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Novel Mn(III)chlorins as versatile catalysts for oxyfunctionalisation of hydrocarbons under homogeneous conditions

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Abstract

The novel fluorinated metallochlorin 5,10,15,20-tetrakis(pentafluorophenyl)-tetrahydro-1*H*-*N*-methyl-pyrrolo[3,4-*b*]-porphyrinato manganese(III), **Mn(chlor)-1**, and its methylated derivative, **Mn(chlor)-2**, have been studied as catalysts in the oxyfunctionalisation of cyclohexane with two oxidants, namely iodosylbenzene (PhIO) and H_2O_2. For comparison reasons two metalloporphyrins have been also used: the neutral 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato manganese(III), **Mn(porph)-1**, and the cationic 5,10,15,20-tetrakis(2,3,5,6-tetrafluoro-4-trimethylammoniumphenyl)porphyrinato manganese(III), **Mn(porph)-2**. It has been possible to verify a different reactivity in the H_2O_2-oxyfunctionalisation of alkanes from studies using the radical inhibitor bromotrichloromethane and competitive cyclooctane/*cis*-cyclooctene oxidations. The results suggest that the formation of alcohols and ketones from the oxidation of cyclohexane occurs mainly from a free alkyl radical mechanism, which requires a $Mn^V{=}O$ species to abstract a hydrogen atom from the alkane to generate the alkyl radical. On the other hand, the Mn(chlor)/H_2O_2 system possibly yields, in a first step, the $Mn^{III}{-}OOH$ species, but this is not reactive enough to generate $Mn^V{=}O$. The Mn(chlor) hydroperoxy complex shows low efficiency in the production of the alkyl radical, leading to small amounts of alcohol and ketone. However, it seems to be an efficient species for selective epoxidation, as can be observed in the competitive cyclooctane/*cis*-cyclooctene oxidation reaction.

Keywords: Manganese(III); Chlorin; Porphyrin; Cyclohexane; Oxidation

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1. Introduction

Synthetic metalloporphyrins, mainly with Fe(III) or Mn(III) as metal ions, have been often used as catalysts in several oxidation reactions, mimicking the activity of cytochrome P450 monooxygenases, enzymes which contain iron(III)porphyrin moieties in their active sites. Synthetic manganese(III)porphyrins have also been used as catalysts for oxidation reactions of organic compounds by single oxygen donors (iodosylarenes, $KHSO_5$, NaOCl or H_2O_2). High catalytic activities have been observed, mainly with catalysts containing electron-withdrawing substituents at the *meso*- and/or β-pyrrolic positions of the porphyrin ring [1–3]. It is often described that manganese or iron porphyrin complexes containing pentafluorophenyl groups at the *meso* positions, such as **Mn(porph)-1** (Fig. 1), act as very efficient catalysts for oxyfunctionalisations of hydrocarbons; the fluorine electron-withdrawing atoms give rise to more active catalysts, by shifting the redox potential of the metal and, in addition, making the active intermediate to be more electrophilic and, hence, more reactive towards poor reactive substrates like alkanes [4,5].

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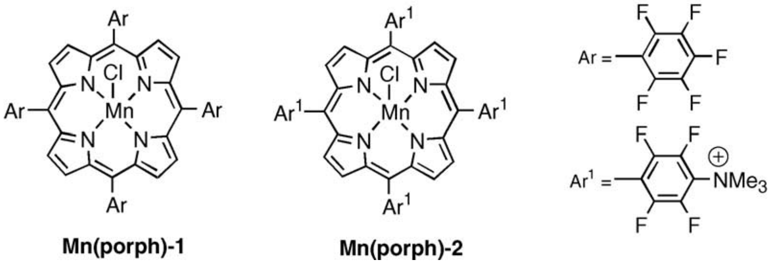


Fig. 1. Mn(III)porphyrins.

A modification of the 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ligand could result in improved or different catalytic properties. The introduction of certain functional groups can either promote changes in selectivity (chemo-, regio-, stereo-) or the binding of the porphyrin to other molecules or solid supports can bring several advantages [6]. For this reason, Silva et al. [7] have modified the structure of the 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, yielding a novel ligand, corresponding to the chlorin **1** (Fig. 2). This is easily obtained with the 1,3-dipole derived from the reaction between paraformaldehyde and *N*-methylglycine, in 61% yield.

