Catalysed Epoxidation and Hydroxylation of Alkene by Osmium(III)–Porphyrin Complexes

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Osmium(III)–porphyrin complexes have been prepared by Br_2 oxidation of $Os^{II}(P)(PBu^n{}_3)(CO)$ in CH_2Cl_2 [H_2P = H_2OEP (octaethylporphyrin) and H_2TPP (meso-tetraphenylporphyrin)]; the '$Os^{III}(P)(PBu^n{}_3)Br$ + PhIO' system is capable of performing epoxidation and hydroxylation of styrene and cyclohexene.

The study of 'metalloporphyrin complex + PhIO' as a biomimetic system for the oxidative enzymatic reactions of cytochrome P-450 is a matter of current interest.[1] It has been shown that the high-valent $Fe^V{=}O$ or $Fe^{IV}(P^{\cdot +}){=}O$ [$(P^{\cdot +})$ = porphyrinato radical cation] species is responsible for the cytochrome P-450 catalysed epoxidation and hydroxylation of alkenes.[2] Studies on this putative 'FeO' intermediate are in general difficult owing to its instability. Attention has been directed in modelling the reactivities of this enzyme toward the isoelectronic ruthenium and osmium porphyrin complexes that exhibit greater kinetic stabilities over the iron species. In this communication, we report preliminary results showing that the 'Os^{III}–porphyrin + PhIO' system performs epoxidation and hydroxylation of cyclohexene and styrene under simple and mild conditions as 'Fe^{III}–porphyrin + PhIO' did.[1,2]

The Os^{III}–porphyrin complexes $Os^{III}(P)(PBu^n{}_3)(Br)$ [(**2a**) H_2P = H_2OEP (octaethylporphyrin); (**2b**) H_2P = H_2TPP (meso-tetraphenylporphyrin)] have been prepared by Br_2 oxidation of $Os^{II}(P)(PBu^n{}_3)(CO)$ species in CH_2Cl_2 (Scheme 1). As expected for low spin d^5-Os^{III} complexes, the measured $\mu_{eff.}$ of 1.75—1.77 μ_B for (**2a**) and (**2b**) is characteristic of a spin-only value for one unpaired electron.† The observed low $E_f°$ values of the Os^{IV}/Os^{III} couple for (**2a**) and (**2b**) (0.06 and

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† Satisfactory elemental analyses have been obtained for (**1a**), (**1b**), (**2a**), and (**2b**).

Table 1. Oxidation of alkene with PhIO in CH_2Cl_2 catalysed by Fe^{III}, Ru^{III}, and Os^{III}–porphyrin complexes.

Catalyst	Substrate	Products	Reaction time (h)	Yield (%)[a]	Total turnover on metal
Fe (TPP)Cl[b]	cyclohexene	**(3)** **(4)** (55 : 15)	0.5	70	—
$Ru(OEP)(PPh_3)Br$[c]	cyclohexene	**(3)** **(4)** **(5)** **(6)** (1 : 1.7 : 0.5 : 3.4)	6	3	1.5
(2a)	cyclohexene	**(3)** **(6)** (9 : 14)	4.5	23	120
(2b)	cyclohexene	**(3)** **(6)** (18 : 9)	5	27	70
(2b)	styrene	styrene oxide	2.5	4	40
$Ru(OEP)(PPh_3)Br$[c]	styrene	styrene oxide	6	21	10

[a] Based on PhIO; this does not include loss of PhIO due to self decomposition in CH_2Cl_2 solution in the absence of catalyst. [b] J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, 1979, **101**, 1032. [c] Reference 6.

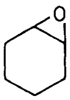
0.5 V *vs.* cp_2Fe^+/cp_2Fe^0 couple respectively) strongly indicate that high-valent osmium porphyrin complexes are more stable than the analogous ruthenium and iron species.

The catalytic oxidation of cyclohexene was carried out by stirring **(2a)** (3 mg, 3×10^{-3} mmol), cyclohexene (0.5 ml), and PhIO (250 mg, 1.23 mmol) in CH_2Cl_2 (3 ml) at 25 °C under *degassed, dry*, and *dark conditions*. Studies on the course of the reaction by gas chromatography showed a concomitant formation of cyclohexene oxide and cyclohexenone with 9 and 14% yield respectively after 4½ h reaction (see Table 1). For the first 2 h, the yields of the organic products increased linearly with the time of reaction. No induction period for this catalytic oxidative reaction was found. PhIO has been found to be transformed into PhI after the reaction. The organic products were identified by g.c.–mass spectroscopy.‡ As the oxidative reaction was unaffected by room light, this was neither a photocatalytic nor a photochemical process. If either **(2a)** or PhIO was omitted, only trace amounts of cyclohexene oxide and cyclohexenone were produced. The results on similar studies of the oxidation of cyclohexene and styrene by **(2b)** + PhIO are summarized in Table 1.

