Isolation of a High-valent 'Oxo-like' Manganese Porphyrin Complex obtained from NaOCl Oxidation

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We report the isolation and characterization of a high-valent manganese porphyrin complex which epoxidizes styrene both catalytically and stoicheiometrically.

There is renewed interest in manganese porphyrin complexes in connection with their ability to facilitate the oxidative decomposition of water[1] and as catalysts in the oxidation of alkanes, alkenes, alcohols, ethers, amines, and phosphines.[2] It has been suggested that high-valent manganese porphyrin complexes are possible intermediates, but little is known about the mechanism of these reactions even though some Mn^{IV} [3] and Mn^{V} [4] porphyrin complexes have recently been isolated and characterized both physically and chemically. Previously,[2c,d] we have published details of the manganese

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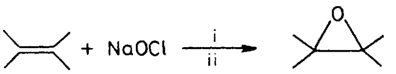

Scheme 1. i, Mn(TPP)OAc (TPP = tetraphenylporphyrinato)–pyridine–R_4NCl; ii, CH_2Cl–H_2O.

porphyrin catalysed epoxidation of many di- and tri-substituted olefins with NaOCl and the influence of added pyridine on the epoxidation rate, product selectivity, and stereoselectivity (Scheme 1).

In particular stereochemical studies[5] demonstrated that chlorohydrins are not involved in this catalytic epoxidation but suggested that manganese porphyrin complexes, in an oxidation state higher than 3+, are the active species. Recently it has been shown that NaOCl is a strong oxidant which can generate Mn^{V} porphyrin nitrido complexes in the presence of NH_3.[4a] Here we report the isolation and the preliminary characterization of an oxidized manganese porphyrin complex, obtained from chloro(tetramesitylporphyrinato)-manganese(III) Mn(TMP)Cl in the presence of NaOCl, which can epoxidize styrene both catalytically and stoicheiometrically. Mn(TMP)Cl (2×10^{-2} M) was dissolved in CH_2Cl_2 in the presence of benzyldimethyltetradecylammonium chloride as phase transfer agent. The solution was transferred to a separating funnel and shaken vigorously with an excess of aqueous sodium hypochlorite. The organic green layer rapidly turned brown. After separation, the organic phase was transferred into a receiver containing cold pentane, maintained at −80 °C. A brown microcrystalline solid (**1**) precipitated within 24 h. This complex, stable in the solid state, at ambient temperature, for one day, is reduced back to $[Mn^{III}(TMP)]^+$ [Figure 1(a)] when dissolved in various organic solvents at room temperature. On the other hand solutions of (**1**) are reasonably stable at low temperatures and we were able to obtain a visible spectrum of (**1**) at −36 °C in CH_2Cl_2 [Figure 1(b)]. This spectrum is identical to that obtained after oxidation *in situ* of a methylene chloride solution of Mn(TMP)Cl with aqueous NaOCl in the presence of a phase transfer agent [Figure 1(c)].

[Mn(TMP)O]Cl
(**1**)

Styrene and triphenylphosphine are stoicheiometrically oxidized by (**1**) at room temperature‡ in various organic solvents affording $Ph_3P{=}O$ (*ca.* 90%) and styrene oxide (22%). Yields are expressed with respect to the oxidant and confirm that (**1**) can transfer only one oxygen atom.

The visible absorption spectrum of (**1**) [Figure 1(b)] displays a Soret band at 425 nm and a well resolved absorption band at 520 nm, as described for a monomeric manganese(IV) porphyrin.[6] The variable-temperature magnetic susceptibility was determined in the solid state from 77 to 300 K. A plot of $1/\chi_M$ *vs.* temperature yielded a straight line with an intercept of −1.8 K, indicating Curie–Weiss behaviour. The effective magnetic moment was $\mu_{eff} = 4.00 \pm 0.05\ \mu_B$ for all the data points. This is consistent with a manganese(IV) $S = 3/2$[7] slightly coupled with a radical $S = 1/2$ on the ligands (porphyrin or oxygen atom).[8] Cyclic voltammetry of (**1**) indicated two reversible reduction steps: $Ep(1) = +1.47$ V and $Ep(2) = +0.85$ V.§ The elemental analysis of (**1**) gave one chlorine atom per manganese atom. The infrared spectrum of (**1**) (KBr pellets) displays a small band at 1260 cm^{-1}, usually considered characteristic of a π radical–cation structure in metalloporphyrins,[9] and a strong band at 950 cm^{-1} (both bands are absent in the parent porphyrin). The M=O band is in the 1020—1040 cm^{-1} region for chromium complexes;[10] in the case of manganese porphyrins no oxo-complexes have been fully characterized.[7,11] The apparent absence of oxygen exchange with $H_2{}^{18}O$[12,13] does not permit a definite assignment of the 950 cm^{-1} band. These facts show the important differences between the complex reported here and the high-valent manganese porphyrin complexes prepared *via* iodosylbenzene oxidation.[2a,3a,b]

