters and (2) a "rigid" binding cavity of the size and shape of the alkane molecule to be converted. It is anticipated that the octa-alkyl(aryl)-tetraphenylporphyrins (OATPPs) will possess the rigidity required to form a sturdy foundation upon which additional molecular architecture can be added as a consequence of the severe steric congestion (crowding) of the peripheral substituents. Previous designed catalysts based on the tetraphenylporphyrins (TPPs) did not have the necessary degree of rigidity. All of the required structural features have now been designed into a single molecule derived from the OATPPs. The OATPP class of catalysts are being developed and characterized in collaboration with K. Smith and C. Medforth at the University of California at Davis and K. Barkigia and J. Fajer at Brookhaven National Laboratories.

The OATPP group of catalysts were used as the basis for designing a single catalysts with all of the structural features presently thought to be important for an efficient, robust and selective alkane-oxidation catalyst. Energy optimization was used to determine the likelihood that the catalyst was synthesizable, and molecular dynamics calculations were carried out to investigate the binding of ethane.

Sun Refining & Marketing is pursuing an alternative approach using a gas phase reaction based on a porphyrin catalyst with considerable success. O_2 is the oxidant; no co-reductant is required for the

Sun process. Our biomimetic approach has the potential for improving the specificity of the Sun process for oxidation of light alkanes. This would be accomplished by providing a shape selective cavity adjacent to the porphyrinic metal center at which the Sun reaction takes place. The cavity can determine the region of the hydrocarbon at which oxidation takes place, and, further, may influence the product ratios by trapping of radical intermediates thought to be involved in the Sun process. The autooxidation reaction occurring in this reaction proceeds by a mechanism different from the biological reaction which gives only alcohols. Trapping of free radical intermediates is one possible mechanism by which the P_{450} enzyme may select specific oxidation products.

We are initiating a new study of cytochrome P_{450} and a series of reaction intermediates to help to further elucidate the biological reaction. In this regard, we have recently established a collaborative effort with Paul Ortiz de Montellano and Barbara Swanson of the University of California at San Francisco to investigate the suicide intermediates in the reaction of phenylhydrazine with the Fe-porphyrin group from the active site of cytochrome P_{450}. Preliminary results and future studies of these important cytochrome-P_{450} intermediates are described below.

We are rapidly progressing on the molecular design work for a new generation of catalysts; therefore, as the work continues to progress we plan to place increasing emphasis on the synthesis and testing of the tailored catalysts.

SIGNIFICANT ACCOMPLISHMENTS: We briefly list here the major accomplishments to date, followed by a more complete description of the significance of the work. Further details of the work are given in the listed publications. First, a molecular mechanics force field was developed specifically for metalloporphyrins. Structural predictions of the mechanics calculations for the NiOATPPs were tested by comparison with spectroscopic structural information and X-ray structures. About 20 OATPPs were synthesized and structurally characterized. For a series of ten NiOATPP derivatives, Raman studies identified spectroscopic markers of the molecular structure, and systematic distortions of the catalysts were related to reactivity. Metal derivatives were synthesized for the most promising OATPPs, including Zn(II), Ni(II), and Co(II) and Co(III)(py) derivatives that have small molecule binding cavities. CAMD studies predict that several metal-OATPP catalysts may bind methane, ethane and carbon dioxide for substantial times even in vacuum at room temperature. Co derivatives were synthesized for ^{13}C-NMR studies of substrate binding to the cavity. H-NMR studies were used to determine the stability (lifetime) of the cavity (1). Synthesis of Fe(III) and Mn(III) OATPPs for activity, selectivity, and stability testing in hydrocarbon gas conversion reactions is underway. A photochemical alkane-oxidation process using dioxygen at ambient conditions was discovered and patented (2,3). Finally, a unique, new dual-channel *transient* Raman spectrometer was built and used to detect substrate-catalyst interactions in intermediates (4).

Computer-Aided Molecular Design of Natural Gas Conversion Catalysts: *Evaluation of CAMD Predictions.* A fundamental aspect of the application of molecular modelling to the design of natural gas conversion catalysts is the validation of our structural predictions, especially those predictions for the class of catalysts to be engineered. We have made substantial progress in this area of the work in the last year. Our current parameterization of the porphyrin force field gives extraordinarily accurate agreement with experimentally determined porphyrin structures. The new parameters give much improved predictions of molecular structure. We modified the DREIDING-II parameters to include nickel and to model the porphyrin structure better. The latter are extensive modifications based on the recently published nickel-octaethylporphyrin (NiOEP) force constants and the NiOEP X-ray crystal structures.

We have completed modelling studies of ten of the porphyrins in the octa-*alkyl(aryl)*-tetra*phenyl*porphyrin (OATPP) series using the new metalloporphyrin force field. The structural predictions for the series of catalysts have now been compared with experimental structural information as described below. Both the calculations and the new experimental data indicate that the conformation of the OATPP catalysts varies in a systematic fashion for members of the series.

Table 1. Raman frequencies (in cm^{-1}) of the structure-sensitive marker lines and selected structural parameters (calculated) of nickel porphyrins.

