

Letter

## On the mechanism of catalytic alkene oxidation by molecular oxygen and halogenated iron porphyrins

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### Abstract

The halogenated porphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato-iron(III) chloride,  $[\text{Fe}(\text{TFPPBr}_8)\text{Cl}]$ , catalyzes the oxidation of cyclohexene in the presence of molecular oxygen or iodosobenzene. With PhIO, 77% epoxide is observed, consistent with a mechanism involving a high-valent metal-oxo species. With dioxygen, however, allylic alcohol and ketone are observed, suggesting a different mechanism. The relatively high activity of the  $[\text{Fe}(\text{TFPPBr}_8)\text{Cl}]/\text{O}_2$  system suggests that the reaction involves the formation and decomposition of alkyl peroxides.

Halogenated porphyrins have been widely investigated in the search for biomimetic metalloporphyrin oxidation catalysts [1]. Electron-withdrawing halogen substituents at the pyrrole or meso positions have been found to increase the catalytic efficiency of metalloporphyrins and retard catalyst decomposition [2–8]. In addition, the bulky halogens at the  $\beta$ -positions induce severe distortions of the porphyrin macrocycle, minimizing dimerization of the porphyrins in solution [9–14].

The perhalogenated porphyrin, 2, 3, 7, 8, 12, 13, 17, 18-octabromo-5, 10, 15, 20-tetrakis (pentafluorophenyl) porphyrinato-iron(III) chloride,  $[\text{Fe}(\text{TFPPBr}_8)\text{Cl}]$ , is an active catalyst for the selective oxidation of light alkanes under 4 atm of dioxygen [2,3]. Recently, we reported at room temperature and one atmosphere of molecular oxygen,  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$  will oxidize 3-methyl-

pentane to 3-methylpentan-3-ol [4]. We have now found that this metalloporphyrin is an even more efficient catalyst for the oxidation of cyclohexene with either dioxygen or single O-atom donors such as iodosylbenzene (PhIO).

In the presence of  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}^1$ , cyclohexene oxidation to a mixture of cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one, was observed (Fig. 1). The product distribution and activity varied greatly with the oxidant. With PhIO, the majority of product (77%) consisted of the epoxide. With dioxygen, mainly allylic oxidation products were generated (49 and

<sup>1</sup> Substrate (1 ml freshly distilled) was added to a solution of  $\text{Fe}(\text{TFPPBr}_8)\text{Cl}$  in methylene chloride (0.2 mM) and stirred in a closed container for 48 h. During this time, aliquots were taken and analyzed by GC to detect any product formation. For reactions with dioxygen, the methylene chloride was oxygen saturated, and the head space in the reaction vessel was filled with oxygen (~450 eq  $\text{O}_2/\text{Fe}$ ). For iodosylbenzene reactions, the solutions were argon-purged (~50 eq PhIO/Fe).

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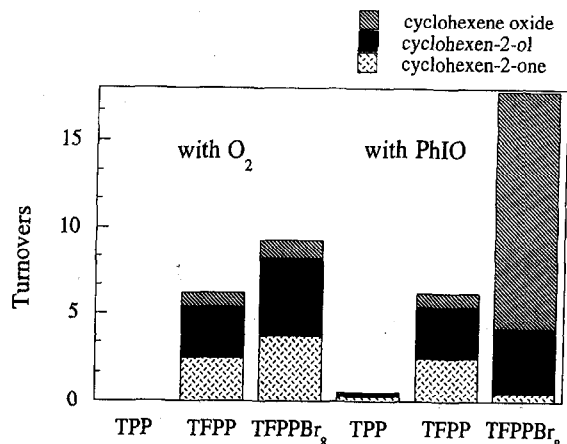


Fig. 1. Turnovers and product distributions with cyclohexene and iron(III) porphyrins with dioxygen (at 3 h) and PhIO (at 4 h).

44% of alcohol and ketone, respectively). Reactions with styrene (data not shown) exhibited similar differences in product distribution with oxidant. With PhIO, the majority of the product (67%) was styrene oxide, while with dioxygen, only the cleavage product, benzaldehyde (>95%), was observed.

