Oxidation of alkanes catalyzed by manganese(III) porphyrin in an ionic liquid at room temperature

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Abstract—Efficient oxidation of alkanes is achieved by using an electron-deficient manganese(III) porphyrin catalyst in combination with iodobenzene diacetate in an ionic liquid at room temperature; a high-valent manganese-oxo porphyrin complex ($Mn^V=O$) was considered as the reactive oxidation intermediate.
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In view of today's environmental consciousness, the use of environmentally benign reaction mediums is very important. In this connection, room temperature ionic liquids that are air and moisture stable have received in recent years a good deal of attention as potential cleaner solvents.[1–3] More recently, it has been reported that classical organic oxidation can be performed in ionic liquids with great advantages (yield and selectivity) as compared to those performed in organic solvents.[4,5] We have described the epoxidation of several alkenes catalyzed by a manganese porphyrin **1**, carrying four pentafluorophenyl substituents, in an ionic liquid [bmim]PF$_6$ at room temperature.[6] Epoxidation, using iodobenzene diacetate [PhI(OAc)$_2$] as the oxygen source, of various alkenes led to the corresponding epoxides with good to excellent yields. PhI(OAc)$_2$, which is soluble in most organic solvents, safe to use, and commercially available, has been employed as an efficient oxidant in metal complex-catalyzed oxidation reactions.[7,8] Since the oxidation of saturated hydrocarbons under mild reaction conditions is of importance in both synthetic chemistry and industrial processes, biomimetic catalysts based on metalloporphyrins associated with various oxidants have been used as cytochrome P-450 models and their potential for saturated hydrocarbons oxidation has received considerable interest in recent years.[9–12] In this paper, we hope to further report the development of this MnTFPPCl-[bmim]PF$_6$ catalyst system for the oxidation of the inert carbon–hydrogen bond of alkanes.

Table 1. Catalytic oxidation of alkanes with metalloporphyrins and PhI(OAc)$_2$ in [bmim]PF$_6$/CH$_2$Cl$_2$[a]

Entry	Substrate	Axial ligand[c]	Conv. (%)	Products yield (%)[b]	
				Alcohol	Ketone
1	**2a**	–	38 (9)	24 (2)	13 (7)
		Imidazole	81	36	45
2	**2b**	–	56 (16)	49 (3)	7 (13)
		Imidazole	57	51	5
3	**5**	–	96 (90)	1 (31)	95 (59)
		Imidazole	91	49	42
4	**8**	–	90 (9)	90 (7)	<1 (2)
		Imidazole	55	54	<1

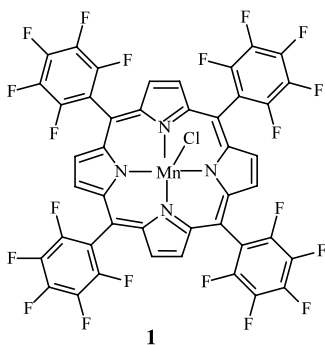[a] All reactions were performed in capped vials in 2.5 mL of [bmim]PF$_6$/CH$_2$Cl$_2$ (3/2, v/v) using a 225/150/1 oxidant/substrate/catalyst ratio.
[b] The yields are based on the substrate and are determined by GC. Results obtained in the absence of ionic liquid are given in parentheses.
[c] Molar ratio of axial ligand to catalyst is 50/1.

1

The catalytic oxidation of alkanes by **1** using PhI(OAc)$_2$ as the oxidant was carried out in [bmim]PF$_6$/CH$_2$Cl$_2$ (3:2, v/v) at room temperature. The results of the oxidation of alkanes were summarized in Table 1. It was shown that **1** functioned as a good catalyst in the reaction of PhI(OAc)$_2$ with various alkanes such as cyclohexane (**2a**), cyclooctane (**2b**), tetrahydronaphthalene (**5**) and adamantane (**8**). Transformation of alkanes to their corresponding alcohols and ketones was found to proceed with moderate to very high yields depending on the alkane structures (Fig. 1).

Cyclohexane was oxidized to cyclohexanol (**3a**) and cyclohexanone (**4a**) in yields of 24% and 13% after 2 h under identical conditions. In the oxidation of cyclooctane (**2b**) and adamantane (**8**), alcohols were yielded as the major products with the formation of small amounts of ketone products (Table 1, entries 2 and 4). In the case of tetrahydronaphthalene (**5**), the main product detected was ketone (**7**) (Table 1, entry 3).