Ni Porphyrin	Ct-N	$C_\alpha NC_\alpha$	ν_4	ν_3	ν_2	ν_{19}	ν_{10}	ν_ϕ	Raman data from:
NiP	1.938	104.5		1505.5			1649.0		NiP/CH_2Cl_2
NiOEP_triB	1.953	104.5	1383.3	1519.9	1602.7	1603.0	1656.0		NiOEP/CS_2
NiTPP	1.953	104.8	1374.3	1505.0	1571.9	1547.0		1600.5	NiTPP/CS_2
NiTC$_5$TPP	1.969	105.3	1395.6	1531.2	1594.0	1569.0			NiTC$_5$TPP/xtals
NiTC$_6$TPP	1.920	105.7	1371.3	1512.9	1576.9	1525.7		1599.9	NiTC$_6$TPP/CS_2
NiTC$_7$TPP	1.900	105.7	1368.7	1505.3	1564.1			1598.1	NiTC$_7$TPP/CS2
NiOMTPP	1.884	106.0	1362.3	1512.1	1574.3	1520.0		1598.5	NiOMTPP/CS_2
NiOETPP	1.878	106.1	1359.7	1504.7	1562.0	~1507		1599.1	NiOETPP/CS_2
NiOPTPP	1.878	106.1	1359.9	1504.5	1559.9	~1504		1598.5	NiOPTPP/CS_2
NiDPP	1.896	105.6	1367.3	1510.7	1575.7	1503.0		1600.6	NiDPP/CS_2
			1353.1	~1500	1545.1			1606.2	
NiOETPP/planar	1.953	104.8							
NiP									NiP/xtals
NiOEP/triA	1.956	104.5	1380.4	1520.5		1605.5	1659.0		NiOEP/triA
NiOEP/triB	1.953	104.5	1382.9	1524.8		1608.4	1662.2		NiOEP/triB
NiOEP/tet	1.953	104.5	1383.0	1514.0		1595.0	1641.0		NiOEP/tet
NiOEP/alt	1.952	104.5							
NiTPP									NiTPP/xtals
NiTC$_5$TPP			1395.6	1531.2	1594.0	1569.0		1603.4	NiTC$_5$TPP/xtals
NiTC$_6$TPP			1375.6	1515.8	1575.6			1602.4	NiTC$_6$TPP/xtals
NiTC$_7$TPP			1371.8	1509.6	1567.4			1601.4	NiTC$_7$TPP/xtals
NiOMTPP									NiOMTPP/xtals
NiOETPP			1363.0	1510.0	1568.8			1603.0	NiOETPP/xtals
NiOPTPP			1361.0	1508.6	1562.4			1599.8	NiOPTPP/xtals

Table 1 lists members of the NiOATPP series whose structures have been calculated by energy optimization to date. The structural formulas are given in Figure 1 and the calculated 3-dimensional structures are shown in Figure 2. The newest member is NiDPP, which has phenyl substituents at the eight β-pyrrole and four bridging carbon positions of the porphyrin. Also listed in the table are the frequencies of several of the structure-sensitive Raman lines and two calculated structural parameters that define the metal core geometry and that may affect the catalytic activity of the metal center. Table 2 gives several other geometrical properties and the energies of the optimized structures for the NiOATPP series.

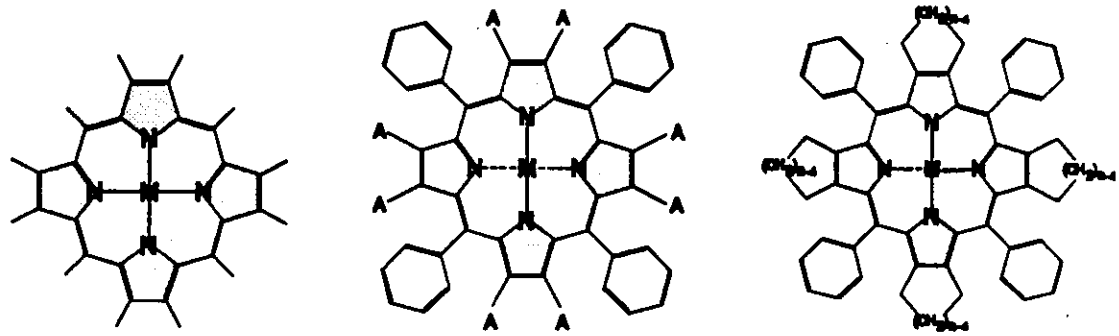
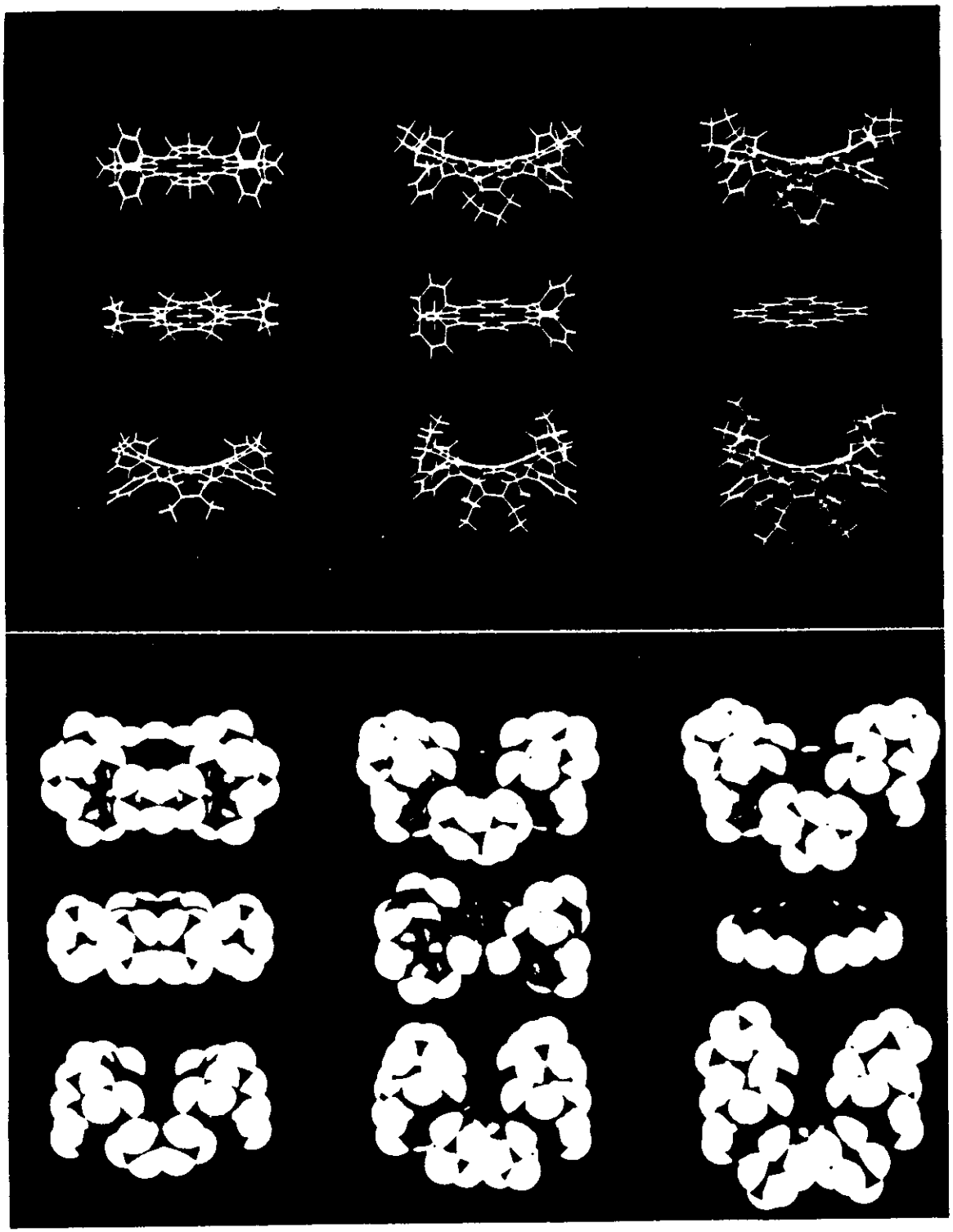


