

PHOTOCHEMICALLY-DRIVEN BIOMIMETIC OXIDATION
OF ALKANES AND OLEFINS

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ABSTRACT

A photochemical reaction for oxidation of hydrocarbons that uses molecular oxygen as the oxidant is described. A reductive photoredox cycle that uses a tin(IV)- or antimony(V)-porphyrin photosensitizer generates the co-reductant equivalents required to activate oxygen. This "artificial" photosynthesis system drives a second catalytic cycle, mimicking the cytochrome P_{450} reaction, which oxidizes hydrocarbons. An iron(III)- or manganese(III)-porphyrin is used as the hydrocarbon-oxidation catalyst. Methylviologen can be used as a redox relay molecule to provide for electron-transfer from the reduced photosensitizer to the Fe or Mn porphyrin, but appears not to enhance efficiency of the process. The system is long-lived and may be used in time-resolved spectroscopic studies of the photo-initiated reaction to determine reaction rates and intermediates.

INTRODUCTION

Many alkane and olefin oxidation systems that mimic biological oxidation of hydrocarbons by cytochrome P_{450} have been reported. Most use an iron, manganese, or ruthenium porphyrin as the analog of the heme (iron porphyrin) functional group of the enzyme.¹⁻⁸ In the great majority of these chemistries a single oxygen atom donor, such as iodosylbenzene or hypochlorite, is used as the oxidant rather than molecular oxygen.¹⁻⁴ When molecular oxygen is used as the oxidant, as is the case for cytochrome P_{450} , reducing equivalents must be supplied to reduce the Fe porphyrin causing it to bind and split dioxygen and, subsequently, oxidize the alkane substrate. Several biomimetic systems have been demonstrated using either sodium borohydride, hydrogen/Pt, ascorbate, or zinc metal as the co-reductant.⁵⁻⁸

We have been investigating these reactions from the standpoint of stereochemically controlling the reaction at the metal site by designing metalloporphyrins with a shape- and size-selective pocket at the metal center.^{9,10} The pockets designed so far are small, and thus require an oxidant, like O_2 , that is small enough to enter the cavity. It is also desirable that the system be stable and operate over many hours. We are interested also in the possibility of photo-initiating the reaction so that reaction intermediates can be followed using time-resolved spectroscopic techniques for kinetic studies. This can be accomplished if the reductant is the product of a photoredox cycle.

Here we describe such a photochemically driven system for oxidation of alkanes and olefins. The system is illustrated in Figure 1. The cycle on the left is the photoredox chemistry that produces the reductant, a long-lived tin(IV)-porphyrin radical anion. In the cycle, a tin(IV)- or antimony(V)-porphyrin absorbs a photon of visible light resulting in the formation of the triplet excited state of the porphyrin. The porphyrin photosensitizer in its excited state is reduced by a sacrificial electron donor such as triethanolamine (TEOA).¹¹⁻¹³ The resulting long-lived π anion of the porphyrin has a

redox potential low enough to reduce either a Fe(III) or Mn(III) porphyrin, which acts as a catalyst for the biomimetic oxidation of hydrocarbons.^{13,14} After reduction of the FeP, the photosensitizer anion (SnP⁻) returns to the resting redox state (SnP). Actually, two molecules of the porphyrin anion are required in the biomimetic P₄₅₀ cycle as indicated in Figure 1; the first to reduce Fe(II) to Fe(III), allowing O₂ to bind and a second to split dioxygen to form the reactive O=FeP intermediate. In some cases a molecule such as heptylviologen (HV²⁺) is used to relay the electron from the SnP anion to the P₄₅₀ cycle. Acetic or benzoic anhydride is sometimes used as an oxygen atom acceptor (replacing H⁺) in the splitting of dioxygen in the hydrocarbon (RH) oxidation cycle.

RESULTS AND DISCUSSION

A photochemical reaction like that illustrated in Figure 1 was carried out in acetonitrile under an O₂ or air atmosphere. In a typical reaction, 0.24 μmol of Fe(III) tetra(pentafluoro-phenyl)porphyrin (FeTF₅PP) chloride, 0.45 μmol of Sn(IV) protoporphyrin IX (SnProtoP) dichloride, 1.1 mmol of TEOA, 1.4 μmol of heptylviologen (N,N'-diheptyl-4,4'-dipyridinium dichloride), and 11 μmol of benzoic (or acetic) anhydride, were added to 1 ml of acetonitrile. Hexane (4.7 mmol) was added as a substrate. The samples, contained in a 1-cm path length cuvette, were irradiated with a tungsten lamp for 1-6 hr. Light of wavelengths less than 380 nm was filtered to insure that photosensitization of the reaction was only due to visible light absorption by the porphyrin. 1-, 2-, and 3-Hexanol and 2- and 3-hexanone products were quantified at the end of the run by gas chromatography. Table 1 gives yields and hexanol to hexanone product ratios for typical runs and control experiments.