$$[\mathrm{Os^{II}(P)(CO)}] \xrightarrow{\text{i}} \underset{\textbf{(1)}}{\mathrm{Os^{II}(P)(PBu^n{}_3)(CO)}} \xrightarrow{\text{ii}} \underset{\textbf{(2)}}{\mathrm{Os^{III}(P)(PBu^n{}_3)(Br)}}$$

a; P = OEP
b; P = TPP

Scheme 1. *Reagents:* i, excess of $PBu^n{}_3$ in CH_2Cl_2; ii, Br_2 in CH_2Cl_2.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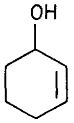
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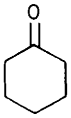
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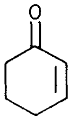
(6)

The observed epoxidation of alkene by **(2a)** [or **(2b)**] + PhIO is similar to the analogous reactions found for Mn^{III}, Fe^{III}, and Cr^{III} metalloporphyrin complexes;[2,3] a high-valent osmium oxo intermediate may be responsible for the epoxidation reaction. However, the active form of the catalyst is not *trans*-$[Os^{VI}(P)O_2]$ (H_2P = H_2OEP and H_2TPP) as this has been found to be inert towards styrene and cyclohexene at room temperature.[4]

Replacement of PhIO by t-butylhydroperoxide gave cyclohexenol as the major product in the **(2a)** [or **(2b)**] catalysed oxidation of cyclohexene. In this case, the osmium porphyrin complex may induce the decomposition of t-butylhydroperoxide and the oxidative reaction is likely to be a free radical auto-oxidation process.[5]

The observed large catalytic turnover number (Table 1) for the **(2a)** [or **(2b)**] + PhIO system is in contrast to Dolphin's work[6] where a 1.5 turnover number has been found for the '$Ru(OEP)(PPh_3)Br$ + PhIO' catalysed oxidation of cyclohexene. The underlying reason is uncertain; however, we are currently exploring the catalytic oxidative reactions of the 'Ru^{III}–porphyrin + PhIO' system. With **(2b)** as the catalyst, the visible spectrum of the solution after the oxidative reaction

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‡ G.l.c. conditions: styrene, 6′ × 1/8″ stainless steel (10% Carbowax on 60/80 mesh Chromosorb W) at 110 °C and a nitrogen flow rate of 10 ml min^{-1}. Cyclohexanol was used as internal standard; cyclohexene, 6′ × 1/8″ stainless steel (10% Carbowax on 60/80 mesh Chromosorb W) at 80 °C and a nitrogen flow rate of 8 ml min^{-1}.

Selected spectroscopic and electrochemical data (u.v.–visible spectra measured in CH_2Cl_2).

(1a) u.v.–vis.: $\lambda_{max.}$/nm (log ε), 257(4.74), 331(4.57), 348(4.59), 405(5.51), 516(4.24), 541(4.24); i.r.: ν(C≡O), 1920 cm^{-1}; ^1H n.m.r.: δ (CD_2Cl_2), 9.48 (s, 4H), 3.90(q, 16H), 1.86(t, 24H), 0.24 (m, 15H), −1.77 (m, 6H), −3.05(m, 6H).

(2a) u.v.–vis.: $\lambda_{max.}$/nm (log ε), 272(4.45), 347(4.58), 400(4.87), 495(4.01); $\mu_{eff.}$, 1.75 μ_B; $E_f°(Os^{IV}/Os^{III})$ = 0.06 V *vs.* cp_2Fe^+/cp_2Fe^0 couple in 0.1 M $[Bu_4N][BF_4]CH_2Cl_2$ solution (scan rate, 100 mV s^{-1}; working electrode, Pt).

(1b) u.v.–vis.: $\lambda_{max.}$/nm (log ε), 253(4.67), 282(4.44), 324(4.47), 418(5.51), 529(4.19), 562(3.80), 592(3.55); i.r.: ν(C≡O), 1950 cm^{-1}; ^1H n.m.r.: δ(CD_2Cl_2), 8.42(s, 8H), 8.07(m, 8H), 7.68(m, 12H), 0.33(m, 15H), −1.36(m, 6H), −2.52(m, 6H).

(2b) u.v.–vis.: $\lambda_{max.}$/nm(log ε), 276(4.62), 365(4.70), 420(5.13), 509(4.20); $\mu_{eff.}$, 1.77 μ_B; $E_f°(Os^{IV}/Os^{III})$ = 0.50 V *vs.* cp_2Fe^+/cp_2Fe^0 couple in 0.1 M $[Bu_4N][BF_4]CH_2Cl_2$ solution (scan rate, 100 mV s^{-1}; working electrode, Pt).

exhibited a broad absorption band from 510 nm tailing down to 650 nm. However the Soret band of the transformed osmium porphyrin complex remained at 420 nm. The mechanisms of these reactions have yet to be elucidated.

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