Shape Selective Oxidations of Hydrocarbons

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The oxidation of hydrocarbons is extremely important in both biological and chemical systems [1]. The development of selective catalysts for the oxidation of simple hydrocarbons (i.e., alkanes and alkenes) has received extensive attention due to the vast hydrocarbon feedstocks available from coal and oil. Cytochrome P-450, a heme monooxygenase, catalyzes the insertion of a single atom of oxygen from dioxygen to various hydrocarbon substrates [2]. Certain isozymes of P-450 are capable of catalyzing the shape selective oxidation of these hydrocarbon substrates [3]. Nonsterically protected metalloporphyrins also catalyze these hydrocarbon oxidations, however they do not exhibit enzyme like regioselectivity [4].

Tetrakis-5,10,15,20-(2',4',6'-triphenylphenyl)porphyrinate (TTPPP) manganese(III) and iron(III) acetate were both found to be shape selective alkane hydroxylation catalysts when iodosobenzene was used as oxidant [5,6]. The selectivity observed was the same when these catalysts were used with meta-chloroperoxybenzoic acid. This demonstrates the intermediacy of a common manganese porphyrin based oxidant. The ratio of 1-heptanol to 2, 3, and 4-heptanol was found to be smaller for FeTTPPP(OAc) relative to MnTTPPP(OAc). This is consistent with a greater amount of C-H bond breaking in the iron porphyrin catalyzed reactions. The measured isotope effect from hydroxylation of d_4-pentane was found to be 3.5 for manganese [6] as compared to 12.9 found in the iron systems [4]. This shape selectivity was also used as a sensitive probe for metalloporphyrin involvement in the hydroxylation transition state [6]. Both tert-butylhydroperoxide and trifluoroethanol solubilized pentafluoroiodosobenzene were found not to be shape selective with manganese porphyrin catalysts indicating that the oxidation is not occurring at the metal (e.g., radical chain).

MnTTPPP(OAc) and FeTTPPP(OAc) were also found to be shape selective epoxidation catalysts for diene substrates using a wide variety of oxidants [7,8]. Collman [9] has proposed a metallaoxetane intermediate for both manganese and iron porphyrin catalyzed epoxidations, while Traylor [10] has proposed an electron transfer pathway to form a carbenium ion intermediate. Vastly diminished selectivities were observed when conjugated dienes are epoxidized by MnTTPPP using hypochlorite as oxidant [7]. This indicates the presence of at least two different pathways for the manganese catalyzed epoxidations, and the latter pathway has a transition state with lessened steric constraint. Diminished selectivity was also observed for the iron catalyzed systems compared to manganese [8]. This indicates a different principal pathway for the iron porphyrin epoxidations. The selectivities observed for both iron and manganese were found to be insensitive to changes in oxidant or the addition of added imidazole. This indicates that the reactive species does not contain the oxidant (e.g., a metallo-iodosobenzene complex), and that imidazole does not change the steric constraints of the transition state.

The photochemistry and specifically the photooxidation chemistry of metalloporphyrins has not been extensively explored. Manganese(III) and chromium(III) porphyrins do not exhibit normal porphyrin visible absorption spectra [11]. The absorption bands observed in both manganese and chromium porphyrin

spectra have a large porphyrin (π) to metal charge transfer character [12]. Photolysis of 5,10,15,20-tetraphenylporphyrinate manganese(III) perchlorate (MnTPP(ClO$_4$) and CrTPP(ClO$_4$) leads to clean transformation to MnTPP(Cl) and Cr(IV)TPP(O) respectively [13]. MnTPP(ClO$_4$) was found to photooxidize stoichiometrically cyclopentane, toluene, and cyclohexene. Photocatalytic oxidations of the same three hydrocarbon substrates were accomplished using MnTPP(OAc) and excess tetra-n-butylammonium periodate. Kinetic investigation indicates a preequilibrium displacement of acetate with periodate followed by photolysis to form the active Mn(V)TPP(O) species.

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