In the presence of the P₄₅₀ catalyst, a generally higher overall yield of products is observed when illumination and other conditions were identical; however, a lower average hexanol to hexanone ratio of 1.3:1 is observed. However, in the absence of the catalyst FeTF₅PP, photosensitized production of hexanols and hexanones is observed in an average ratio of 2.3:1. In the absence of O₂, light, photosensitizer, or triethanolamine, there is no significant yield of oxidized hexane.

It is apparent that more than one oxygen activation pathway exists. The excited triplet state of tin porphyrins is known to be quenched in the presence of O₂,¹⁴ suggesting a possible direct mechanism of O₂ activation by the photosensitizer. We have examined reactions of both singlet O₂ and superoxide anion under our reaction conditions. Chemically-produced superoxide (KO₂/18-crown-6) is not reactive under our experimental conditions. On the other hand, singlet oxygen, produced by irradiation of free base protoporphyrin (H₂ProtoP),¹⁵ is reactive in the presence of tertiary amines and gives about the same hexanol to hexanone ratio (2.7, see Table 1) as is observed in the presence of the SnP photosensitizer. Sn-, Sb-, and H₂ProtoP all have triplet lifetimes of 10 ms or longer, and form singlet O₂ by intermolecular triplet-triplet annihilation. In fact, the photophysical parameters and singlet oxygen sensitizing properties of SnProtoP^{14,16} are similar to metal-free porphyrins.¹⁷ The similarity of photosensitizing characteristics of Sn-, Sb-, and H₂-porphyrins explains the similarity of their properties in the FeP-free reaction (Table 1). However, only the Sn and Sb porphyrins form the stable anions capable of driving the Fe-porphyrin catalyzed reaction.

In the presence of the iron-porphyrin, the alcohol/ketone product

ratio is modified (-ol/-one \approx 1) indicating that a competing reaction comes into play. If the FeP-catalyzed reaction is to account for the low product ratio, then this reaction necessarily must give a lower hexanol to hexanone ratio. We can test this hypothesis by determining the product ratio for the P_{450} cycle when driven by addition of a suitable reductant in the absence of light. Table 1 includes the yield and product ratio for the dark reaction of hexane and O_2 catalyzed by $FeTF_3PP$ using a Zn/Hg amalgam as the co-reductant.¹⁸ (The ranges of yields and product ratios are for a range of solution conditions. The reaction is run for 2 hr, but is complete in about 10 min in most cases. Although the yields in some cases represent less than one catalyst turnover, the reaction can be continued by adding more amalgam. The FeP or MnP catalyst is required for significant yields of oxidized hexane. In some cases methylviologen is used as a relay molecule, and acetic anhydride is used as an oxygen atom acceptor. The product yield is sensitive to the amount of water in the acetonitrile solvent, and, in addition, acetic acid improved the overall yield and raised the alcohol/ketone product ratio. Presumably, acetic acid aids is the dioxygen lysis step in the reaction.)

Most importantly, when the FeP catalyst is present in the dark reaction the product ratio is one or less. Therefore, the dark reaction appears to compete favorably with the formation of singlet O_2 and the photochemical reaction proceeds as shown in Figure 1. The dark reaction, which also occurs in the presence of light, results in the observed lowering in the alcohol/ketone ratio and higher yield measured for the light-driven reaction in the presence of the FeP catalyst. Also, viologen appears not to aid the reaction, since the yield generally remains unchanged or is slightly lowered in its presence (data not shown).

When cyclohexene is the substrate in the dark reaction, the products cyclohexene oxide (1.0), 2-cyclohexen-1-ol (2.2), and 2-cyclohexen-1-one (1.8) are observed in the ratios (relative product yields are given in parenthesis) observed in other dioxygen-based systems that mimic the cytochrome P_{450} reaction.^{19,20} Also, when Mn tetraphenyl porphyrin is used as the catalyst, imidazole binding as a fifth ligand acts as a promoter for P_{450} reaction as has been noted in earlier studies.²¹ Both of these results support the contention that the reaction is occurring at the porphyrin catalyst under these solution conditions.

