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Novel iron meso-nitrooctaethylporphine complexes for the catalytic reaction of alkanes with molecular oxygen

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Introducing nitro groups into the *meso*-positions of a metalloporphyrin converts a catalytically inactive complex into a highly active catalyst for the oxidation of alkanes with molecular oxygen. The degree of nitration correlates with both the Fe(III)/Fe(II) reduction potential and the catalytic activity.

Keywords: Metallonitroporphines; oxidation; isobutane; propane

1. Introduction

The development of a catalyst for the selective oxidation of alkanes to alcohols with air or oxygen remains an important goal of both synthetic and industrial chemistry. Synthetic metalloporphyrin catalysts inspired by enzymic systems such as the monooxygenase cytochrome P450, are of interest as catalysts for alkane hydroxylations using a number of oxidants including molecular oxygen [1].

A key to the biomimetic approach to modeling cytochrome P450 and producing catalysts which can mimic the hydroxylation activity of the enzyme, has been the development of synthetic metalloporphyrin chemistry. Nearly all of the metalloporphyrins used as oxidation catalysts have been based on the meso-tetraphenylporphine, TPP, ligand system. A number of metalloporphyrin complexes have been synthesized by ourselves and others in which the meso-phenyl groups have been substituted in order to adjust the electronic nature of TPP or modify the geometry of the porphyrin plane and thereby control access to the metal center [2–6].

In this regard, it is interesting to note that the prosthetic group of cytochrome P450, iron-protoporphyrin IX, contains no phenyl groups in the meso positions and in fact is unsubstituted in those positions. Synthetic "flat" metalloporphyrin complexes that have no meso-phenyl groups and are not protected by the protein as in the natural enzyme, have been ineffective for alkane oxidation [7]. It is thought that the meso-unsubstituted metalloporphyrin complexes are prone to attack at the meso-carbon during oxidation leading to facile porphyrin degradation [8,9].

Thus, the nature of the meso-substituent can play a critical role in catalytic oxidation reactions. We have shown that the tetraphenylporphyrin metal complexes whose meso-phenyl groups bear halogen substituents are active catalysts for the reaction of unsubstituted light alkanes with oxygen [2,10,11]. In particular, complexes having meso-pentafluorophenyl substituents exhibit high activity for the air-oxidation of alkanes. We have further shown that this activity is related to the electron withdrawing character of the halogen substituents and may be due to increased M(III)/M(II) reduction potential at the central metal atom.

In this communication we report for the first time that incorporating highly electron-withdrawing nitro groups in the meso-position of a porphyrinato iron complex provides soluble, active catalysts for the liquid phase oxidation of alkanes. We further describe the synthesis of nitrated iron octaethylporphyrins and the effect of the degree of meso-nitration on catalytic activity. *These are the first metalloporphyrin complexes having nitro substituents in the meso-position which are efficient catalysts for the oxidation of hydrocarbons with dioxygen.*

2. Experimental

The μ-oxo dimer of (meso-tetranitrooctaethylporphinato)iron(III), $[Fe(OEP)(NO_2)_4]_2O$, was prepared by nitration similar to the method of Gong and Dolphin [12] wherein a 12/1 molar ratio of NO_2 to Fe(OEP)Cl is stirred under N_2 in CH_2Cl_2 for 1 h at room temperature. After chromatography on neutral alumina eluting with chloroform/hexane, the pure μ-oxo dimer is obtained. FAB/MS gives a M^+ of 767.5 for the complex, corresponding to $Fe(OEP)(NO_2)_4^+$. The IR (KBr) spectrum shows N–O stretches at 1368 and 1537 cm^{-1} and the Fe–O–Fe stretch at 853 cm^{-1}. The ^1H NMR ($CDCl_3$) spectrum is very similar to that of the μ-oxo dimer of $Fe(OEP)^9$ with broad resonances at 5.8 and 4.5 ($-CH_2-$) and 1.36 ($-CH_3$) ppm.

The chloride salt, $Fe(OEP)(NO_2)_4Cl$ is obtained by treatment of the μ-oxo dimer with 6 N HCl in CH_2Cl_2. The ^1H NMR ($CDCl_3$) spectrum of this material shows resonances at 39.2 ($-CH_2-$) and 5.4 ($-CH_3$) ppm.

$\{Fe[5,15\text{-}(NO_2)_2OEP]\}_2O$ [#1] [14] a by-product of nitration, is obtained via chromatography on neutral alumina eluting with a 1/3 CH_2Cl_2/hexane mixture. This material is recrystallized from slow addition of an isopropanol/hexane mixture to a CH_2Cl_2 solution of the dinitro iron porphyrin. ^1H NMR ($CDCl_3$) has broad resonances at 6.5 (meso C–*H*), 6.0, 5.8, 5.0, 4.3 ($-CH_2-$) and 1.7 and 1.5 ($-CH_3$). The IR (KBr) spectrum shows N–O stretches at 1367 and 1533 cm^{-1} and the Fe–O–Fe stretch of the μ-oxo dimer is seen as a shoulder at 860 cm^{-1}. The IR also shows a

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[#1] The X-ray crystal structure of this complex has recently been completed showing the trans geometry of the nitro groups [16].

strong band at 875 cm^{-1} attributable to a meso-CH deformation mode [15] which is not present in the tetranitrated material in which all four meso-CH bands have been nitrated. $[Fe(OEP)]_2O$ was prepared [13] by reaction of Fe(OEP)Cl with aqueous sodium hydroxide.

