

PHOTOCHEMICALLY-DRIVEN BIOMIMETIC OXIDATION OF ALKANES AND OLEFINS

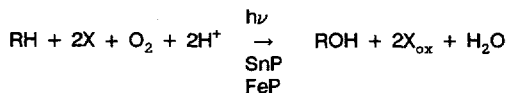
J. A. Shelnutz* and D. E. Trudell

Fuel Science Division 6211, Sandia National Laboratories, Albuquerque, NM 87185

Abstract: Photochemical oxidation of hydrocarbons using molecular oxygen as oxidant and Sn(IV)- or Sb(V)-porphyrin as photosensitizer to generate the required co-reductant is described. Fe(III)- or Mn(III)-porphyrin is the hydrocarbon-oxidation catalyst. The system is long-lived and may be used in photo-initiated spectroscopic kinetic studies.

A great variety of alkane and olefin oxidation systems that mimic biological oxidation of hydrocarbons by cytochrome P₄₅₀ have been reported.¹⁻⁸ Most use an iron, manganese, or ruthenium porphyrin as the analog of the heme (iron porphyrin) functional group of the enzyme. 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 P₄₅₀, two 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 reducing agent.⁵⁻⁸

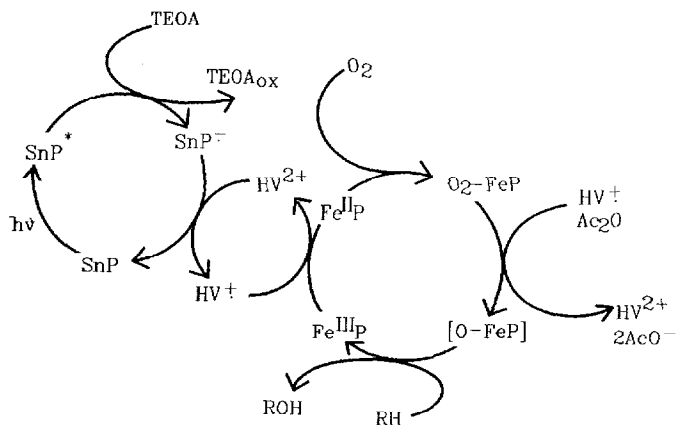
We have been investigating these reactions from the standpoint of stereochemically controlling the reaction at the metal site by designing metalloporphyrins with a shape and size selective pocket at the metal center.^{9,10} The pockets designed so far are small, and thus require an oxidant, like O₂, that is small enough to enter the cavity. It is also desirable that the system be stable and operate over many hours. Finally, 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 Scheme 1. The net reaction is:



where X is a poor reductant, RH is an alkane or olefin, and SnP and FeP are metalloporphyrins. The cycle on the left is the photoredox chemistry that produces the reductant, in this case the reduced form of heptylviologen (HV²⁺). In the cycle, tin(IV)- or antimony(V)-porphyrin, in its triplet excited state, is reduced by a sacrificial electron donor such as triethanolamine (TEOA; E_s = +0.8 V).¹¹⁻¹³ The resulting long-lived π radical anion of the porphyrin has a redox potential low enough to reduce HV²⁺, which is detected by its characteristic red absorption at 602 nm.^{13,14} After reduction of the relay (or the FeP directly, see below), the photosensitizer (SnP) returns to the resting redox state.

A molecule like heptylviologen could act as an electron relay molecule between the photocycle and the cytochrome-P₄₅₀-like chemical cycle on the right. Actually, two molecules of reduced HV²⁺ (HV^{•+}) or of the porphyrin anion would be required in the biomimetic P₄₅₀ cycle as indicated in Scheme 1. It is also possible that the SnP radical

anion can directly transfer an electron to FeP, in which case the relay molecule is not required. Acetic anhydride (Ac_2O) acts as an oxygen atom acceptor in the splitting of dioxygen in the hydrocarbon (RH) oxidation cycle.



Scheme 1

A photochemical reaction like that illustrated in Scheme 1 was carried out in acetonitrile under an O_2 or air atmosphere at room temperature. In a typical reaction, $0.24 \mu\text{mol}$ of Fe(III) tetra(pentafluoro-phenyl)porphyrin (FeTF_3PP) chloride, $0.45 \mu\text{mol}$ of Sn(IV) protoporphyrin IX (SnProtoP) dichloride, 1.1 mmol of TEOA, $1.4 \mu\text{mol}$ of heptylviologen (N,N' -diheptyl-4,4'-dipyridinium dichloride), and $11 \mu\text{mol}$ 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 $1\text{-}6 \text{ hr}$. Light of wavelengths less than 380 nm was filtered to insure that photosensitization of the reaction was only due to visible absorption by the porphyrin. Hexanol and hexanone products were quantified at the end of the run by gas chromatography. Table 1 gives typical yields and hexanol to hexanone product ratios for typical runs and control experiments. The system produced stable yields of oxidized hydrocarbons for more than 6 hr .

