# Iron Porphyrin catalysed Oxidation of Propanal and Cyclohexene by Molecular Oxygen

**Kenton R. Rodgers, Isam M. Arafa and Harold M. Goff***

*Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, USA*

A variety of tetraphenylporphinatoiron(III) complexes are shown to catalyse the aerobic oxidation of propanal to propionic acid, and with cyclohexene as a co-substrate to effect conversion to cyclohexene oxide.

The ability of cytochrome P-450 to activate oxygen for the oxidation of hydrocarbons has inspired a multitude of studies that involve metalloporphyrins as potential catalysts for the oxidation of alkanes and alkenes.[1,2] Porphinatocobalt(II) derivatives are known to catalyse the aerobic oxidation of aldehydes to the corresponding peroxycarboxylic acids.[3,4] In contrast, this report describes the tetraphenylporphinatoiron(III) catalysed aerobic oxidation of propanal to propionic acid. The inclusion of cyclohexene as a co-substrate with the porphinatoiron catalyst also leads to predominant conversion to the epoxide. The present report elaborates on the initial description of the reactions,[5] and offers a comparison with related observations made primarily for a porphinatomanganese(III) catalyst.[6–8]

Example reaction conditions are listed in Table 1. Bleaching of the intense porphyrin colour takes place in periods of less than 1 h when millimolar concentrations of tetraphenylporphinatoiron(III), (tpp)Fe (as the chloride, fluoride or oxo-bridged dimer complex) in benzene solution with an excess of (purified[9]) propanal are vigorously stirred under an oxygen (or air) atmosphere. A strong odour of propionic acid is evident, and this product is quantitated by gas chromatographic analysis and acid–base titration. The peroxy acid is not detected as a final product, although it is likely to be the intermediate responsible for ultimate porphyrin ring destruction following several hundred catalytic turnovers. Carbon dioxide is identified as a significant product, presumably from activation and heterolytic cleavage of the peracid. All the

**Table 1** Product distributions for catalytic autoxidation of propanal and cyclohexene[a]

| Solution composition[b] | | | | Turnover numbers[c] | | | | |
|---|---|---|---|---|---|---|---|---|
| Benzene (ml) | HPr (mmol) | $C_6H_{10}$ (mmol) | $P_{O_2}$ | $CO_2$ | Oxide | -ol | -one | HOPr |
| 1.5 | 6.9 | — | 500 Torr | 19 | — | — | — | 500 |
| 1.5 | 6.9 | — | 390 Torr | 18 | — | — | — | 380 |
| 1.0 | 6.9 | 4.9 | 530 Torr | 49 | 56 | 14 | 13 | 120 |
| 1.5 | 3.5 | 2.5[d] | 472 Torr | 0 (10 μmol oxide after 6 h) | | | | |

[a] All reactions were carried out at ambient temperature until the catalyst was completely bleached. [b] Unless otherwise indicated, all reaction mixtures initially contained 5.0 mg Fe(tpp)Cl (7 μmol) and excess $O_2$. HPr = propanal, $C_6H_{10}$ = cyclohexene. [c] Reported as moles of product per initial moles of catalyst. Oxide = cyclohexene oxide, -ol = cyclohex-2-en-1-ol, -one = cyclohex-2-en-1-one, and HOPr = propionic acid. [d] No catalyst was present.

oxygen consumed in the reaction is accounted for in production of propionic acid and carbon dioxide.

Light is not required for catalysis. Only traces of propionic acid are produced in controls that lack the catalyst or that contain metal-free tetraphenylporphyrin. In the absence of oxygen no propionic acid is produced and the porphinatoiron(III) chloride is unchanged. No porphinatoiron(II) species was detected (5% conversion would have been detected) by NMR spectroscopy during a period of one month for a mixture of (tpp)FeCl and propanal in benzene in a vacuum sealed NMR tube. Hence, if the +2 oxidation state is involved as previously suggested,[7] this reduced species must be present only at a low steady-state concentration.

Addition of (purified) cyclohexene to a mixture of benzene, propanal, and the porphinatoiron catalyst under a partial atmosphere of oxygen results in ultimate bleaching of the porphyrin ring following variable induction periods of up to several hours. Gas chromatographic analysis of the reaction mixture reveals cyclohexene oxide as a major product, with substantial quantities of the allylic products cyclohex-2-en-1-one and cyclohex-2-en-1-ol (Table 1). The turnover number for propionic acid is reduced, but relatively more carbon dioxide is produced. It is perhaps noteworthy that the yield of carbon dioxide matches the yield of epoxide. The long induction period is suggestive of initiation by accumulation of free radical species. The radical mediated cooxidation of valeraldehyde and cyclohexene is known,[10] but the rate is considerably slower than the porphinatoiron-catalysed reaction.

The ratio of aldehyde to alkene oxidation products is dependent on the initial substrate concentrations, thus suggesting competition for an active oxidant. Total turnover number generally increases as the initial oxygen pressure increases and as the initial catalyst concentration decreases. Addition of 3.5 to 7% pyridine to the co-substrate system results in much lower turnover numbers and higher yields of allylic oxidation products, presumably due to blockage of iron coordination sites essential for oxygen atom transfer.

Peracid decarboxylation by cytochrome P-450 is well established,[11] and the appearance of a carbon dioxide product in the presently described system implicates peracid involvement. The detailed mechanism for porphinatoiron(III) catalysed oxygenation of aldehydes remains to be elucidated.

Support from the US National Science Foundation Grant CHE 87-05703 is gratefully acknowledged.

*Received, 13th November 1989; Com. 9/04858H*

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