Figure 1. Structural formula of the parent metal porphine and octaalkyl-tetraphenylporphyrins.



Calculated NiOATPP Structures.

The structures of the ten molecules of the NiOATPP series were predicted using a molecular mechanics model based on the X-ray structure and the most recent normal coordinate analysis for NiOEP. The figure shows nine of the energy-optimized structures. They are (from upper left): $NiTC_5TPP$, $NiTC_6TPP$, $NiTC_7TPP$, NiOEP, NiTPP, NiP, NiOMTPP, NiOETPP, and NiOPTPP (bottom right). The nickel porphyrins have increasing steric congestion at the periphery of the macrocycle. Members of the group with the bulkiest substituents exhibit a high degree of non-planar distortion.

Figure 2.

To develop confidence in the accuracy of the calculated structures, it is imperative that these structures be verified experimentally. The X-ray crystal structures of several of the OATPP's are being determined by Jack Fajer and Kathy Barkigia at Brookhaven National Laboratory. They have provided preliminary results for the structure refinement of nickel octa-propyl-tetraphenylporphyrin (NiOPTPP), the most non-planar porphyrin of the series.

Table 2. Calculated minimum energies (kcal/mol) and some structural parameters for the nickel octa-alkyl(aryl)-tetraphenylporphyrins.

Raman data from:	Tot. E	Torsion	VDW	Angle	Bond	Ni-N	dihedral	<NNiN	φ dihedral
NiP/CH_2Cl_2	86.2	0.0	10.9	71.6	3.7	1.938	0.0	180.0	
NiOEP/CS_2	120.8	0.4	32.3	77.8	10.3	1.953	0.2	180.0	
NiTPP/CS_2	242.1	79.3	73.9	74.3	14.4	1.952	0.8	180.0	
$NiTC_5TPP$/xtals	338.1	108.0	66.2	142	21.9	1.969	0.1	179.9	89.9
$NiTC_6TPP/CS_2$	345.4	127.9	103.6	91.4	21.6	1.935	0.8	165.8	78.8 (81.6, 68.9)
$NiTC_7TPP/CS_2$	388.6	142.6	112.8	106.4	25.9	1.920	2.2	163.3	74.3 (88.1, 60.4)
NiOMTPP/CS_2	324.2	127.3	86.7	90.6	19.0	1.907	3.7	162.0	62.1
NiOETPP/CS_2	360.2	149.1	87.1	98.7	23.2	1.903	7.8	161.3	70.1
NiOPTPP/CS_2	370.0	149.3	93.6	99.9	25.0	1.903	8.6	161.5	70.1
NiDPP/CS_2	535.5	279.6	139.5	82.8	28.9	1.915	1.7	163.8	
Ni OETPP/planar	426.9	105.7	169.3	120.0	31.1	1.952	0.8	180.0	
NiOEP/triA	122.6	0.3	33.1	78.5	10.8	1.953	0.2	180.0	
NiOEP/triB	120.8	0.4	32.3	77.8	10.3	1.953	0.2	180.0	
NiOEP/tet	122.7	0.4	33.1	78.5	10.7	1.953	0.1	179.1	
NiOEP/alt	119.2	0.5	31.7	77.2	9.9	1.953	0.6	180.0	

The only true test of the accuracy of the molecular modelling calculations is the direct comparison with the X-ray crystal structures of one of the OATPPs. The first NiOATPP structure to be obtained is that of NiOPTPP. Two almost identical structures were obtained, one at room temperature and another at 200° K. Both structures have been refined to better than 5 % error. Because the calculations predict this nickel OATPP derivative has the most ruffled structure of the series, the calculation of its structure provides the most demanding test of our predictive capability (which was based on planar NiOEP).

