# Effect of Fluorination of the *meso*-Phenyl Groups on Selective Tetraphenylporphyrinatoiron(III)-catalysed Reactions of Propane with Molecular Oxygen

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A series of tetrakis(pentafluorophenyl)iron(III) complexes are active catalysts for the selective air oxidation of propane to isopropyl alcohol and acetone under mild conditions, and provide hundreds of catalytic turnovers in the absence of any added co-reductants.

The hydroxylation of simple aliphatic hydrocarbons with molecular oxygen to form alcohols is a challenging and synthetically important goal that might be met by transition metal complexes which are capable of forming active metal oxo intermediates *via* direct reaction with molecular oxygen.[1] We recently reported that first row azidotetraphenylporphyrinatometal(III) complexes $M(TPP)N_3$ (M = Fe, Mn, Cr) are capable of catalysing the direct hydroxylation of isobutane to t-butyl alcohol with molecular oxygen at low temperature.[2] When the *meso*-phenyl substituents bear five fluorines, as in azidotetrakis(pentafluorophenyl)porphyrinatometal(III), $M(TFPP)N_3$, catalytic activity can be increased by more than an order of magnitude.[3] Because of the unusually high activity of these complexes, we were encouraged to attempt the catalytic oxidation of a more difficult secondary C–H bond. The substrate which we chose to study was propane. Propane is an interesting substrate not only because of the difficulty of C–H bond cleavage, but also because of the possibility of further oxidation of the alcohol produced. The ability to form either isopropyl alcohol, equation (1), or acetone, equation (2), allows us to examine another aspect of reaction selectivity not provided by the hydroxylation of isobutane.

$$MeCH_2Me + 1/2\ O_2 \rightarrow MeCH(OH)Me \qquad (1)$$

$$MeCH_2Me + O_2 \rightarrow MeC(O)Me + H_2O \qquad (2)$$
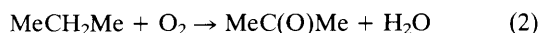
In this Communication we report that the tetrakis(pentafluorophenyl)porphyrinatoiron(III) complexes $Fe(TFPP)N_3$, $Fe(TFPP)Cl$, $Fe(TFPP)OH$, and $[Fe(TFPP)]_2O$, are uniquely active catalysts for selective air oxidation of propane to a mixture of isopropyl alcohol and acetone, equations (1) and (2), at temperatures as low as 100 °C. The tetraphenylporphyrinato complexes $Fe(TPP)N_3$, $Fe(TPP)Cl$, and $[Fe(TPP)]_2O$, on the other hand, are inactive at or below 125 °C. The analogous manganese and chromium complexes $M(TFPP)X$ and $M(TPP)X$ (M = Mn, Cr; X = N_3, Cl), which are active for isobutane oxidations,[2,3] were also found to have little or no activity for air oxidation of propane under these mild conditions.

Table 1 shows the pronounced effect of the porphyrin ligand on the activity of iron(III)-catalysed oxidation of propane in benzene at 125 °C. The higher activity of iron TFPP complexes for air oxidation is reminiscent of that observed for alkane oxidations using iodosylbenzene as the oxidant in which iron oxo species were implicated.[4,5] It is of interest that the di-iron μ-oxo complex, $[Fe(TFPP)]_2O$, has activity comparable to the chloride and the azide. It is likely that the μ-oxo species is a reactive intermediate in all cases. The hydroxo complex, $Fe(TFPP)OH$, was also found to be active for propane oxidation, giving nearly 300 turnovers at 125 °C. Table 2 demonstrates that $Fe(TFPP)N_3$ has considerable activity even at 100 °C, and appears to be more active in acetonitrile than in benzene. Figure 1 shows that the activity of $Fe(TFPP)N_3$, though initially very high, diminishes with time. At 150 °C the catalyst is nearly inactive after 3 h, whereas at 125 °C there is still considerable activity after 3 h. The loss of activity and the considerable bleaching of the catalyst after a long time,

Table 1. Propane oxidations catalysed by iron(III) porphyrin complexes.[a]

Iron(III) complex[b]	Catalyst turnovers[c]	Isopropyl alcohol /acetone[d]
Fe(TPP)Cl	0	—
Fe(TPP)N_3	2	N.a.[e]
[Fe(TPP)]$_2$O	0	—
Fe(TFPP)Cl	230	0.8
Fe(TFPP)N_3	330	0.8
[Fe(TFPP)]$_2$O	440	0.8

[a] Propane (1.36 mol) was added to benzene (42.2 g) containing the catalyst (0.023 mmol). The solution was stirred for 3 h at 125 °C under 1000 psig of air in a glass-lined autoclave. Liquids and gases were analysed by g.c. Production of carbon oxides never exceeded 5% of total products. Isopropyl alcohol and acetone exceeded 90 mol% of carbon-containing reaction products in all cases. [b] TPP = tetraphenylporphyrinato, TFPP = tetrakis(pentafluorophenyl)porphyrinato. [c] Moles of acetone plus isopropyl alcohol formed per mole of catalyst used. [d] Molar ratio of isopropyl alcohol to acetone formed. [e] N.a. = not applicable.