Catalytic activity also varied with oxidant. Iodosylbenzene reactions deactivated in 1 to 5 h, accompanied by a shift in the Soret band from 442 to 418 nm. However,  $18 \pm 4$  TO were completed during this time period, and product distribution (Fig. 1) was consistent between runs. Although the initial activity with PhIO was greater, overall activity was higher with dioxygen, suggesting an induction period for the latter reaction<sup>2</sup>. Furthermore, in reactions with dioxygen, the perhalogenated porphyrin showed much higher activity (73 TO/24 h) as compared to the related porphyrins tetrakis(pentafluorophenyl)porphyrinato-iron(III) chloride (Fe(TFPP)Cl) (31 TO) and tetraphenylporphyrinato-iron(III) chloride (Fe(TPP)Cl) (<1 TO) (Fig. 2).

The variations in selectivity with Fe(TFPPBr<sub>8</sub>)Cl can be explained by invoking different mechanisms for the two oxidants. With

<sup>2</sup> Reactions with dioxygen continued after 24 h, indicating that the catalyst does not decompose in this time period. Addition of more oxygen resulted in further oxidation of substrate. Iodosylbenzene reactions never utilized more than 50% of the added PhIO. Greater amounts of PhIO did not result in higher activity.

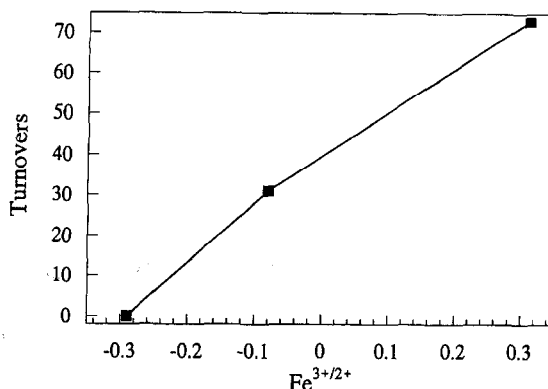


Fig. 2. Plot of the catalytic activity (turnovers at 24 h) observed for cyclohexene oxidation with dioxygen versus the iron(III)-porphyrin reduction potential ( $E^\circ$  values: Fe(TPP)Cl < Fe(TFPP)Cl < Fe(TFPPBr<sub>8</sub>)Cl).

dioxygen, the reaction has been shown to involve formation and porphyrin-catalyzed decomposition of alkyl peroxides [4,15]. The radicals generated by the Fe(TFPPBr<sub>8</sub>)Cl-catalyzed peroxide decomposition react with additional molecules of substrate to form the observed products, propagating a radical chain reaction (Fig. 3). Competitive experiments with cyclohexene and cyclohexene-*d*<sub>10</sub> result in an isotope effect of 8.2<sup>3</sup>, consistent with a mechanism involving hydrogen abstraction in the rate-determining step. Addition of a radical trap, BHT, completely inhibits the reaction. The radical chain mechanism is also consistent with the high percentage of allylic radical products observed in the reaction of cyclohexene with dioxygen.

Moreover, this mechanism explains the greater reactivity observed with dioxygen and Fe(TFPPBr<sub>8</sub>)Cl compared to tetraphenylporphyrinato-iron(III) chloride or tetrakis(pentafluorophenyl)porphyrinato-iron(III) chloride. The electron-withdrawing TFPPBr<sub>8</sub> ligand stabilizes the ferrous state ( $E^\circ$  Fe<sup>3+/2+</sup> = 0.31 V vs. AgCl/Ag) [4], thereby enhancing the rate of alkyl peroxide oxidation [16]. In contrast, the lower reduction potentials of Fe(TFPP)Cl (-0.08 V) [4] and Fe(TPP)Cl (-0.29 V vs. SCE) [17] make these species poor oxidants,

<sup>3</sup> Calculated from a competitive substrate experiment: isotope effect = (moles non-deuterated product) / (moles deuterated product).