The catalysis in the absence of the ionic liquid, gave much lower conversions (between 9 and 16%, see values in parentheses in Table 1) except for tetrahydronaphthalene in which 90% conversion was obtained. As for the role of ionic liquids played during the catalytical oxidation, we considered that the active site
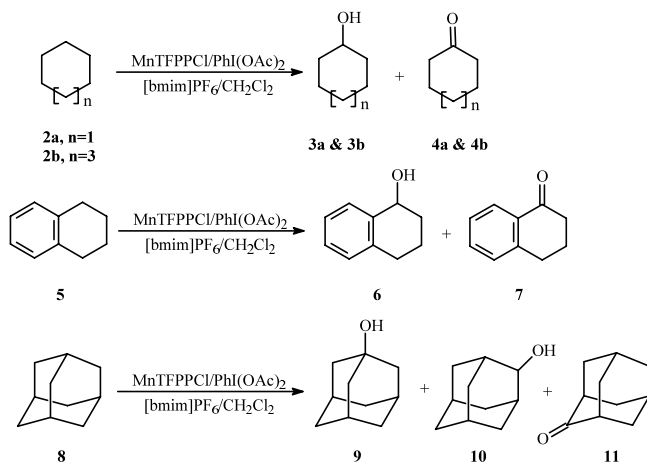
of the catalyst is very accessible to organic substrates because of the non-coordination of [bmim]PF$_6$. Furthermore, ionic liquids are generally chemically inert towards both catalysts and reactive intermediates, meaning that catalyst stability is not a problem. Unfortunately, up until recently, the nature of interactions between ionic liquids and different types of solute is not clear.

It is well known that the catalytic ability of manganese porphyrins can be improved by the use of nitrogen bases as an axial ligand.[13,14] To study the effect of an axial ligand on the oxidation of alkanes catalyzed by **1** in [bmim]PF$_6$/CH$_2$Cl$_2$ with PhI(OAc)$_2$, we chose imidazole as the axial ligand. The results of Table 1 showed that the conversion was greatly dependent on the substrate structure. It is clear that the yield of hydroxylation products was improved in the presence of imidazole in the case of cyclohexane and cyclooctane. The proportions of alcohol and ketone were found to be 4:5 for cyclohexane and 10:1 for cyclooctane. This is because the ligand favors the formation of the high-valent oxo-manganese species, OMn^V(P), which is responsible for oxygen insertion into the substrates. However, in the case of adamantane and tetrahydronaphthalene, the conversion was reduced, especially for the oxidation of adamantane. This happens probably due to the fact that the approach of the bulky adamantane to the active site of the catalyst is difficult in the presence of imidazole.

One of the primary aims of our study was to investigate the recycling of the catalyst **1**. Clearly this is important in the context of economic feasibility and sustainable development. Thus, at the end of the reactions the products were removed from the catalytic system by extraction with *n*-hexane and the recovery and recyclability of the brown–red oily ionic liquid phase containing the catalyst were examined. The catalyst was tested for its activity in the oxidation of cyclohexane and cyclooctane using PhI(OAc)$_2$ as oxidant leading to five recycling steps without decrease of activity. Moreover, no manganeseporphyrin was detected in the extracted solution when analyzed by UV–vis spectroscopy.

The UV–vis analysis revealed that the Soret band of metalloporphyrin **1** in mixed [bmim]PF$_6$/CH$_2$Cl$_2$ showed a blue shift relative to the Soret band at 474 nm as obtained in CH$_2$Cl$_2$. This change could be attributed, in part, to the possibility that [bmim]PF$_6$ is more dipolar than CH$_2$Cl$_2$. The reaction of **1** with PhI(OAc)$_2$ in [bmim]PF$_6$/CH$_2$Cl$_2$ and CH$_2$Cl$_2$ was also monitored by UV–vis spectroscopy (Fig. 2). In CH$_2$Cl$_2$, addition of PhI(OAc)$_2$ to a solution containing **1** caused immediate generation of a new species with a broad Soret band at 422 nm indicating the formation of a Mn^{IV}=O derivative, as shown in Figure 2c.[15–17] This derivative was very stable and unchanged even after one day. When cyclooctane was added to the solution, after 2 h, GC analysis of the reaction mixture showed little formation

Figure 1. The oxidation of alkanes by PhI(OAc)$_2$ catalyzed by **1** in [bmim]PF$_6$/CH$_2$Cl$_2$.
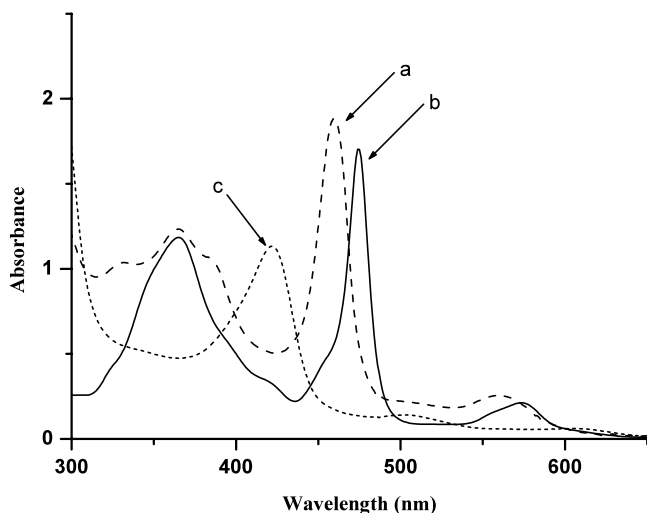
Figure 2. (a) UV–vis spectrum of manganese porphyrin **1** in [bmim]PF$_6$/CH$_2$Cl$_2$ (3/2, v/v). (b) In CH$_2$Cl$_2$. (c) Spectrum of **1** in the presence of PhI(OAc)$_2$ in CH$_2$Cl$_2$.