We report in this paper a strategy to develop a cationic Mn complex obtained from the *N*-methylation of **1**, yielding the corresponding chlorin **2** (Fig. 2). Insertion of Mn(III) into chlorin derivatives **1** and **2**, gave the **Mn(chlor)-1** and **Mn(chlor)-2** complexes, which were characterised by thin layer chromatography (TLC), UV–vis spectroscopy and elemental analysis.

The new complexes **Mn(chlor)-1** and **Mn(chlor)-2** have been used as catalysts in the homogeneous oxidation of cyclohexane with iodosylbenzene (PhIO) and H_2O_2. Their catalytical action was also compared with the results obtained with two manganese fluorinated porphyrin complexes,

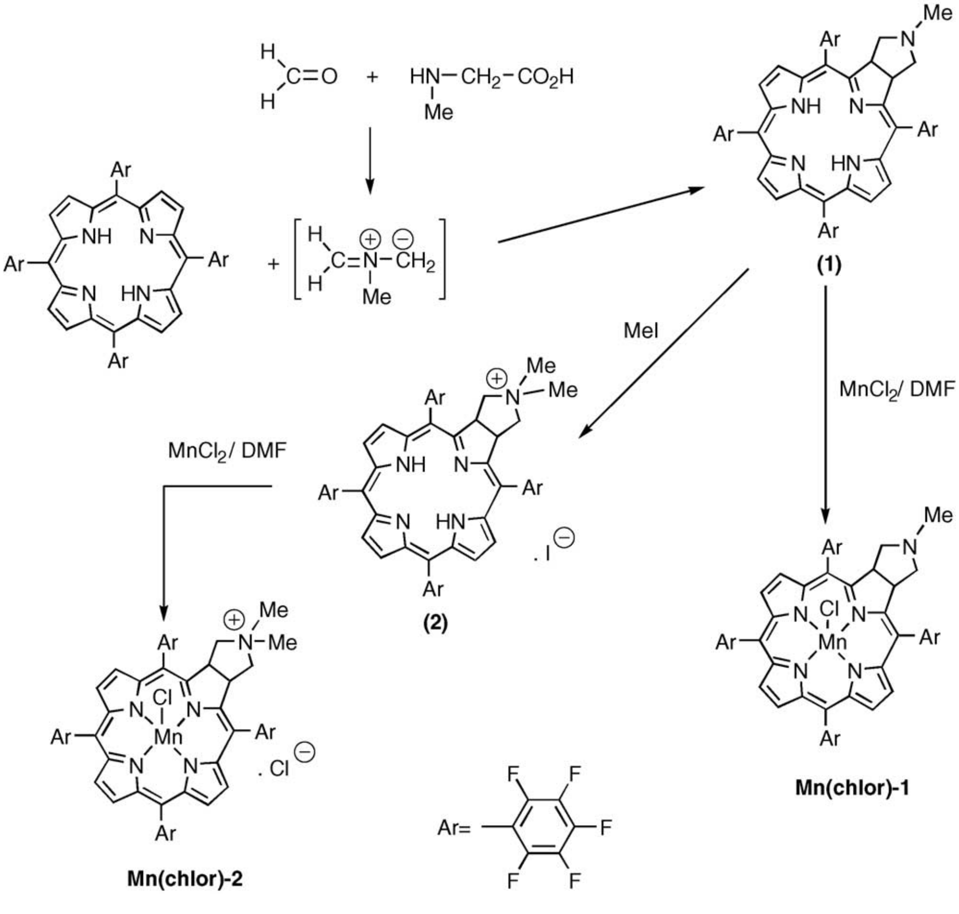


Fig. 2. Syntheses of chlorins **1** and **2** and their corresponding Mn(III) derivatives, **Mn(chlor)-1** and **Mn(chlor)-2**.

Mn(porph)-1 and **Mn(porph)-2** (Fig. 1). Studies on competitive oxidations between cyclooctane and *cis*-cyclooctene as well as experiments on cyclohexane oxyfunctionalisation in the presence of bromotrichloromethane, an alkyl radical trapping, have been carried out in order to have a deeper insight into the mechanism and, in addition, to try to understand the different reactivity features observed when a Mn(chlor)/H_2O_2 system is used.

