# Oxidation of Cycloalkanes and Arylalkanes with Sodium Periodate Catalysed by Manganese Porphyrins†

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**Daryoush Mohajer,* Reza Tayebee and Hameed Goudarziafshar**

*Department of Chemistry, Shiraz University, Shiraz, 71454, Iran*

Cycloalkanes and arylalkanes are transformed into their related alcohols and ketones in moderate to high yields and selectivities at room temperature with sodium periodate in the presence of manganese(III) tetraarylporphyrin complexes associated with imidazole and tetra-*n*-butylammonium bromide in $CH_2Cl_2$–$H_2O$ solution.

Partial catalytic oxidation of unactivated saturated C–H bonds under mild conditions has been of great interest to chemists.[1] Effective mediation of oxygenation of hydrocarbons by cytochrome P-450 has led to diverse efforts to develop synthetic systems for mimicking the activity of this enzyme.[2] To achieve this goal catalytic systems involving manganese porphyrins in conjunction with various oxygen sources[2] have been extensively studied. Recently, it has been shown that $NaIO_4$ in the presence of Mn(TPP)Cl and imidazole can efficiently be employed for epoxidation of alkenes.[3] We now present the results of oxidation of cycloalkanes and arylalkanes with sodium periodate by different manganese tetraphenylporphyrin catalysts with or without substituents on the *meso*-aryl groups of tetraphenylporphyrin in the presence of imidazole, and a phase-transfer catalyst (tetra-*n*-butylammonium bromide) in a two-phase ($CH_2Cl_2$–$H_2O$) solvent system at room temperature.

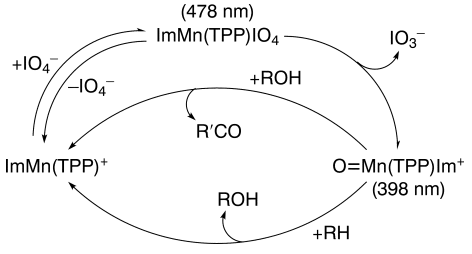
Catalytic systems consisting of various manganese porphyrins and $NaIO_4$ exhibit moderate to high activities for oxidation of cycloalkanes and arylalkanes (Table 1). Transformation of cycloalkanes to their corresponding alcohols and ketones proceeds with moderate to very high selectivities, whereas benzylic C–H bonds are virtually oxidised with an absolute selectivity [except for Mn(TMP)OAc catalyst] to a mixture of alcohols and ketones under our experimental conditions. Competitive oxidation of cyclohexane (0.5 mmol) and methylcyclohexanol (mixture of isomers) (0.01 mmol) by Mn(TNP)OAc catalyst, under the general conditions described in Table 1, showed a relatively low conversion (16%) of cyclohexane to the corresponding oxygenated products in 2 h, while methylcyclohexanol produced 90% methylcyclohexanone in the same period. This result and observation of an increase in ketone/alcohol ratio in the course of oxidation of cycloalkanes and arylalkanes suggests that ketone products are formed by sequential hydrocarbon hydroxylation and alcohol dehydrogenation, rather than by a direct pathway,[4] Scheme 1.

As far as the relative catalytic ability of various manganese porphyrins in the oxidation of different substrates is concerned, the simple Mn(TPP)OAc complex shows a higher efficacy for oxidation of tetralin and indane than for cycloalkanes. It leads to a conversion of 55% of tetralin to 1-tetralol and 1-tetralone and 47% of indane to indan-1-ol and indan-1-one, whereas much lower conversion of cyclohexane (5%) and cyclooctane (28%) to their corresponding alcohols and ketones is observed in the same period. It is noteworthy that although some degradation of Mn(TPP)OAc occurs during the oxidation of benzylic C–H bonds, as monitored by the gradual loss of its Soret band at $\lambda_{max} = 478$ nm, the catalyst is still active after 3.5 h. However, this contrasts with complete destruction and deactivation of the Mn(TPP)OAc catalyst when cycloalkanes are oxidised within the same time.

**Table 1** Oxidation of cycloalkanes and arylalkanes with various manganese(III) porphyrins and imidazole[a]

| (Substrate) Catalyst[b] | Conversion (%)[c] | Alcohol[d] yield (%)[c] | Ketone[d] yield (%)[c] | Combined selectivity[e] |
|---|---|---|---|---|
| (*Cyclohexane*) | | | | |
| A | 5 | 2 | 1 | 60 |
| B | 28 | 13 | 8 | 75 |
| C | 30 | 11 | 7 | 60 |
| D | 45 | 21 | 18 | 87 |
| (*Cyclooctane*) | | | | |
| A | 28 | 8 | 19 | 96 |
| B | 58 | 20 | 36 | 97 |
| C | 55 | 18 | 33 | 93 |
| D | 87 | 29 | 46 | 86 |
| (*Ethylbenzene*) | | | | |
| A | 13 | 5 | 8 | 100 |
| B | 26 | 9 | 17 | 100 |
| C | 26 | 12 | 12 | 92 |
| D | 80 | 16 | 64 | 100 |
| (*Indane*) | | | | |
| A | 47 | 16 | 31 | 100 |
| B | 53 | 19 | 34 | 100 |
| C | 38 | 15 | 23 | 100 |
| D | 87 | 26 | 60 | 99 |
| (*Tetralin*) | | | | |
| A | 55 | 19 | 35 | 98 |
| B | 63 | 12 | 50 | 98 |
| C | 33 | 10 | 23 | 100 |
| D | 85 | 14 | 70 | 99 |