Generally, the NiOPTPP structures are similar to the previously reported structure of zinc octa-ethyl-tetraphenylporphyrin with methanol bound to the metal (Barkigia *et al.*, personal communication). The calculated and experimental structural parameters for the porphyrin core are compared in Table 3. In particular, the macrocyle of NiOPTPP is strongly ruffled with the pyrrole rings alternately tilted above and below the mean porphyrin plane. The tilting of the pyrrole rings results in the nitrogens being alternately above and below the mean plane by from 0.199 to 0.173 Å (0.188 to 0.187 Å at room temperature). The calculated structure gives the same general structure, although some twisting of the pyrroles occurs in addition to the pyrrole tilting. The calculated distance for the out-of-plane distance of the nitrogens due to pyrrole tilting is 0.306 Å. Thus, the calculation slightly overestimates the degree of ruffling while, nevertheless, reproducing the basic non-planar distortion of the macrocycle.

For the determining the catalytic activity, the metal core geometry of is of vital importance. The Ni-N distance for the low temperature structure is 1.901±0.003 Å; the Ni-N distance for the room temperature structure is the same within experimental uncertainty, 1.899±0.003 Å. The experimental values compare exceptionally well with the calculated Ni-N distance of 1.903 Å. The average center-to-nitrogen distance is about 1.89 Å, slightly larger than the predicted core size of 1.88 Å. The Ni ion itself is less than 0.02 Å from the average plane of the porphyrin in both structures as is also the calculated result.

The C_aNC_a angle is also fairly accurately predicted by the energy minimized structure. The calculated value of 106.1° is to be compared with 105.8±0.1° for the low temperature structure and

105.7±0.3° for the room temperature structure.

Table 3. Comparison of calculated and X-ray structural parameters for the metal core of nickel(II) octapropyl-tetraphenylporphyrin.

Structural Parameter	Calculated	Experimental	
		Low Temp.	High Temp.
Ni-N bond distance	1.903 Å	1.902±0.002 Å	1.899±0.003 Å
Metal Core Size	1.878 Å	1.890 Å	
$C_\alpha NC_\alpha$ Angle	106.1°	105.8°	105.7°
N Out-of-Plane Dist.	0.3 Å	0.2 Å	
Ni Out-of-Plane Dist.	0.00 Å	<0.02 Å	

The slight overestimates of the nitrogen out-of-plane distance and the Ni-N distance suggest that slightly stiffer torsion force constants are necessary to more accurately predict porphyrin structures in the crystal phase. Nevertheless, it is evident that the energy-optimization calculations using our NiOEP force field are exceptionally precise in predicting the core geometry even in the most difficult case of NiOPTPP. Thus, we can with some confidence now believe the calculated porphyrin structures. This is even true for fairly elaborate and strained structures like NiOPTPP. NiOPTPP is predicted to have the best alkane binding site of all of the OATPPs synthesized to date, although more promising hydrocarbon-oxidation catalysts have been designed.

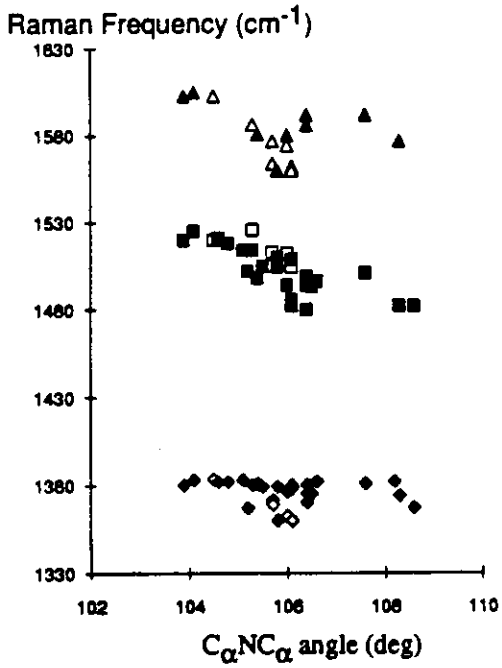


Figure 3.

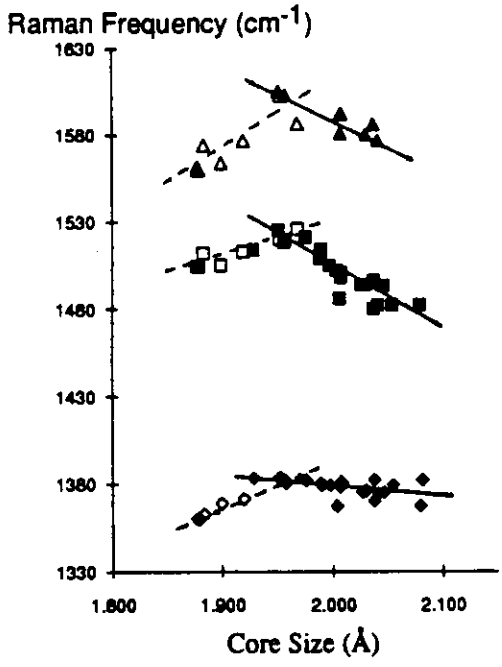


Figure 4.

Determination of Structure-Reactivity Relationships. We cannot always rely on obtaining full X-ray crystal structures to verify the molecular modelling predictions. Consequently, a more hopeful approach is to correlate easily obtainable spectroscopic parameters with molecular structure, and, in turn, relate the structure to reactivity. Such structure-reactivity relationships are essential to any program of rational catalyst design. In this regard, we have now successfully correlated Raman line frequencies with the structural parameters for the NiOATPP series of catalysts. Further, we have also succeeded in connecting variations in molecular structure of the NiOATPPs with the ligand affinity of the metal.