2. Experimental

2.1. Materials and solvents

All solvents and reagents were of commercial grade unless otherwise stated and were purchased from Mallinckrodt, Acros, Fluka and Aldrich. Dichloromethane, methanol, *N*,*N*-dimethylformamide and acetonitrile HPLC grade were used as received. **Mn(porph)-1** and **Mn(porph)-2** were purchased from Midcentury (Posen, IL, USA). Cyclohexane was purified by column chromatography on basic alumina prior to use and the purity was checked by gas chromatographic analysis. Hydrogen peroxide (H_2O_2 30% in H_2O, Fluka) was stored at 5 °C and checked by titration every 3 months [8]. Iodosylbenzene was synthesised according to the procedure previously described and stored in a freezer and analysed every 6 months by iodometric assay [9]. Chlorin **1** was prepared according to a literature procedure [7].

2.2. Methylation of **1**

Methylation of **1** was achieved by adding a large excess of methyl iodide to a solution of **1** in toluene and the mixture was stirred for 72 h at 40 °C. At the end of the reaction, the solid was filtered and washed with petroleum ether. Then, the solid was dissolved in dichloromethane and washed with water and dried (Na_2SO_4). The product was obtained after partial evaporation of the solvent and addition of hexane. Yield: 91%; m.p. > 300 °C; ^{1}H NMR δ: −1.99 (s, 2H, N*H*), 3.09 (s, 3H, CH_3), 3.48–3.58 (m, 2H, H-pyrrolidine), 3.68 (s, 3H, CH_3), 4.68–4.74 (m, 2H, H-pyrrolidine), 5.88–5.98 (m, H-2, 3), 8.38 (d, 2H, $J = 4.9$ Hz, H-β), 8.51 (s, 2H, H-12, 13), 8.76 (d, 2H, $J = 4.9$ Hz, H-β); UV–vis (CH_2Cl_2, λ_{max} (nm) (rel. int.)): 400 (100%); 500 (11%); 527 (6%); 594 (5%); 647 (27%); MS (LSIMS) 1046 $(M - I)^+$.

2.3. Synthesis of **Mn(chlor)-1** and **Mn(chlor)-2**

The manganese insertion into **1** and **2** has been achieved in 95% yield by heating the free-base chlorins and $MnCl_2 \cdot 4H_2O$ at reflux in *N*,*N*-dimethylformamide, according to the literature report [10]. At the end of the reaction, the solvent was removed under vacuum and the Mn(III)chlorin obtained was purified by column chromatography on alumina. After the evaporation of the solvent, the product was recrystallised from dichloromethane/hexane. **Mn(chlor)-1**: one spot on alumina coated TLC plates using dichloromethane/methanol (4:1); UV–vis (CH_2Cl_2, λ_{max} (nm) (ε)): 365, 494 (4.9×10^4 mol^{-1} cm^{-1} l), 565 and 662; Anal. Calcd. for $C_{47}H_{15}ClF_{20}MnN_5 \cdot (1/2)C_6H_{14}$: C, 51.63; H, 1.91; N, 6.02. Found: C, 51.52; H, 1.97; N, 6.51. **Mn(chlor)-2**: one spot on alumina coated TLC plates using dichloromethane/methanol (4:1); UV–vis (CH_2Cl_2, λ_{max} (nm) (ε)): 367, 480 (1.0×10^5 mol^{-1} cm^{-1} l); Anal. Calcd. for $C_{48}H_{18}Cl_2F_{20}MnN_5 \cdot H_2O$: C, 48.51; H, 1.70; N, 5.85. Found: C, 48.65; H, 2.06; N, 5.95.

2.4. General procedure for catalytic oxidations

All solvents and substrates have been checked prior to use, by gas chromatography, to ensure that they were pure. Reactions were performed in a 4 cm^3 vial under air and inert atmosphere at room temperature in dichloromethane/acetonitrile (1:1) as solvent. For the inert atmosphere oxidation reactions, a vial capped with a Teflon-coated silicone septum was used. Imidazole was used as a co-catalyst according to reports in the literature [3,11], and bromobenzene as the internal standard. Yields based on the oxidant added have been determined by removing aliquots of the reaction mixture and analysing them by gas chromatography. No transformation took place in the control experiments in the absence of Mn(III)chlorins or Mn(III)porphyrins. For competitive reactions between cyclooctane and *cis*-cyclooctene a 10:1 molar ratio of alkane/alkene has been used.

