Effect of Axial Azide on the Selective, Low Temperature Metalloporphyrin-catalysed Reactions of Isobutane with Molecular Oxygen

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Azido(tetraphenylporphyrinato) complexes of Cr^{III}, Mn^{III}, and Fe^{III} catalyse selective, low temperature hydroxylation of isobutane with molecular oxygen and provide many turnovers in the absence of added co-reductants.

The direct catalytic conversion of alkanes to alcohols using molecular oxygen as the oxidant is of great interest as a means of converting these available and inexpensive hydrocarbons to valuable products.¹ It is believed that mono-oxygenase enzymes such as cytochrome P-450 catalyse the conversion of alkanes to alcohols through metal oxo intermediates.² The high oxidation state metal oxo intermediates that are generated in the biological systems require stoicheiometric consumption of two electrons and two protons, equation (1). Most biomimetic analogues require oxygen atom transfer reagents such as iodosylbenzene,3,4 peroxides,5,6 hypohalites,⁷ or others⁸⁻¹⁰ to generate the active metal oxo moiety. The catalytic hydroxylation of alkanes using oxygen as the source of O-atoms has been accomplished with added co-reductants such as Pt/H2¹¹ or ascorbic acid.¹² Recent work¹³ has shown that a low oxidation state porphyrinatoruthenium complex can form the metal oxo moiety by direct reaction with molecular oxygen. This complex catalyses the epoxidation of cyclo-octene using O₂ and no added coreductant.14

$$Fe^{II} + O_2 + 2H^+ + 2e^- \rightarrow Fe=O' + H_2O \qquad (1)$$

We report results that demonstrate for the first time that the first row azido(tetraphenylporphyrinato)metal(III) complexes, $M(tpp)N_3$ (M = Cr, Mn, Fe), are active catalysts for the selective formation of t-butyl alcohol from isobutane and molecular oxygen at 80 °C, equation (2), Table 1. These catalysts efficiently hydroxylate the alkane without the addition of stoicheiometric amounts of co-reductants. In contrast to the catalytic activity of the first row metal azides, the chloro- or acetato-(tetraphenylporphyrinato)metal(III) comp-

lexes (metal, M = Cr, Mn, Fe) were found to be ineffective as catalysts for the mild oxidation of isobutane, equation (2).

$$Me_3CH + \frac{1}{2}O_2 \xrightarrow{M(tpp)N_3} Me_3COH$$
 (2)

Under the conditions of our study the azido(tetraphenylporphyrinato)metal(III) complexes (M = Cr, Mn, Fe) are more active than typical radical initiators or cobalt salts and have activity which is quite comparable to that of the highly active alkylperoxo[bis(pyridylimino)isoindolinato]cobalt(II) complexes,^{15,16} (Table 2) which have been investigated recently. We have also found that azido[bis(pyridylimino)isoindolinato]cobalt(II), Co(bpi)N₃,† is of comparable activity to the alkylperoxo complex, Co(bpi)OOBu^t, but far more active than the acetate, Co(bpi)OAc.

In contrast to the first row azido(tetraphenylporphyrinato)metal(III) complexes, the corresponding nitrides are not active under mild conditions, Table 1. In fact, it is possible to observe the transformation of the tetraphenylporphyrinatoiron(III) azide, Fe(tpp)N₃, into the corresponding μ -nitride, [Fe(tpp)]₂N, in benzene using Fourier transform i.r. spectroscopy.¹⁸ The azide N–N stretch at 2050 cm⁻¹ disappears and new bands at 920 and 870 cm⁻¹ attributable to the μ -nitrido species appear. This may be a catalyst deactivation process. Whereas the μ -oxo di-iron species, [Fe(tpp)]₂O, was active for autoxidation of allylic and benzylic C–H bonds,¹⁹ it has very low activity for hydroxylation of isobutane at low tempera-

^{\dagger} Co(bpi)N₃ is prepared by the reacting of Co(bpi)OAc¹⁷ with sodium azide in methanol. I.r.(KBr) shows the N–N stretch of the azide ligand at 2030 cm⁻¹.

Table 1. Oxidation of isobutane ca	atalysed by	metalloporphyrin	complexes. ^a
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Catalyst	Catalyst /mmol	O2 uptake /mmol ^b	Catalyst turnovers ^c	Products/mmol		Selectivity
				Me ₂ CO	Bu ^t OH	to Bu ^t OH /% ^d
Fe(tpp)Cl ^e	0.025	0	0	0	0	
Mn(tpp)Cl	0.025	0	0	0	0	
Mn(tpp)OAc	0.050	0	0	0	0	
Cr(tpp)Cl	0.025	0	0	0	0	—
Fe(tpp)N ₃	0.013	1.7	130	0.2	2.2	92
$Mn(tpp)N_3$	0.013	2.3	177	0.4	3.0	88
$Mn(tpp)N_3$	0.025	5.5	220	0.7	6.2	90
$Cr(tpp)N_3$	0.013	3.4	262	0.4	3.3	89
Cr(tpp)N ₃	0.025	6.6	264	0.8	6.3	89
[Fe(tpp)] ₂ N	0.013	0	0	0	0	
Mn(tpp)N	0.025	0	0	0	0	
Cr(tpp)N	0.013	0	0	0	0	

^a Isobutane (6—7 g) was added to a solution of the catalyst in benzene (25 ml). The solution was stirred under 100 psig of O_2 at 80 °C for 6 h. ^b Oxygen was added in 10 psig increments as consumed. Gas was analysed by g.c.-m.s. and corrected for small amounts of CO_2 formed. *Caution:* Any experiments run within the explosive limits must be properly barricaded. ^c Mol oxygen consumed/mol catalyst used. ^d (Mol ButOH produced/total mol liquid product) ×100. The only products detected were the major product, ButOH, and the minor oxidative cleavage products, acetone and CO_2 . ^e tpp = tetraphenylporphyrinato.

Table 2. Oxidation of isobutane catalysed by cobalt complexes.^a

Catalyst	Catalyst /mmol	O ₂ uptake /mmol ^b	Catalyst turnovers ^c	Products/mmol		Selectivity
				Me ₂ CO	ButOH	10 Bu'OH /% d
None	0	0	0	0	0	
AIBN ^e	1.00	4.9	5	1.2	4.2	78
	0.10	17	1.7	0.3	0.7	70
$Co(acac)_{2}^{f}$	0.100	5.2	52	0.6	4.5	88
$Co(acac)_3$	0.100	1.5	15	0.3	2.1	88
Co(bpi)(OAc)f	0.025	0.6	24	0.1	0.7	88
Co(bpi)N ₃	0.025	4.9	196	0.7	4.7	87
Co(bpi)(O ₂ Bu ^t)	0.025	6.6	264	0.6	5.0	89

a - c See Table 1. ^d (Mol ButOH produced/total mol liquid product) ×100. The only liquid products detected were ButOH and acetone. ^e Azoisobutyronitrile. ^f bpi = bis(pyridylimino)isoindolinato; Hacac = pentane-2,4-dione.

tures. Thus, it would appear that an active catalyst which is converted to this species loses activity for alkane hydroxylation. Another deactivation process involves the oxidative decomposition of the porphyrin ring structure, which can be followed by electronic absorption spectroscopy. Work continues in an effort to understand the role of the azido ligand in oxidation activity and to synthesise and test active first row metalloporphyrin complexes which are more robust to oxidation by oxygen.

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