Raman data has been obtained for all ten of the nickel derivatives and three copper derivatives

(CuOETPP, CuTPP, and CuOEP), and more compounds of the series are being synthesized for additional experimental structural studies (see below). The experimental structural data reflect the systematic variation in the structures of the NiOATPPs. Figures 3 and 4 show plots of the correlations between two calculated structural parameters and some Raman line frequencies for the series on NiOATPPs. (A paper submitted to Journal of the American Chemical Society describes the experimental studies, modelling calculations, and relationships between experimental data and molecular structure in considerable detail.)

The structural differences among the NiOATPPs influence the ligand reactivity in a systematic way. Thus, we plan to redirect the work on the OATPP series into an investigation of reactivity and alkane-activation activity of the Fe and Mn derivatives. This will be coupled with CAMD calculations for the these new derivatives and their interactions with reaction partners in the catalytic environment. What follows is a brief description of the NiOATPP results and their importance for the CAMD facets of alkane-activation catalyst design.

It is clear from the data in the Table 1 and Figures 3 and 4 that linear relationships exists between the Raman frequencies of the ν_4, ν_3, ν_2, and ν_{19} vibrations and either the metal core size (Ct-N) or the pyrrole $C_\alpha NC_\alpha$ angle. For the core size two separate linear relationships are noted in the data of Figure 4. The slope of the correlation between metal core size and the Raman frequencies for the NiOATPP data is *positive*, whereas for the usual core size-frequency relationship the slope is *negative*. This new relationship between core size and frequency is a result of the substituent induced distortion of the planarity that occurs for the OATPP series. The usual core-size correlation is for mostly planar porphyrins.

Figure 5 gives the relationship between core size and pyrrole angle for the old and new structural data. For the old data, the two structural parameters are seen to be correlated with each other (filled squares); therefore, either core size or angle could be the determining factor for the so-called core-size correlation. Because the correlation breaks down for the new structural data (open squares), the influence of the angle and the core size can be separated. Examination of Figures 3 and 4 suggest that the relevant parameter in determining the Raman frequency is the $C_\alpha NC_\alpha$ angle, not the core size. The implications of this result reaches far beyond molecular modelling for catalyst design.

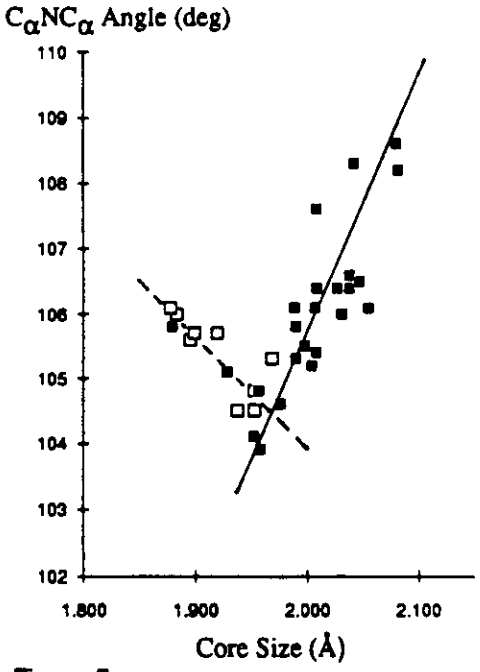


Figure 5.

The upshot is that we now have an easily obtained experimental measure of the planarity of the porphyrin macrocycle and related changes at the metal center. This is valuable in our catalyst design studies because we are using the non-planarity of the porphyrins to construct the alkane binding cavity, and we now have an experimental technique for verifying the calculated non-planarity of the designed catalysts.

Thus, the energy optimized structures appear to give an accurate reflection of the actual molecular structure, even for the most distorted case. Detailed comparisons with the full crystal structure of NiOPTPP and other porphyrins of the OATPP series should be possible soon.

Molecular Modelling of Catalytic Intermediates. Classical molecular modelling of N-phenyl protoporphyrins has begun and will be described in the Future Work section. We have also initiated INDO/CI (intermediate neglect of differential overlap/configuration interaction) molecular orbital calculations of model cytochrome P_{450} porphyrin complexes. The purpose of this work is to better understand the catalysis of the metal contained in the porphyrin ring, so that improvements in catalytic

activity can be designed into the tailored catalyst. Initially, we chose the vanadyl porphyrin complex for investigation of the electronic structure of a metal-oxo bond, mimicking the Fe=O and Mn=O bonds of alkane activation catalysts. The vanadium-oxo complex is more tractible from the standpoint of the INDO/CI calculations and there use in the interpretation of experimental data on the excited states. The V=O porphyrin calculation will serve as a useful point of comparison for future INDO/CI MO calculations for the Fe and Mn analogs. The calculations give qualitatively different results for the low lying, and therefore chemically active, excited states compared with interative extended Hückel (IEH) MO methods (See Publication 1, 24b.). In fact, the lowest excited state predicted by the INDO/CI is a metal-to-porphyrin charge-transfer state rather than a porphyrin-to-metal or d-d state as predicted by the IEH MO calculation (See Publication 1, 24b.). The INDO/CI prediction is in better agreement with the transient Raman spectra of this excited state. A manuscript is in preparation on the application of the INDO/CI methods for vanadyl tetraphenylporphyrins.

CAMD Calculations of Specific Interactions. We have designed a porphyrin catalyst with all of the structural features now thought to be required for an efficient and selective ethane-oxidation catalyst. These features include a catalytic metal center with an iron atom in the porphyrin core coordinated to a mercaptide sulfur ligand acting as a promoter. The mercapto group is tethered to one of the pyrrole groups by a $-(CH_2)_4-$ chain. The other seven b-carbon pyrrole positions are occupied by methyl-cyano (CH_2CN) groups. These groups serve to cause the non-planar distortion needed to form a deep groove on both faces of the porphyrin that is suitable for binding ethane. The severe steric interactions among the peripheral methyl-cyano and meso-phenyl substituents results in the required inflexibility of the ethane binding cavity. Also important for alkane binding is the negative partial charges of many of the atoms lining the cavity.