TABLE 1. Photo-oxidation of hexane in acetonitrile by air.

Catalyst	Photosensitizer	Reductant	-ol/-one	Yield ^a (turnovers/hr)
FeTF_3PP	SnProtoP	TEOA	1.3 ^b	4.3
-	SnProtoP	TEOA	2.3 ^b	1.7
-	H_2ProtoP	TEOA	2.7	0.6
-	SbProtoP	TEOA	2.2	1.4
FeTF_3PP	SbProtoP	TEOA	1.0	0.8
-	-	TEOA	-	0.0
-	SnProtoP	-	-	0.0
FeTF_3PP	-	TEOA	0.8	0.2
MnTPP	SnProtoP	TEOA	0.9	0.2

a. Yield is for selected run.

b. hexanol/hexanone value is average for all (~ 20) runs with turnovers > 1 .

In the presence of the P_{450} catalyst, a generally higher overall yield of products is observed when illumination and other conditions were identical; however, a low average hexanol-to-hexanone ratio of 1.3:1 is observed. In the

absence of the catalyst FeTF_3PP , photosensitized production of hexanols and hexanones is observed in an average ratio of 2.3:1.

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 O_2 ,¹⁴ suggesting a possible direct mechanism of O_2 activation by the photosensitizer. We have examined reactions of both singlet O_2 and superoxide anion under our reaction conditions. Chemically produced superoxide (KO_2 -18-crown-6) is not reactive under our experimental conditions. On the other hand, singlet oxygen, produced by irradiation of free base porphyrin,¹⁵ is reactive in the presence of tertiary amines and gives about the same hexanol to hexanone ratio (2.7, see Table 1) with the SnP photosensitizer and in the absence of FeP catalyst. Sn-, Sb-, and free base porphyrins all have triplet lifetimes of 10 ms or longer, and form singlet O_2 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 H_2 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. Table 2 shows the yield and product ratio for the dark reaction of hexane and O_2 catalyzed by FeTF_3PP . The reaction is run for 2 hr, but is complete in about 10 min in most cases. In this case, Zn/Hg amalgam provides the reducing equivalents for activating O_2 at the FeP.¹⁸ 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 (as illustrated in Scheme 1). Also, the product yield is sensitive to the amount of water in the acetonitrile solvent, since the sodium sulfate-dried solvent gave almost no oxidation. In addition, acetic acid improved the overall yield and also raised the alcohol/ketone product ratio. Presumably, acetic acid aids is the dioxygen lysis step in the reaction.

TABLE 2. Oxidation of hexane in acetonitrile by O_2 using Zn/Hg amalgam.

Catalyst	Addend(s)	-ol/-one	Tot. Yield (turnovers)
FeTF_3PP	Ac_2O , MV	0.2 ^a	1.0 ^a
-	Ac_2O , MV	4.4 ^b	0.0
$\text{H}_2\text{TF}_3\text{PP}$	Ac_2O , MV	1.2	0.1
FeTF_3PP	Na_2SO_4 -dried Ac_2O , MV	0.1	0.1
FeTF_3PP	Ac_2O , MV, 5% H_2O	0.3	0.5
FeTF_3PP	Ac_2O , MV	0.2	0.8
FeTF_3PP	CH_3COOH , \pm MV	0.6	1.1
FeTF_3PP	Ac_2O , CH_3COOH , MV	0.4	0.3
FeTF_3PP	H_2O , CH_3COOH , MV	0.7	0.8
MnTPP	Ac_2O , MV	1.3 ^b	0.0
MnTPP	Ac_2O , MV, Im	1.1	0.5

a. Average of 6 runs. All other data is for single run.

b. Probable large errors because of low yield.

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 relative proportions 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 conditions.

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 singlet O_2 reaction in the photochemical reaction as shown in Scheme 1. The dark reaction results in the observed lowering in the alcohol/ketone ratio and higher yield measured in the presence of the FeP catalyst. Also, viologen appears not to aid the reaction, since the yield generally remains unchanged or is lowered in its presence (data not shown). This is also true of the dark reaction (Table 2).

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. 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.

Acknowledgements. This work performed at Sandia National Laboratories and supported by the United States Department of Energy Contract DE-AC04-76DP00789.

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(Received in USA 19 June 1989)