2.5. Physical measurements

Thin layer chromatography (TLC) was done on alumina plates (Merck). Column chromatography experiments were performed on silica gel (Merck silica gel 70–230 mesh). UV–vis measurements were performed with a diode array HP 8453 spectrophotometer. Mass spectra were obtained using a VG Autospec Q mass spectrometer. Gas chromatography analyses were performed on a Hewlett-Packard HP 6890 Series GC System, coupled to a flame ionisation detector using a capillary column (HP-INNOWAX, cross linked polyethylene glycol, length 30 m; i.d. 0.25 mm, film thickness 0.25 μm) and nitrogen as the carrier gas.

3. Results and discussion

For testing the catalytic properties of the new class of Mn(III)chlorin complexes, a comparison with the catalytic activity of electron-deficient Mn(III)porphyrins was considered. For such purpose, a neutral Mn(III)porphyrin, **Mn(porph)-1** and a tetracationic one, **Mn(porph)-2** (Fig. 1) were used. Results on the oxyfunctionalisation of cyclohexane with PhIO and H_2O_2 catalysed by **Mn(chlor)-1**, **Mn(chlor)-2**, **Mn(porph)-1** and **Mn(porph)-2** systems are now reported.

Table 1
Oxidation of cyclohexane with H_2O_2 and PhIO catalysed by synthetic Mn(III)chlorins and Mn(III)porphyrins

Entry	Catalyst	Oxidant	Imidazole	Cyclohexanol selectivity (%)	Cyclohexanone selectivity (%)	Alcohol/ketone ratio	Total yield (%)
1	**Mn(chlor)-1**	H_2O_2	–	–	–	–	–
2	**Mn(chlor)-1**	H_2O_2	+	100	–	–	13
3	**Mn(chlor)-1**	PhIO	–	66	34	1.9	41
4	**Mn(chlor)-1**	PhIO	+	78	22	3.6	60
5	**Mn(chlor)-2**	H_2O_2	–	–	–	–	–
6	**Mn(chlor)-2**	H_2O_2	+	92	8	11	24
7	**Mn(chlor)-2**	PhIO	–	69	31	2.2	49
8	**Mn(chlor)-2**	PhIO	+	78	22	3.5	54
9	**Mn(porph)-1**	H_2O_2	–	–	–	–	–
10	**Mn(porph)-1**	H_2O_2	+	83	17	4.9	41
11	**Mn(porph)-1**	PhIO	–	71	29	2.5	42
12	**Mn(porph)-1**	PhIO	+	83	17	4.9	47
13	**Mn(porph)-2**	H_2O_2	–	–	–	–	–
14	**Mn(porph)-2**	H_2O_2	+	75	25	3	28
15	**Mn(porph)-2**	PhIO	–	69	31	2.2	48
16	**Mn(porph)-2**	PhIO	+	79	21	3.8	48

Maximum yields based on the oxidant added. Reaction mixtures analysed by GC after 1 h of reaction. No modification of the reaction products profile was observed after 2 and 24 h. Conditions: molar ratio Mn(complexes)/imidazole/oxidant/substrate = 1:20:40:7440 (for H_2O_2 oxidations) and 1:10:40:7440 (for PhIO oxidations); magnetic stirring, under air and at room temperature. Quantities: Mn(complexes) = 0.25 μmol; cyclohexane = 200 μl; solvent = 800 μl. All reactions were run at least in duplicate.

Firstly, it can be observed from Table 1 that moderate to good yields (up to 60%) of oxygenated products are obtained in the oxyfunctionalisation of the poor reactive cyclohexane. Furthermore, alcohol/ketone ratios ranging from about 66:34 to 100:0 have been obtained.

Hydroxylation of alkanes by Mn(porph)/PhIO are reported in the literature to operate by an oxygen rebound mechanism [12], having a high-valent $Mn^V{=}O$ intermediate believed to be the active species, which abstracts a hydrogen atom from the alkane, generating a short-lived alkyl radical and a Mn^{IV}–OH complex in a solvent cage. Rapid hydroxyl transfer from this complex to the alkyl radical produces the alcohol (reactions (1)–(3)). For reactions under air, escape of alkyl radicals from the solvent cage should yield higher amounts of ketones due to the very fast reaction ($k > 10^9\,mol^{-1}\,l\,s^{-1}$) between the carbon centred radicals and the O_2 generating peroxyl radicals [13] (reaction (4)):

$$Mn^{III}L + PhIO \rightarrow LMn^{V}O + PhI \qquad (1)$$

$$LMn^{V}O + RH \rightarrow LMn^{IV}OH + R^{\bullet} \qquad (2)$$

$$R^{\bullet} + LMn^{IV}OH \rightarrow ROH + Mn^{III}L,$$
$$L = \text{porphyrin or chlorin} \qquad (3)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (4)$$

