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OXONE AS OXYGEN DONOR IN THE CATALYTIC HYDROXYLATION OF SATURATED HYDROCARBONS

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Summary: Manganese porphyrin complexes catalyze the hydroxylation of saturated hydrocarbons by potassium hydrogen persulfate (or Oxone) at room temperature. High conversions of hydrocarbons are obtained.

Many studies have been devoted to the catalytic oxygenation of olefins or saturated hydrocarbons catalyzed by metalloporphyrins in order to (i) mimic cytochrome P-450 enzymes and (ii) to develop new homogeneous catalytic oxidation reactions (for a recent review, see references 1 and 2 for leading references). Recently, we have shown that $KHSO_5$ (or potassium hydrogen persulfate, trademark: Oxone) behaves as a good single oxygen donor in catalytic epoxidation reactions.[3] (For an X-ray structure of $KHSO_5$, see reference[4] and[5-7] for non-catalytic oxidations of organic molecules with this peroxo compound).

Here we report the catalytic hydroxylation of saturated hydrocarbons by $KHSO_5$ in the presence of manganese-porphyrin complexes.

All the data reported in Table 1 for cyclohexane and Table 2 for adamantane were obtained according to the same experimental procedure: saturated hydrocarbon (1 mmol), pyridine (0.155 mmol), manganese complex (6.25 µmol) and benzyldimethyltetradecylammonium chloride (12.5 µmol) are dissolved in 2.5 mL of dichloromethane. Onto this organic phase, 20 mL of a phosphate buffer solution (pH 8) of Oxone are added (0.65 g, ca. 1.8 mmol of $KHSO_5$). With 0.6% of catalyst vs. hydrocarbon, turnover rates in the range 50-130 cycles/ hour can be observed.

For both hydrocarbons, the best conversions are obtained with substituted-phenyl-porphyrinato ligands instead of TPP[8] itself. With Mn(TFPP)Cl,[8] up to 55% of cyclohexane are converted in one hour at room temperature, and cyclohexanol is the major oxidation product detected in the organic phase (Table 1).

Furthermore, the adamantane conversion is nearly complete within one hour with the $KHSO_5$/Mn(Por)Cl system (Por = porphyrin) (see Table 2). 30-50% of the corresponding alcohols are obtained with a high predominance of hydroxylation on tertiary C-H vs. secondary C-H bonds (C_3/C_2 ratio = 15-45, after statistical correction). Such high values for C_3/C_2 hydroxylation ratio

Table 1. Catalytic Oxidation of Cyclohexane Using the $KHSO_5$/Manganese-Porphyrin System.[a]

Catalyst[b]	Hydrocarbon conversion (%)	Alcohol (%)[c]	Ketone (%)[c]
-	1	-	-
Mn(TPP)OAc	3	-	-
Mn(TMP)Cl	35	3	2
Mn(oFPP)Cl	22	2	7
Mn(TFPP)Cl	55	13	6

[a] Hydrocarbon/$KHSO_5$/catalyst ratio = 160/290/1. Data expressed in Table correspond to a reaction time of one hour at room temperature.

[b] TPP = meso-tetraphenylporphyrinato dianion ; TMP = meso-tetramesitylporphyrinato ; oFPP = meso-tetrakis (ortho-monofluorophenyl)porphyrinato ; TFPP = meso-tetrakis(pentafluorophenyl)porphyrinato.

[c] Yields determinated by GLC analysis and expressed vs. the initial amount of hydrocarbon.

Table 2. Catalytic Oxidation of Adamantane Using the $KHSO_5$/Manganese-Porphyrin System.

Catalyst[a]	Hydrocarbon conversion (%)	Alcohol (%)[b]	Ketone (%)[b]
-	5	-	-
Mn(TPP)OAc	31	13(12; 1)[c]	1
Mn(TMP)Cl	48	29(24; 5)	4
Mn(oFPP)Cl	80	46(43; 3)	6
Mn(TFPP)Cl	94	36(32; 4)	5

[a] For abbreviations, see Table 1.

[b] Yields are expressed vs. the starting hydrocarbon.

[c] The two numbers indicated in parentheses correspond to 1-adamantanol and 2-adamantanol respectively

have been previously observed by Groves with PhIO/Iron-porphyrin.[9] These data strongly support the abstraction of H· from the hydrocarbon as the key step of the hydroxylation reaction.

As previously observed in the case of terminal olefin epoxidation by NaOCl/Mn(porphyrin)Cl,[10] the best results obtained with Mn(TMP)Cl, Mn(oFPP)Cl and Mn(TFPP)Cl evidence once again the predominant role of ortho-substituents on the phenyl rings of the porphyrin macrocycle

to prevent dimerization of the catalyst via μ-oxo bridge formation or oxidative destruction via intermolecular oxygen transfer from one metalloporphyrin to another one.

From these preliminary data on the catalytic hydroxylation with $KHSO_5$ several points must be noted:

(i) the lower pH value of the aqueous phase (pH 8) compared to that of NaOCl (pH 12-13), another water-soluble oxygen donor for hydroxylation[11] favors selective oxygenation reactions by diminishing side-reactions of oxidized products due to basic pH values. In similar experimental conditions, with NaOCl as oxygen source, lower yields of alcohol are obtained either from cyclohexane or adamantane;[11b]

(ii) the quasi-complete oxidation of adamantane (see Table 2) at room temperature and with a fair rate (∿ 100 cycles/hour) makes "$KHSO_5$/Mn(porphyrin)Cl" one of the most efficient homogeneous catalytic systems for the hydroxylation of saturated hydrocarbons;

(iii) a small amount of adamantanone is obtained during adamantane oxidation (alcohol/ ketone = 7.2 to 7.6 for catalyst with ortho-substituents on the phenyl ring of the macrocyclic ligand). Such a good selectivity for the formation of alcohols during the hydroxylation process is expected for a good model of cytochrome P-450 enzymes;

(iv) with a molar ratio dichloromethane/ adamantane/oxidant of 39/1/1.8, the fact that adamantane is nearly completely oxidized with Mn(TFPP)Cl also indicates that the hydroxylation is sufficiently selective to distinguish between two hydrocarbons: adamantane versus dichloromethane.

We are presently working on the development of this new hydroxylation method using a cheap and readily available oxidant and giving reasonable yields in alcohol compared to other similar catalytic systems.

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