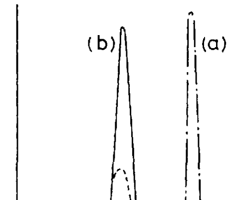

Figure 1. Visible absorption spectrum of: (a) Mn(TMP)Cl in CH_2Cl_2 at 25 °C, (b) complex (**1**) in CH_2Cl_2 at −36 °C, (c) Mn(TMP)Cl (4.3×10^{-5} M), phase transfer agent (1.5×10^{-5} M) in CH_2Cl_2 (2.5 ml), after shaking for 2 min with aqueous NaOCl (0.35 M, 0.3 ml) and separation; the spectrum is recorded in the presence of the oxidant at 25 °C.

The data presented here, lead us to suggest two possible structures for (**1**) shown in Figure 2.

Besides the stoicheiometric oxidations reported above it should be noted that (**1**) is also an effective catalyst for styrene epoxidation. Figure 3 shows that a better catalytic activity is

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‡ The reactions were performed by mixing 4 equiv. of substrate and 1 equiv. of complex (**1**) at low temperature and gradually warming to 25 °C.

§ A 'home microcomputer-controlled instrument' with *iR* compensation was used for electrochemical studies. All voltammograms were recorded at −10 °C; complex (**1**) 1×10^{-3} M in CH_2Cl_2. A platinum auxiliary electrode and an Ag/AgCl (0.1 M KCl) reference electrode were used in conjunction with the hanging-drop mercury electrode (static mercury electrode, Princeton Applied Research).

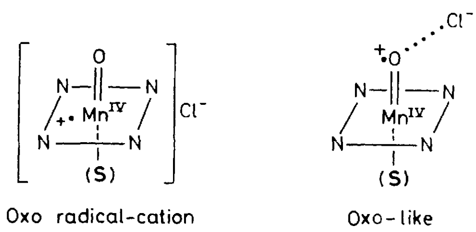

Figure 2. Proposed structures for complex (**1**). S = solvent, H_2O, or neutral ligand (pyridine).

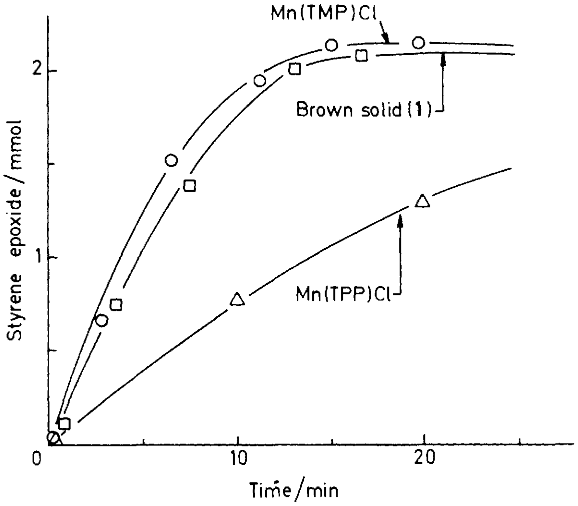

Figure 3. A plot of time *vs.* conversion for the catalytic oxidation of styrene to the corresponding epoxide with NaOCl under standard phase transfer conditions: manganese complex (0.0125 mmol), phase transfer agent (0.025 mmol), pyridine (0.31 mmol), styrene (2.1 mmol), and NaOCl (3.5 mmol) in CH_2Cl_2–H_2O (5—10 ml) at 25 °C under nitrogen. In all cases: conversion 100%, yield and selectivity >90%.

obtained with the sterically hindered porphyrin (TMP) compared with the 'normal' TPP ligand.

Further work is in progress (EXAFS) to confirm the structure of this high-valent 'oxo-like' manganese porphyrin complex obtained from NaOCl oxidation.

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