In a dynamics calculation in which ethane is initially inserted into the binding cavity, ethane remains bound for 65 ps (the full length of the 3-day calculation on a MicroVAX II computer) at room temperature *in a vacuum*. This was a worst case senario for the catalyst, since the oxygen atom bound to Fe of the reactive ferryl intermediate partially occupied the ethane binding cavity. We are currently pursuing the synthesis of this catalyst and other potential catalysts with Michiko Miura of Brookhaven National Laboratory.

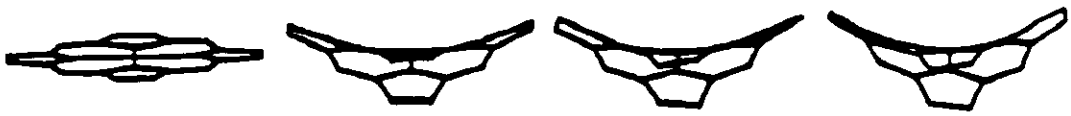
Gaseous molecule interactions with the tailored binding site of a octa*propyl*-tetraphenyl-porphyrin (OPTPP) catalyst have been investigated in preparation for experimental studies of the binding of methane and other alkane natural gas components to the tailored cavity. Molecular dynamics calculations show that CO_2 will stay bound to NiOPTPP for greater than 65 ps, but ethane is bound much more weakly. The stronger binding of CO_2 is a result of the complimentary partial charges of the cavity of the catalyst.

The critical nature of the binding site's rigidity is demonstrated by a dynamics calculation in which n-butane was bound to the groove of metal-free OPTPP. By only 1 ps at 300° K the butane molecule evaporates from the cavity. The lack of significant binding is most likely due to the increased macrocycle flexibility resulting from the absence of a metal ion in the porphyrin core. The butane-H_2OPTPP dynamics calculation was the first carried out using a new and faster Silicon Graphics workstation.

An important question is how long the cavity itself is stable. Molecular dynamics calculations at 300 °K show that the substrate binding groove exists for at least 65 ps and that methane or CO_2 will stay bound to the cavity for at least this long. To determine whether the lifetime of the binding cavity is on the order of the turnover time of the catalyst, we have undertaken detailed molecular mechanics calculations and spectroscopic structural characterization of the OATPP series. (A report on this work is in *Tetrahedron Lett.*1990, 31, 3719.) We have (1) calculated energy-minimized molecular structures of the nickel OATPP series and obtained H-NMR spectra at several temperatures between 200 and 293 °K for the nickel OATPP series, the H_2OATPP (free base) series, and the $H_4TC_nTPP^{2+}$ (dication) series. The calculated structures show increasing non-planarity of the porphyrin skeleton as shown in Figure 6. The cavity is formed by forcing a highly non-planar conformation upon the porphyrin macrocycle. The non-planarity makes the pyrrole substituents form a deep, rigid groove on both faces of the porphyrin

ring, especially for OETPP. Our dynamics calculations show that binding of light alkanes of natural gas to the groove is favorable, even in a vacuum.

The NMR results give information concerning the *lifetime* of the groove configuration in which the alkane is expected to bind. As an example, for nickel octaethyl-tetraphenyl porphyrin (NiOETPP) the substrate binding groove exists for 4 to 400 ms at 300 °K, a time that is on the order of typical catalyst turnover times. Larger metals, such as Fe, Mn, and Ru that are active alkane oxidation catalysts, appear to stabilize the alkane binding groove (e.g. 0.6-6 s for ZnOETPP).



n=5 n=6 n=7 NiOETPP

Figure 6. Energy minimized structures of the porphyrin ring (substituents have been removed for clarity) for $NiTC_5TPP$, $NiTC_6TPP$, $NiTC_7TPP$, and NiOETPP.

In an extension of the work on substrate-metalloporphyrin complexes, we have investigated the effects on stacking interactions resulting from transient formation of a metal-centered excited state. The excited state formed results in the expansion of the central core of the porphyrin in which the nickel ion resides. Core expansion removes the forces which drive the ruffling of Ni porphyrins; therefore, the formation of the excited state results in a short lived (~300 ps) transition from a ruffled to a planar conformation. We have observed the effects of this conformational transition on complex formation using a unique, new transient Raman difference spectrometer.

Transient Raman difference spectroscopy (RDS) is being developed at Sandia as a probe of transient reaction intermediates and excited states. We now have the first working transient RDS instrument and, as a test case, have used the new technique to measure the effect of π–π complex formation in the excited d-d state of Ni porphyrins (4).

In other work on CAMD evaluation of interactions between designed catalysts and substrates, we have carried out molecular dynamics calculations of the interaction of the alkane (2,2-dimethylbutane) with the oxo-ruthenium tetrakis(9-anthracenyl) porphyrin. Based on the calculation, we predict that little if any shape or size selectivity of alkane activation will be observed as a result of the steric constraints imposed by the anthracenyl groups. Some benefit may be observed in preventing catalyst self-destruction, however.

Synthesis of Designed Natural Gas Conversion Catalysts: *Synthesis of Metal Octa-alkyl-tetraphenylporphyrin Catalysts.* The catalysts of the OATPP series are being synthesized by Prof. Kevin Smith at UC, Davis. A large collection of metal OATPPs have now been synthesized and characterized as described above and in the attached reprint and preprint. Craig Medforth and Kevin Smith will continue to make new members of this class of catalysts. In the last month they have provided the first derivatives containing metals other than nickel. These include two copper(II) derivatives and three cobalt(II) derivatives. The cobalt derivatives were required for the NMR gaseous ligand binding studies.