Table 2. Propane oxidations catalysed by $Fe(TFPP)N_3$.[a]

Reaction temp. /°C	Reaction time /h	Catalyst turnovers[b]	Isopropyl alcohol /acetone[c]
150	1	490	1.1
100	3	30	0.6
125	3	330	0.8
125[d]	3	250	0.9
150	3	620	1.0
150	3	870[e]	0.5
100	6	190[e]	0.7
125	6	410	0.7
125	7.5	430	0.8
150	7.5	640	0.8

[a] Propane (1.36 mol) was added to benzene (42.2 g) containing the catalyst (0.023 mmol). The solution was stirred at the reaction temperature under 1000 psig of air for the designated time in a glass-lined autoclave. Liquids and gases were analysed by g.c. Production of carbon oxides never exceeded 10% of total products. Isopropyl alcohol and acetone exceeded 90 mol% of carbon-containing reaction products in all cases. [b] Moles of acetone plus isopropyl alcohol formed per mole of catalyst used. [c] Molar ratio of isopropyl alcohol to acetone formed. [d] 2,6-Di-t-butyl-*p*-cresol (0.23 mmol) added as a radical inhibitor. [e] Reactions run in acetonitrile rather than benzene.
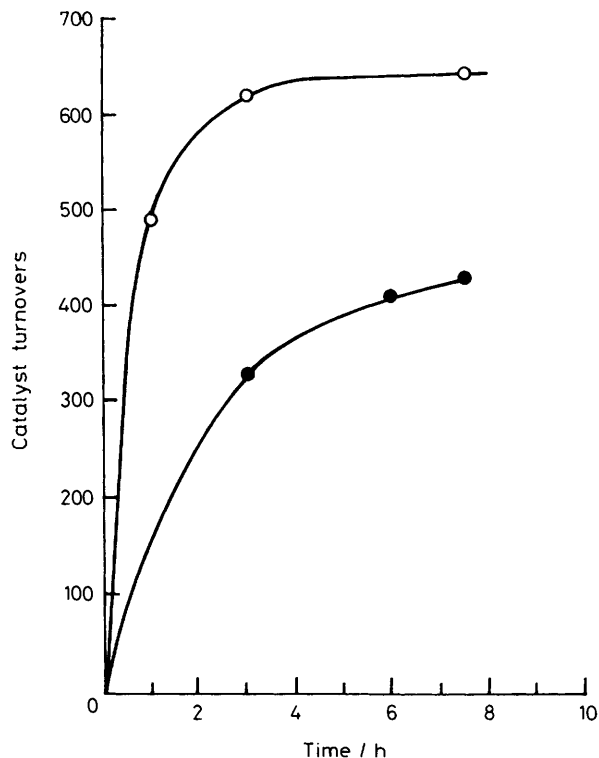
Recent work[6] has indicated that ruthenium oxo species are formed by direct reaction of oxygen with a porphyrinatoruthenium complex. It has also been postulated[7] that a ruthenium oxo complex is formed from a μ-peroxo ruthenium complex derived from oxygen during a catalytic alkane oxidation. High oxidation states of ruthenium are more accessible than are those of iron in most instances. The role of the fluorinated macrocycle might be to permit the existence of high oxidation state iron oxo while preventing rapid oxidative degradation of the macrocyclic system. Such a high oxidation state iron oxo complex might directly hydroxylate a carbon–hydrogen bond in a biomimetic manner.[4,5,8] We are continuing our work to ascertain whether the species responsible for selective oxidation of propane are very active iron oxo intermediates formed directly by interaction of Fe(TFPP) complexes with molecular oxygen.

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Figure 1. Fe(TFPP)N$_3$-catalysed propane oxidations: (a) see footnotes in Table 2; (b) ○ 150 °C, ● 125 °C.

especially at higher temperatures, indicate that the fluorinated ligand, though far more oxidation resistant than TPP, is still subject to significant oxidative degradation and demetallation.[5]

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