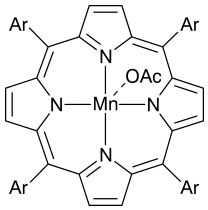
[a]Reactions are performed under air at 25 ± 3 °C. Molar ratio for substrate:oxidant:Mn-catalyst:imidazole is 83.3:166.6:1:10. [b]Catalysts: A, Mn(TPP)OAc; B, Mn(TNP)OAc; C, Mn(TMP)OAc; D, Mn(TDCPP)OAc. For Mn(TPP)OAc, Mn(TNP)OAc and Mn(TMP)OAc molar ratio for phase transfer catalyst (PTC) : Mn catalyst is 10:1 and reaction time is 3.5 h. For Mn(TDCPP)OAc catalyst PTC molar ratio is 40 and reaction time is 24 h. [c]GLC conversions and yields are based on the starting substrates. Reported values are within ±5%. [d]Alcohols: Cyclohexanol for cyclohexane, cyclooctanol for cyclooctane, 1-phenylethanol for ethylbenzene, indan-1-ol for indane, and 1-tetralol for tetralin. Ketones: Cyclohexanone for cyclohexane, cyclooctanone for cyclooctane, acetophenone for ethylbenzene, indan-1-one for indane, and tetral-1-one for tetralin. [e]Combined selectivity = [alcohol yield (%) + ketone yield (%)]/[conversion(%)] × 100.




**Scheme 1**

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.




| Mn-Porphyrin | Ar |
|---|---|
| Mn(TPP)OAc | Phenyl |
| Mn(TNP)OAc | 1-Naphthyl |
| Mn(TMP)OAc | 2,4,6-Trimethylphenyl |
| Mn(TDCPP)OAc | 2,6-Dichlorophenyl |

Results of oxygenation of the arylalkanes and cycloalkanes, and also consideration of the smaller number of benzylic C–H bonds relative to those of secondary C–H bonds, clearly demonstrate that the latter bonds are less susceptible to oxidation than the former ones. Low conversion competitive oxidation of cyclooctane and tetralin with an Mn(TPP)OAc:imidazole:cyclooctane:tetralin:oxidant ratio of 1:10:83.33:83.33:166.66 led to a conversion of 18% of tetralin and 4% of cyclooctane to their oxidised forms in 30 min. These results are consistent with the greater reactivity of the benzylic C–H bonds [$\sim(18/4)\times(16/4)=$ 18-fold] relative to those of cyclooctane, under our experimental conditions.

Mn(TNP)OAc is a better catalyst than Mn(TPP)OAc for oxygenation of all the substrates and particularly for cycloalkanes and ethylbenzene. The sterically hindered Mn(TMP)OAc complex acts very similarly to Mn(TNP)OAc in the oxidation of cycloalkanes and ethylbenzene, whereas in the oxygenation of indane and tetralin Mn(TMP)OAc shows a relatively poor activity. This may be related to the steric effects of the *ortho*-methyl substituents of the phenyl groups of the TMP ligand.

The high stability of the halogenated Mn(TDCPP)OAc, under the oxidising conditions, and also the relatively slower oxidation reactions that are induced by this complex, led us to increase both the reaction time (24 *vs.* 3.5 h) and concentration of the oxidation in the $CH_2Cl_2$ phase by enhancing the PTC/Mn–porphyrin molar ratio (40 *vs.* 10), for this catalyst. Under these conditions high conversion of cycloalkanes (45–87%), and arylalkanes (80–87%) to their oxidised forms is observed.

Treatment of the green $CH_2Cl_2$ solution of Mn(TPP)OAc with $NaIO_4$ under the catalytic reaction conditions in the absence of a substrate produced a new broad band at 398 nm at room temperature. Addition of tetralin to the solution caused a gradual loss of intensity of the Soret absorbance at 398 nm with a concomitant increase in absorbance at 478 nm. The band at 398 nm, although not very close to that expected for a classical high-valent oxo-manganese complex (Soret band at 420–425 nm)[5] is attributed to the presence of an active high-valent manganese oxidising species. The possible complexation of periodate and other anionic ligands, existing in the reaction mixture, to $Mn(TPP)^+$ is expected to give Soret bands at $>478$ nm.[6]

Maximum turnover numbers for various catalysts (assuming two oxidations for generation of cyclooctanone) with a molar ratio of 1:10:167:1250 for Mn-catalyst:imidazole:oxidant:cyclooctane are Mn(TPP)OAc (100 in 7 h), Mn(TNP)OAc (130 in 15 h), Mn(TMP)OAc (350 in 36 h) and Mn(TDCPP)OAc (475 in 72 h). It should be noted that while complete destruction of Mn(TPP)OAc and Mn(TNP)OAc occurred in the process, reactions with Mn(TMP)OAc and Mn(TDCPP)OAc were stopped with some catalyst still remaining. In the course of measuring the turnover numbers, the aqueous phase was renewed whenever the reaction stopped.

By correlating the intensity of the Soret bands of various Mn–porphyrins with their concentrations in the oxidation of cyclooctane, according to the conditions described in Table 1, consumption percentages of Mn(TPP)OAc of 81%, Mn(TNP)OAc of 56%, Mn(TMP)OAc of 24% and Mn(TDCPP)OAc of 17% were obtained at the end of the reactions.

## Experimental

In a standard reaction procedure, to a solution of Mn(porphyrin)OAc (0.006 mmol) in dichloromethane (2 ml) the phase-transfer catalyst (0.024 or 0.24 mmol) imidazole (0.06 mmol) and then substrate (0.5 mmol) were successively added. To the resulting solution mixture, a solution of $NaIO_4$ (1 mmol) in $H_2O$ (10 ml) was added and the two phases were stirred vigorously for the appropriate time at room temperature. Formation of products and consumption of substrates were monitored by GLC.

Products were characterised by comparison of their spectroscopic (IR, $^1H$ NMR) properties with those of authentic samples. The purity determination of the substrates and reactions monitoring were accomplished by GLC.

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