Synthesis of Bis-Deep-Pocket Porphyrins. DOE and Sandia intend to apply for a patent on the class of bis-pocket porphyrin catalysts being synthesized at Sandia that are based on the tetra(2,6-dinitrophenyl)porphyrins. We are pursuing additional syntheses based on these metalloporphyrins. We are also synthesizing quantities of the manganese and iron tetra(9-anthracenyl)porphyrins suitable for testing.

Testing and Characterization of Designed Catalysts: *Biomimetic Photochemical Oxidation of Alkanes Using O_2.* Work on this process has resulted in a patent that was awarded in April 1990. Further development of the process is awaiting testable quantities of the designed catalysts having substrate binding cavities.

Evaluation of System Parameters in Catalytic Activity Tests. A spectroscopic study of substrate binding to the designed OATPP catalysts is underway for the purpose of separating the effects of substrate affinity and metal center efficiency upon overall catalytic activity. Co(II)OPTPP, CoDPP, and $CoTC_6TPP$ have now been synthesized for the ^{13}C-NMR light alkane binding studies. See next section for details.

Future Work. Our primary emphasis for the coming year will be on enhancing the testing and synthesis aspects of the catalysts design work. Considerable progress in the computer-aided design of catalysts has been made, and the objective now is to exhaustively test the activity and selectivity of some of the prospective catalysts that have been identified. The general goals for Sandia's natural gas conversion program can be organized into three general areas.

Computer-Aided Molecular Design of Natural Gas Conversion Catalysts. The classical modelling part of the program is mature and well defined goals can be easily identified. These include: (1) Modify the force-field parameter files for operation on a new Silicon Graphics computer. This will allow longer dynamics runs (~1 ns) and/or larger calculation, e. g. solvent interaction studies. (2) Continue improving catalyst designs based on the OATPPs. Investigate other substituents for forming the substrate binding cavity, including substituents that more fully enclose the groove of the OATPP catalysts and substituents that have complementary properties (partial atomic charges, etc.) to enhance substrate binding. (3) Investigate solvent interactions and their influence on substrate and product binding.

Another main goal is to design larger cavities for larger substrate molecules. This will be required for substrates of the size of t-butyl ether and other important oxygenates.

One entirely new direction for the classical molecular modelling work is to develop an understanding of the N-alkyl porphyrin intermediates of the cytochrome P_{450} reaction. The N-phenyl or N-alkyl porphyrin derivatives are thought to be one of four or five intermediates involved in hydroxylation and epoxidation reactions carried out by cytochrome P_{450}. Consequently, we will carry out a molecular modelling study of the N-phenyl porphyrins. Preliminary energy-optimization calculations have been carried out. We have also obtained resonance Raman spectra of one of the zinc(II) N-phenyl-protoporphyrin IX derivatives for comparison with the structural predictions. This preliminary work will be expanded to all four isomers and the phenylhydrazine reacted cytochrome P_{450}.

Quantum mechanical modelling of reaction intermediate will also continue. Emphasis will be placed on INDO/CI and Dmol *ab initio* calculations for the N-phenyl protoporphyrins and high oxidation-state intermediates and analogs. We will complete the V=O porphyrin study and proceed to ferryl porphyrin intermediates. We will investigate the effects of core geometry and substituents on the energy level structure of the Fe=O and V=O intermediates. For the N-phenyl porphyrins, we will perform calculations to determine the relationship between non-planarity of the N-phenyl substituted ring and the ring conjugation of the vinyl substituents.

Synthesis of Natural Gas Conversion Catalysts. Our primary synthesis goal is the synthesis of Fe and Mn OATPP derivatives in quantities suitable for testing in batch reactors. Future work in this area will focus on (1) synthesis of Fe and Mn derivatives for alkane-oxidation studies, in particular the effects of non-planarity on activity and stability of the catalysts, (2) synthesis of variants with deeper, larger, and more fully enclosed cavities, and (3) and synthesis of cobalt derivatives of the OATPPs for ^{13}C- and H-NMR studies of binding of ethane, methane and other light alkanes and alcohols to this series of catalysts.

We will complete the synthesis of Fe and Mn tetra-anthracenyl-porphyrin (TAP) derivatives in quantities suitable for testing. The synthesis of 2,6-substituted anthracenyl porphyrins will also be pursued with the goal of deepening the substrate binding pocket.

The four N-phenyl-protoporphyrin IX isomers in which a phenyl group is attached at the nitrogens of the A, B, C, and D pyrrole rings of both Zn and free base protoporphyrin will be provided by Prof. Ortiz de Mantellano at UCSF. The synthesis of N-phenyl derivatives of protoporphyrin can also be carried out in the protein itself as a means of determining the size and shape of the substrate binding site and its position relative to the Fe-porphyrin group. The shape and location of the substrate binding pocket are inferred by determining which of the four pyrrole rings are phenylated.

Testing of Designed Gaseous Hydrocarbon Conversion Catalysts. Our main goal in the testing

portion of the catalyst design program is to test the Fe and Mn OATPP derivatives and other catalyst for their alkane activation activity. This has not been possible in the past because of the limited availability of these compounds. The steps we have taken to enhance our synthetic capabilities and manpower shortages should alleviate this obstacle to the testing program, since the yields for most of the synthetic procedures are high.