of oxidation products. On the other hand, for a solution of **1** in [bmim]PF$_6$/CH$_2$Cl$_2$, no change in the spectrum was observed after the addition of PhI(OAc)$_2$ with the Soret band at 458 nm being constant and no new absorption appearing. However, in the presence of cyclooctane the catalytic system gave excellent yields. Apparently an active oxidizing species was formed under the experimental conditions but not detected due to its higher reactivity and shorter life time.

According to the above discussion, we assumed that in mixed [bmim]PF$_6$/CH$_2$Cl$_2$ the oxygen atom transfer occurs via the in situ formation of the oxo-manganese complex (Mn^V=O). In order to confirm the proposed Mn^V=O reactive intermediate in this oxidation reaction, the reaction of MnTFPPCl with PhI(OAc)$_2$ (molar ratio = 1:225) in mixed [bmim]PF$_6$/CH$_2$Cl$_2$ was analyzed by stopped-flow spectrophotometry at 20°C (Fig. 3). An intermediate with the characteristic Soret maximum at ca. 428 nm could be observed 5 s after mixing by difference spectroscopy with clear isosbestic points at 447 and 384 nm. Then the Soret band of MnTFPPCl at 458 nm was fully restored. The band at 428 nm has been reported in the literature and was assigned to a Mn^V=O intermediate species.[18–20]

In conclusion, we have shown for the first time that an electron-deficient manganese(III) porphyrin complex was able to catalyze the oxidation of alkanes by PhI(OAc)$_2$ in an ionic liquid at room temperature. The use of an ionic liquid should provide a way for a simple recycling of the catalyst. By the stopped-flow spectrophotometry we observed a higher active and shorter life-time intermediate Mn^V=O during the reaction of **1** with PhI(OAc)$_2$ in mixed [bmim]PF$_6$/CH$_2$Cl$_2$. However, in CH$_2$Cl$_2$ the same reaction only produced a less active intermediate Mn^{IV}=O.
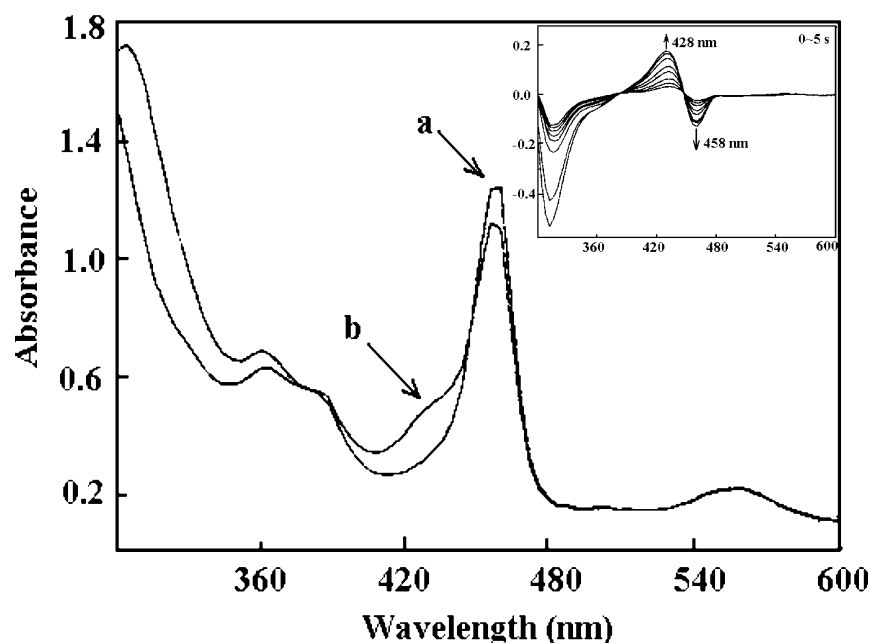
Figure 3. (a) Spectrum of manganese porphyrin **1** (24 μM) in [bmim]PF$_6$/CH$_2$Cl$_2$ (3/2, v/v). (b) Spectrum of manganese porphyrin **1** in 5 s upon addition of PhI(OAc)$_2$ (5400 μM) in [bmim]PF$_6$/CH$_2$Cl$_2$ (3/2, v/v). Inset: Difference spectra define for the first 5 s of the same reaction.

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