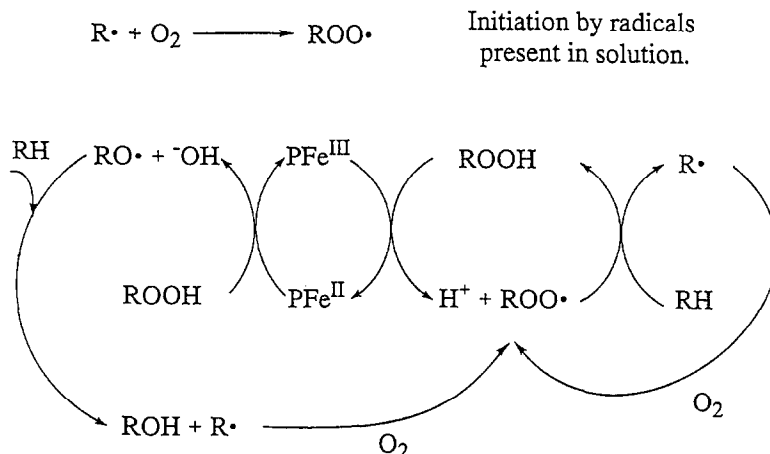


Fig. 3. The alkyl peroxide decomposition mechanism for dioxygen reactions with Fe(TFPPBr<sub>8</sub>)Cl. Initiated by radicals in solution, the peroxides thereby generated are catalytically decomposed by the iron porphyrin. These radicals can then propagate the reaction further.

greatly slowing the ferric  $\rightarrow$  ferrous step in the catalytic cycle. Furthermore, as with ferryl complexes, any radicals generated may attack porphyrin C–H bonds. The peroxide decomposition pathway available to Fe(TFPPBr<sub>8</sub>)Cl explains the significantly greater efficiency with dioxygen. Halogenation of the  $\beta$  positions of the porphyrin also prevents formation of a  $\mu$ -oxo dimer, which is a mode of deactivation for both Fe(TPP)Cl and Fe(TFPP)Cl in reactions with dioxygen [18].

Iodosylbenzene is believed to react with metalloporphyrins to generate a high-valent metal–oxo intermediate, which would favor epoxide formation [19]. Indeed, the large percentage of epoxide formed with PhIO and Fe(TFPPBr<sub>8</sub>)Cl is consistent with a ferryl as the oxidizing species. The increase in activity from Fe(TFPP)Cl is not as great as one might predict: the positive  $E^\circ$  Fe<sup>3+/2+</sup> would make an 'Fe<sup>V</sup>=O' high in energy and difficult to attain. In line with this prediction, reductive generation of a ferryl (O<sub>2</sub>, Zn, H<sup>+</sup>) has been shown to be inefficient for highly halogenated porphyrins [20,21]. The lower potentials of Fe(TFPP)Cl and Fe(TPP)Cl suggest that a ferryl complex can be generated more readily. However, once formed, the ferryl can attack the C–H bonds on other porphyrins, leading to catalyst decomposition and lower net activity with these two complexes.

Fe(TFPPBr<sub>8</sub>)Cl is a remarkably active catalyst for the oxidation of cyclohexene with dioxygen, without added coreductant or light. Other than halogenated porphyrins, only the highly activated porphyrin RuTMP(O)<sub>2</sub> [dioxo (tetramesitylporphyrinato) -ruthenium(VI)] is known to catalyze the aerobic epoxidation of alkenes at ambient temperatures and pressures. Although able to catalyze 26 turnovers of cyclooctene in 24 h (versus 73 TO of cyclohexene by Fe(TFPPBr<sub>8</sub>)Cl), the Ru catalyst decomposes within this time period [22]. Another electron-deficient porphyrin,  $\beta$ -hexanitro-tetrakis (2,6-dichlorophenyl) porphyrinato-iron(III) chloride, has been shown to activate alkanes at higher temperatures and high pressures of O<sub>2</sub> [23]. Considering the similarity of the two porphyrins, it is likely that they operate by the same peroxide decomposition mechanism. Unfortunately, the exceptional reactivity of Fe(TFPPBr<sub>8</sub>)Cl with dioxygen appears to come at the expense of the selectivity found with a high-valent metal–oxo species.

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