

## Oxidation of hydrocarbons with tetra-*n*-butylammonium peroxy monosulfate catalyzed by $\beta$ -tetrabromo-*meso*-tetrakis(4-methoxyphenyl)- and $\beta$ -tetrabromo-*meso*-tetraphenylporphyrinatomanganese(III)

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**Abstract:**  $\beta$ -Tetrabromo-*meso*-tetrakis(4-methoxyphenyl)porphyrin,  $H_2T(4-OCH_3P)PBr_4$ , was synthesized and characterized by UV-Vis and <sup>1</sup>H NMR spectroscopy. Oxidation of alkanes and olefins with tetra-*n*-butylammonium peroxy monosulfate ( $n-Bu_4NHSO_5$ ) was studied in the presence of  $MnT(4-OCH_3P)PBr_4(OAc)$  and  $MnTPPPBr_4(OAc)$  (TPP = *meso*-tetraphenylporphyrin). While significance differences were observed between the catalytic activities of the title complexes in the oxidation of alkanes, the 2 manganese porphyrins showed comparable activities in oxidation of most of the olefins used. However, the latter showed greater catalytic performance in the oxidation of the hydrocarbons. Moreover, the oxidative degradation of the former (60%) was greater than that of the latter (45%) in the oxidation of cyclooctene.

**Key words:**  $\beta$ -Tetrabromo-*meso*-tetrakis(4-methoxyphenyl)porphyrin,  $\beta$ -tetrabromo-*meso*-tetraphenylporphyrin, oxidation, catalyst, alkenes, alkanes, oxone, manganese porphyrins

### 1. Introduction

The catalytic activity of the metal complexes of porphyrins with different substituents at the meso and  $\beta$  positions has been extensively studied as model complexes of cytochrome p-450 enzymes.<sup>1–3</sup> In spite of the general agreement on the better catalytic performance of the metalloporphyrins with electronegative substituents on the periphery of the porphyrin macrocycle, the lack of close correlation between the catalytic activity of the manganese and iron porphyrins and the known electronic properties of the *meso* and  $\beta$  substituents has been evident from recent studies on the oxidation of organic compounds with weak, moderate, and strong terminal oxidants, catalyzed by the metalloporphyrins.<sup>4–16</sup> Herein the oxidation of olefins, alkanes, and sulfides with tetra-*n*-butylammonium peroxy monosulfate ( $n-Bu_4NHSO_5$ ) in the presence of  $\beta$ -tetrabromo-*meso*-tetrakis(4-methoxyphenyl)porphyrinatomanganese(III) acetate is studied and compared with that of the corresponding complex of  $\beta$ -tetrabromo-*meso*-tetrakis(4-methylphenyl)porphyrin.




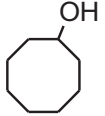
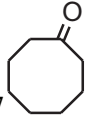
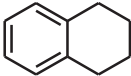
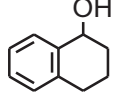
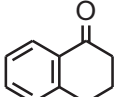
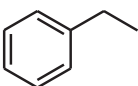
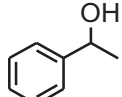
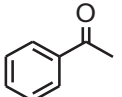
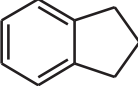
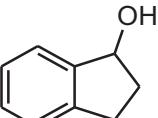
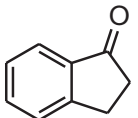

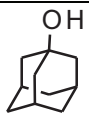
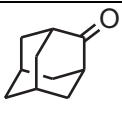
### 2. Results and discussion

Catalytic oxidation of alkanes and olefins with tetra-*n*-butylammonium peroxy monosulfate ( $n-Bu_4NHSO_5$ ) was studied in the presence of  $MnT(4-OCH_3P)PBr_4(OAc)$  and  $MnTPPPBr_4(OAc)$  (TPP = *meso*-tetraphenylpor-

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phyrin). Different solvents were examined for the oxidation reaction and ethanol was found to be the best one. The results of oxidation of alkanes with  $n\text{-Bu}_4\text{NHSO}_5$  in ethanol catalyzed by  $\text{MnTPPBr}_4(\text{OAc})$  and  $\text{MnT}(4\text{-OCH}_3\text{P})\text{PBr}_4(\text{OAc})$  are summarized in Table 1.

**Table 1.** Oxidation of different alkanes with  $n\text{-Bu}_4\text{NHSO}_5$  catalyzed by  $\text{MnTPPBr}_4(\text{OAc})$  and  $\text{MnT}(4\text{-OCH}_3\text{P})\text{PBr}_4(\text{OAc})$  (the data in parentheses) in ethanol. <sup>a,b</sup>

alkane	Conversion(%)	alcohol	ketone
	8.0 (-) <sup>c</sup>	 8 (-)	(-)
	37.0 (3.4)	 28.0 (2.7)	0.7 
	83.0 (39.2)	 37 (16.2)	46.0 (23.0) 
	2.0 (-) <sup>b</sup>	 1.5 (-)	0.5 (-) 
	73.0 (19.4)	 43(12.0)	30.0 (7.4) 
	63.0 (16.7)	 50 (14.0)	13.0 (2.7) 

<sup>a</sup>The molar ratios of catalyst: ImH:olefin: $n\text{-Bu}_4\text{NHSO}_5$  are 1:10:100:200. <sup>b</sup>All reactions were repeated 3 times and averaged. <sup>c</sup>No reaction.

According to the data in Table 1, the oxidation of alkanes gives the corresponding alcohol and ketones as the major and minor products, respectively.  $\text{MnTPPBr}_4(\text{OAc})$  is significantly more efficient than  $\text{MnT}(4\text{-OCH}_3\text{P})\text{PBr}_4(\text{OAc})$ .

OCH<sub>3</sub>P)PBr<sub>4</sub>(OAc). The result is in accord with the general agreement on the better catalytic activity of electron-deficient manganese porphyrins relative to electron-rich ones.<sup>17</sup>

Oxidation of olefins (Table 2), on the other hand, gives the corresponding epoxide as the major product. In spite of the better catalytic activity of MnTPPBr<sub>4</sub>(OAc) in comparison with that of MnT(4-OCH<sub>3</sub>P)PBr<sub>4</sub>(OAc), with the exception of 1-octene, there is no significant preference for the former over the latter. The extent of degradation of metalloporphyrins in the presence of cyclooctene was measured on the basis of the absorbance changes ( $\Delta A$ ) at the  $\lambda_{max}$  of the complexes ( $\Delta A/A$ ). The results show a degradation of 45% and 60% for MnTPPBr<sub>4</sub>(OAc) and MnT(4-OCH<sub>3</sub>P)PBr<sub>4</sub>(OAc), respectively. