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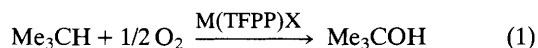
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1989Effect of Fluorination of the *meso*-Phenyl Groups on Selective Tetraphenylporphyrinatometal(III)-catalysed Reactions of Isobutane with Molecular Oxygen

Paul E. Ellis, Jr.,* and James E. Lyons*

Applied Research and Development Department, Sun Company, Marcus Hook, PA 19061, U.S.A.

A series of tetrakis(pentafluorophenyl)porphyrinatoiron(III) complexes are active catalysts for the selective low temperature hydroxylation of isobutane with molecular oxygen and provide thousands of catalytic turnovers in the absence of any added co-reductants.

We have recently reported for the first time that first row azidoporphyrinatometal(III) complexes (metal = Cr, Mn, Fe) are capable of catalysing the direct hydroxylation of an unactivated alkane with molecular oxygen at low temperature.¹ No sacrificial co-reductants such as those used in biological² or biomimetic^{3,4} systems were needed in these reactions. In this Communication we report huge increases in catalytic activity for the reaction of isobutane with molecular oxygen to give *t*-butyl alcohol, equation 1, when the *meso*-phenyl groups in the porphyrin ligand are replaced by pentafluorophenyl substituents.⁵



Oxidations of isobutane catalysed by tetrakis(pentafluorophenyl)porphyrinatometal(III) complexes, $\text{M}^{\text{III}}(\text{TFPP})\text{X}$,† are summarized in Table 1. Increases in activity of more than an order of magnitude over the analogous tetraphenylporphyrinato complexes, $\text{M}(\text{TPP})\text{X}$, were observed for the iron(III)TFPP chloride, azide, and μ -oxide. On the other hand, both the μ -nitrido TPP and TFPP iron complexes were completely inactive for low temperature isobutane oxidation, as were the corresponding manganese and chromium acetates and chlorides. It seems that in the case of manganese and chromium complexes, axial activation with azide is required for high activity even in the fluorinated systems. Fluorination of the *meso*-phenyl groups enhances the catalytic activity of the manganese and chromium azides (Table 1) but not as much as that of the iron azide.

Since $\text{Fe}(\text{TFPP})\text{N}_3$ was such an active catalyst for the direct hydroxylation of an alkane with molecular oxygen, its activity

was examined over a range of temperatures, Table 2. Room temperature hydroxylation of isobutane to *t*-butyl alcohol could be achieved with a very high selectivity (94–95%). The iron catalyst retained good life and still had considerable activity after 24 h at room temperature, Table 2.

Just as was found in the case of $\text{Fe}(\text{TPP})\text{N}_3$,^{1,6} the fluorinated complex, $\text{Fe}(\text{TFPP})\text{N}_3$, could be converted to the μ -nitride, $[\text{Fe}(\text{TFPP})]_2\text{N}$, by warming in benzene. This suggests a possible deactivation pathway. It is of particular interest that although the di-iron TPP μ -oxo complex is not active, the fluorinated complex, $[\text{Fe}(\text{TFPP})]_2\text{O}$, has high catalytic activity. No doubt, this point has significant mechanistic implications and may be related to the high catalytic

Table 1. Oxidation of isobutane catalysed by metalloporphyrin complexes.^a

Complex	Amount used/ mmol	Catalyst turnovers ^b	Selectivity to <i>t</i> -butyl alcohol ^c /%
$\text{Fe}(\text{TPP})\text{dCl}$	0.025	0	—
$\text{Fe}(\text{TFPP})\text{eCl}$	0.016	2040	90
$\text{Fe}(\text{TPP})\text{N}_3$	0.013	130	93
$\text{Fe}(\text{TFPP})\text{N}_3$	0.016	2060	89
$\text{Mn}(\text{TPP})\text{N}_3$	0.013	180	88
$\text{Mn}(\text{TFPP})\text{N}_3$	0.016	750	87
$\text{Cr}(\text{TPP})\text{N}_3$	0.025	280	89
$\text{Cr}(\text{TFPP})\text{N}_3$	0.016	450	97
$[\text{Fe}(\text{TPP})]_2\text{O}$	0.013	0	—
$[\text{Fe}(\text{TFPP})]_2\text{O}$	0.007	1730 ^f	92

^a Isobutane (6–7 g) was added to a solution of the catalyst in 25 ml benzene. The solution was stirred under O_2 (100 psig) at 80 °C for 6 h (O_2 added as used). ^b Moles oxygen consumed/mole catalyst used. ^c (Moles *t*-butyl alcohol produced/total moles liquid product) \times 100. The only products detected were *t*-butyl alcohol, acetone, and CO_2 . ^d TPP = tetraphenylporphyrinato. ^e TFPP = tetrakis(pentafluorophenyl)porphyrinato. ^f Incomplete solubility of $[\text{Fe}(\text{TFPP})]_2\text{O}$ makes this a lower limit value.

† The TFPP complexes were prepared in a manner analogous to the corresponding TPP complexes. Azidometal porphyrins were prepared by metathesis of chloro or acetato complexes with azide ion. Nitridometal porphyrins were prepared by photolysis of the corresponding azidometal porphyrin.

Table 2. Isobutane oxidations catalysed by Fe(TFPP)N₃.^a

Reaction time /h	Reaction temperature /°C	Catalyst turnovers ^b
6	80	2060
6	60	1050
6	40	470
6	27	54
24	27	440

^a Isobutane (6–7 g) was added to a solution of the catalyst (0.016 mmol) in 25 ml benzene. The solution was stirred under O₂ (100 psig) at the designated temperature (O₂ added as consumed). ^b Moles oxygen consumed/mole catalyst used.

activity of the TFPP complexes. The hydroxo complex, Fe(TFPP)(OH), is also catalytically active, producing over 1700 moles of t-butyl alcohol per mole of complex used over a 6 h period. Although somewhat more stable than the tetraphenylporphyrinato complexes, the tetrakis(pentafluoro-

phenyl)porphyrinato species are still too fragile for prolonged alkane oxidation at elevated temperatures. Work continues in an effort to construct more stable macrocyclic ligand environments for highly active transition metal-centred oxidation catalysts.

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