Isobutane oxidations were conducted in glass Fisher-Porter aerosol tubes attached to a gas manifold for addition of pure oxygen as it was consumed. Isobutane was dissolved in a benzene solution of the catalyst which was stirred magnetically and heated by immersion of the tube in an oil bath. Product analyses were conducted by standardized glpc.

Propane oxidations were carried out under air pressure in 300 cm^3 glass lined stainless steel autoclaves equipped with internal thermocouple, magnedrive stirrer and cooling coils for regulating reaction temperature. Internals were teflon-coated. Propane was pressured into a benzene solution of the catalyst and air was then added under pressure. Product analyses were conducted by standardized glpc.

Caution: Some reactions were conducted within the explosive region so care was taken to properly barricade reactor systems. Glass reactors for isobutane oxidations were housed inside hoods surrounded by one-inch polycarbonate shielding. Propane oxidations were carried out behind barricades of steel and sand.

3. Results and discussion

Table 1 shows that the electron-withdrawing nitro group in the meso-position of the porphyrin macrocycle, fig. 1, imparts hydrocarbon oxidation activity to the otherwise inactive iron octaethylporphyrin complex. The greater the number of nitro groups, the more active is the porphyrin complex for air-oxidation of isobutane. The Fe(III)/Fe(II) reduction potentials of the octaethylporphyrin complexes increase steadily with each successive meso-nitro group [14]. In addition, the stability

Table 1
Isobutane oxidation activity of iron porphyrin complexes [a]

Complex	$T = 60°C$		$T = 80°C$	
	TO [c]	Sel. [d]	TO [c]	Sel. [d]
$[FE(OEP)]_2O$ [b]	0	–	0	–
$\{Fe[5,15\text{-}(NO_2)_2OEP]\}_2O$	360	88	970	89
$[FE(OEP)(NO_2)_4]_2O$	800	88	1680	88

[a] Isobutane, 7 g, in 30 ml benzene containing 0.013 mmol complex, heated and stirred at reaction temperature for 5 h under 100 psig of O_2.

[b] OEP = octaethylporphyrinato.

[c] TO = turnovers = mol (TBA + acetone)/mol catalyst.

[d] Sel. = (mol *t*-butyl alcohol produced/total mol liquid product) × 100.

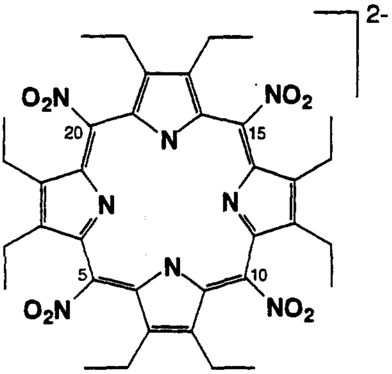

Fig. 1. The meso-tetranitrooctaethylporphinato ligand.

of the complex under oxidation conditions becomes greater as nitro groups are added to the meso-positions around the macrocycle.

As shown in table 1, the diiron μ-oxo complex is highly active for alkane oxidation. It is very soluble in hydrocarbon medium and is a convenient homogeneous catalyst for this reaction. High activity is characteristic of the bismetal μ-oxo complexes of electron deficient porphyrins [2,3] in contrast to typical metalloporphyrins whose μ-oxo dimers are inactive. Selectivity of the isobutane oxidation reactions to the alcohol is high (88%) in the catalytic reactions.

The μ-oxo dimer, $[Fe(OEP)(NO_2)_4]_2O$, also catalyzes the reaction of propane with molecular oxygen. Propane, 1.36 mol, was oxidized using 1500 psi air in a stirred glass-lined autoclave in 48 ml benzene containing 0.023 mmol of $[Fe(OEP)(NO_2)_4]_2O$ at 125°C for 6 h. Acetone and isopropyl alcohol in a 2/1 ratio were the only oxidation products detected in the liquid phase. The number of turnovers was 148 mol of liquid oxidation products per mol of catalyst in the 6 h period. After this time the dark benzene solution had nearly completely bleached and the catalyst had deactivated.

4. Conclusions

Incorporating nitro groups into the meso-position of octaethylporphinato iron complexes introduces a powerful electron withdrawing group which increases the Fe(III)/Fe(II) reduction potential over that of the parent Fe(OEP) complex and provides catalysts for the selective, low temperature oxidation of alkanes. Thus, the nitro groups serve both to protect the reactive meso-position from rapid oxidative attack and to enhance the catalytic oxidation activity. In addition, *these findings show the validity of the general hypothesis that electron withdrawing groups in the meso-position of porphinato iron complexes enhance alkane oxidation activity* [2,3].

Work continues to examine this phenomenon in more details as well as to further enhance catalytic activity and stability for selective alkane oxidations.

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