Specific goals of the testing program are outlined below. One of our main initial goals is to spectroscopically verify light alkane binding to the OATPP class of catalysts. We will develop an experimental method to detect binding of gaseous molecules to the engineered hydrophobic cavity of the catalyst. This is challenging because natural gas components interact with the designed pocket largely by weak non-bonding forces, like van-der-Waals interactions. At present ^{13}C-NMR spectroscopy seems to be our best method for observing and quantifying the binding of gaseous hydrocarbons of natural gas to the cavity of these catalysts. Because of the strong ring current of the porphyrin macrocycle, resonances of bound hydrocarbons species should be significantly shifted relative to the free molecules. We hope to use this method to measure the binding to the pocket. When a catalytic metal center is present, binding of hydrocarbon can be inferred by reaction rates. However, other factors (e.g. turnover rate) complicate determination of the binding affinity by this method. We will use ^{13}C-NMR spectroscopy and, possibly, FTIR spectroscopy to detect the binding of light hydrocarbon gases to the porphyrin catalyst. Paramagnetic NMR provides an additional mechanism by which hydrocarbon binding can be measured. Metals like Fe(III) and Co(II) in the porphyrin core introduce a paramagnetic probe that allows NMR measurements that determine distances between individual atoms of bound substrate molecules and the paramagnetic metal center. Binding is determined by measuring the change in the longitudinal relaxation time of nearby ^{13}C nuclei, and the distance between the paramagnetic ion and the ^{13}C nuclei is calculated from the dipolar term of the Solomon-Bloembergen equation. We have recently obtained three Co(II) OATPP derivatives from Craig Medforth and Kevin Smith for these studies.

We have synthesized tetrakis(9-anthracenyl)porphyrin (TAP) and tetrakis(10-Cl-9-anthracenyl)porphyrin (Cl-TAP) free bases and are scaling up to obtain quantities suitable for testing. Work on these catalysts will emphasize the completion of the synthesis, purification, and alkane activation testing of Mn and Fe tetrakis(anthracenyl) porphyrin catalysts. Stability, shape and size selectivity, and electronic effects on reactivity will be investigated. In particular, we will test the Fe and Mn TAP catalysts to determine the substituent electron withdrawing effect on activity. TAP and Cl-TAP are well suited to answer this important question, because they have different electron withdrawing properties introduced by the chloro substituent on the anthracene groups of Cl-TAP. The activity test should not be complicated as would be the case for porphyrins without the bulky, rigid anthracenyl substituents. Selectivity studies for larger alkanes will also be carried out. This work should serve as baseline studies for derivatized TAPs, if syntheses of these catalysts are successful.

A photochemically driven alkane-oxidation reaction that mimics biological photosynthesis, electron-transfer, and hydrocarbon-oxidation reactions has been patented. The reaction occurs at room temperature and uses O_2 as the oxidant. Most importantly, the reaction can be run for hours without significant degradation. This means that the oxidation of low molecular weight alkanes by O_2, which proceeds at a lower rate than for higher alkanes, can be investigated. Further studies will be performed to determine the detailed reaction mechanisms involved in the photochemical reaction. Using O_2 as the oxidant will allow us to test the catalysts designed to have a small fully enclosed cavity at the metal site. These catalysts cannot be tested with larger oxidants like iodosylbenzene.

Activity test will be carried out in batch reactors using Sandia's gas chromatography capabilities. The goals of the activity testing work will be: (1) Determine the detailed mechanism of the photochemical and dark alkane-activation reaction. (2) Test the engineered catalysts using O_2 as the oxidant while varying the structural parameters outlined in the CAMD section above. (3) Determine the regioselectivity for lower alkanes, especially 2,2-dimethylbutane since it has a 2°, and two distinct 1° sites. (4) Investigate other variables of the photochemical system such as solvent, photosensitizer, possible relays, and phase separation of the light and dark reactions. (5) Perform tests to determine the structural requirements necessary to selectively generate the cytochrome-P_{450} intermediate and, thus,

alcohols as products.

PUBLICATIONS (Relevant Publications and Patents: October 1989 - Present):

(1) Medforth, C. J.; Berber, M. D.; Smith, K. M.; Shelnutt, J. A. *Tetracycloalkenyl-meso-tetraphenylporphyrins as Models for the Effect of Non-Planarity on the Light Absorption Properties of Photosynthetic Chromophores*Tetrahedron Lett. **31**, 3719 (1990).

(2) Shelnutt, J. A. *Process for Light-Driven Hydrocarbon Oxidation at Ambient Temperatures* U.S. Patent No. 4,917,784 (1990).

(3) Shelnutt, J. A.; Trudell, D. E. *Photochemically-Driven Biomimetic Oxidation of Alkanes and Olefins* Tetrahedron Lett. **30**, 5234 (1989).

(4) Crawford, B. A.; Ondrias, M. R.; Shelnutt, J. A. *Transient Raman Difference Spectroscopy of Nickel(II) Uroporphyrin π–π Complexes* J. Phys. Chem. **94**, 6647 (1990).

(5) Alden, R. G.; Sparks, L. D.; Ondrias, M. R.; Crawford, B. A.; Shelnutt, J. A. *Excited State Transient of Vanadyl Uroporphyrin I Detected Using Resonance Raman Spectroscopy* J. Phys. Chem. **94**, 1440 (1990).

(6) *Photochemically-Driven Biomimetic Oxidation of Alkanes and Olefins* Shelnutt, J. A., Trudell, D. E. in *Novel Materials in Heterogeneous Catalysis*, ACS Symp. Ser. 437, Eds. Baker R. T. K.; Murrell, L. L. (American Chemical Society: Washington, DC) Chpt. 24, 1990.

(7) *Biomimetic Oxidation of Alkanes and Olefins Using O_2 and Light* Shelnutt, J. A. in "Methane Activation, Conversion and Utilization" Preprints, PACIFICHEM'89, Honolulu, Hawaii, 40,(1989).

(8) Quintana, C. A.; Shelnutt, J. A. *Synthesis and Spectroscopic Characterization of Bis-Pocket Porphyrins* U. S. Patent Application SD-4796, S-70,606. DOE Intent to File, January 26, 1990.