On the Mn(porph) catalysed oxidations (entries 10 and 12 in Table 1), the alcohol/ketone ratios obtained are the same for either the PhIO or H_2O_2 reactions, as has been previously described in studies focused on oxidations catalysed by Mn(III)porphyrins and those oxidants [11,14]. From these results, it can be assumed that oxidations mediated by Mn(III)porphyrins should be happening by an "in cage" oxygen rebound mechanism and the production of ketones can be explained by the escape of alkyl radicals from the solvent cage, which react with O_2 to produce peroxyl radicals (reaction (4)) and posterior reactions of the peroxyl radicals (reactions (5)–(6)). In contrast to the oxidations mediated by Mn(porph), the results obtained for Mn(chlor)/PhIO (entries 4 and 8, Table 1) and those achieved for Mn(chlor)/H_2O_2 (entries 2 and 6, Table 1) show different reactivities (including different alcohol/ketone ratios), the latter yielding a nearly exclusive formation of the alcohol. Mn(chlor)/PhIO oxidation reactions seem to occur by an oxygen rebound pathway via $Mn^V{=}O$ (reactions (1)–(3)) and the ketones which are formed in these reactions are probably the result of the reaction between the alkyl radicals which escape from the solvent cage and O_2 (reactions (4)–(6)):

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow ROOOOR \rightarrow 2R{=}O + H_2O_2 \qquad (5)$$

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow ROOOOR \rightarrow ROH + R{=}O + O_2 \qquad (6)$$

Table 2
Competitive cyclooctane/*cis*-cyclooctene oxidation reactions promoted by **Mn(chlor)-1**/imidazole or **Mn(porph)-1**/imidazole

Entry	Catalyst	Oxidant	k_{rel}[a]
1	**Mn(chlor)-1**	H_2O_2	–[b]
2	**Mn(chlor)-1**	PhIO	2.3
3	**Mn(porph)-1**	H_2O_2	2.3
4	**Mn(porph)-1**	PhIO	2

Molar ratio Mn(complexes)/imidazole/oxidant/*cis*-cyclooctene/cyclooctane = 1:20:40:740:7440 (for H_2O_2 oxidations) and 1:10:40:740:7440 (for PhIO oxidations).

[a] Determined by GC analysis by dividing the peak areas of the products obtained (1,2-oxycyclooctane/cyclooctanol + cyclooctanone).

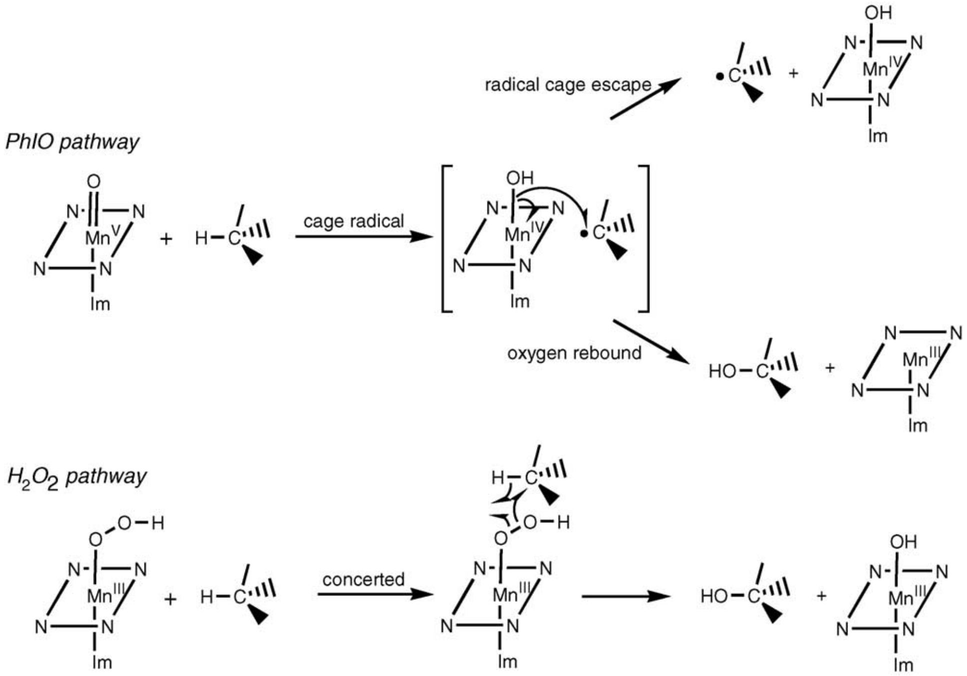
[b] Only the epoxide was detected.