The photochemical system produces stable yields of hydrocarbon oxidation products for more than 6 hr as shown in Figure 2. In Figure 2, the yield of products is given in terms of catalyst turnovers (mol product/mol FeP catalyst) as a function of reaction time. Also plotted in Figure 2 is the yield per hour, which only degrades slightly over the 6 hr reaction time. Finally, the alcohol/ketone ratio is a function of reaction time, increasing slightly as the reaction proceeds. The increase in the product ratio and decrease in oxidation rate both could be explained by slow degradation of the FeP-catalyzed cycle.

In summary, a photochemically driven reaction that mimics biological photosynthesis, electron-transfer, and hydrocarbon-oxidation reactions has been described. 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 hexane, can be investigated. Further studies are underway to determine the detailed reaction mechanisms involved in the photochemical reaction. Transient absorption and Raman spectroscopic techniques will also be applied to determine reaction rates.

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TABLE 1. Oxidation of hexane by air in acetonitrile.

Catalyst	Reductant System	-ol/-one	Yield ^a (turnovers/hr)
FeTF ₅ PP	SnProtoP, hν, TEOA	1.3 ^b	4.3
FeTF ₅ PP	SbProtoP, hν, TEOA	1.0	0.8
FeTF ₅ PP	hν, TEOA	0.8	0.2
MnTPP	SnProtoP, hν, TEOA	0.9	0.2
FeTF ₅ PP	Zn/Hg	0.2-1.1	0.5-1.0 ^c
-	SnProtoP, hν, TEOA	2.3 ^b	1.7
-	H ₂ ProtoP, hν, TEOA	2.7	0.6
-	SbProtoP, hν, TEOA	2.2	1.4 ^d
-	hν, TEOA	-	0.0
-	SnProtoP, hν	-	0.0

- a. Yield is in photosensitizer turnovers (mol product/mol photosensitizer) for selected runs. Catalyst concentrations are about one-half of the photosensitizer concentration.
- b. Hexanol/hexanone value is average for all (~20) runs with turnovers > 1.
- c. Total turnovers under various solvent conditions with O₂ as the oxidant.
- d. Light intensity higher than for SbProtoP/FeTF₅PP run, accounting for higher yield in this case.

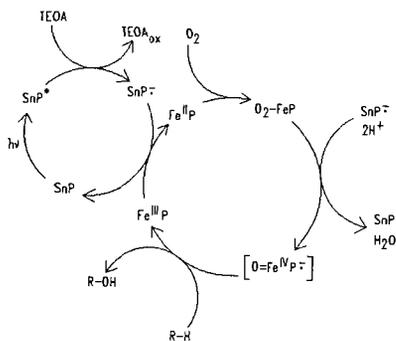


Figure 1. Scheme for photochemical production of co-reductant to drive the oxidation of hydrocarbons by mimicking the cytochrome-P₄₅₀ cycle. The SnP sensitized photoredox cycle is on the left; the P₄₅₀ catalytic cycle is shown on the right.

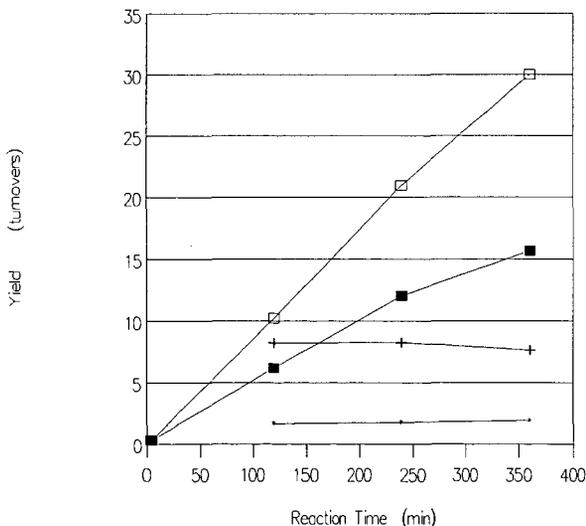


Figure 2. Hexanol and hexanone yields and product ratio as a function of reaction time. Total 1-, 2-, and 3-hexanol yield in catalyst turnovers (□); total 2- and 3-hexanone yield (■); hexanol/hexanone ratio (*); catalyst turnovers/hr (+).