In this sense, an experiment carried out under an inert atmosphere, promoted by **Mn(chlor)-1**/PhIO/imidazole (comparable with the reaction in entry 4, Table 1) resulted in 28% yield of cyclohexanol (85% selectivity) and 5% yield of cyclohexanone (15% selectivity, alcohol/ketone ratio is 5.7). It can be inferred from this result that the absence of O_2 led to a clear dropping of the total substrate conversion, suggesting that the presence of O_2 is important to the alcohol and ketone formation. These results suggest easy escape of the short-lived alkyl radical intermediate from the solvent cage. In order to clarify the contribution of the radical escape mechanism for the conditions used in these studies, we have investigated the cyclohexane oxyfunctionalisation with PhIO catalysed by **Mn(chlor)-1** in the presence of bromotrichloromethane, a carbon centred radical trapping species [15]. Under these reaction conditions, the formation of cyclohexanol (18%), cyclohexanone (5%) and bromocyclohexane (28%) was observed. Remarkably, the alcohol/ketone ratio obtained (3.6) is exactly the same as that obtained in the absence of bromotrichloromethane (see entry 4, Table 1). These results seem to indicate that the same pathway is involved in the alcohol and ketone formation, leading us to believe that these oxygenated products can be formed mainly by a free radical mechanism. Therefore, a possible general pathway could be an “out of cage” mechanism represented by the reactions (4)–(7) [15b–17]. In this way, the “in cage oxygen rebound” mechanism (reactions (1)–(3)) does not appear to be the main reaction pathway under the conditions tested. It is improbable that an “out of cage” reaction (3) may occur due to the slower transfer of the hydroxyl group from Mn(complexes) compared to the reactions (4) and (7) [18,19]:

$$\mathrm{PhIO} + \mathrm{R}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R}^{\bullet} \qquad (7)$$

Based on the free radical mechanism proposed, how can the reactivity presented by the Mn(chlor)/H_2O_2 system be explained? In order to understand this behaviour, competitive experiments between cyclooctane and *cis*-cyclooctene were performed. These competitive studies were carried out with **Mn(chlor)-1** and **Mn(porph)-1** and the results obtained are summarised in Table 2. It is often described that the yield of the epoxide obtained from the epoxidation of *cis*-cyclooctene or the formation of alcohols and ketones in the oxidation of cyclooctane can be an indication of different metal-complex intermediates in the reactions [20]. Presumably, in the reactions promoted by Mn(chlor)/H_2O_2, the Mn^V=O species is not the main intermediate, as it is in the case of the reactions catalysed by Mn(porph) with both oxidants or Mn(chlor) with PhIO.

From the values of k_{rel} in Table 2, it can be observed that only the Mn(chlor)/H_2O_2 system shows a difference in reactivity, leading to the exclusive formation of the epoxide. These results suggest the presence of a different metal complex as the main species in the reaction with Mn(chlor)/H_2O_2. This system seems to favour the formation of a hydroperoxy active species, Mn^{III}–OOH, which is unable to generate the Mn^V=O species as the main entity (the most probable metal complex able to abstract a hydrogen atom from the alkane in order to generate the alkyl radical). Mn^{III}–OOH is capable of epoxidising alkenes [21], but seems to be a less effective species for the oxidation of alkanes.



Scheme 1.

4. Conclusions

Manganese(III)chlorins appear to be promising catalysts for oxidation reactions, since moderate to good yields of oxygenated products were obtained in the cyclohexane oxyfunctionalisation reactions. Furthermore, these Mn(chlor)/H_2O_2 systems showed a different reactivity, favouring the epoxidation reaction. The preference for epoxide formation in the reactions promoted by Mn(chlor)/H_2O_2 lead us to believe that Mn^{III}(chlor)–OOH (Scheme 1) does not seem to favour alkyl radical production, the main active species in the reactions affording the alcohol and the ketone. This implies a pathway without radicals for the Mn(chlor)/H_2O_2 promoted oxidation (Scheme 1). The results obtained with PhIO seem to indicate that the main pathway involves an easy alkyl radical cage escape followed by the radical reactions (4)–(7).

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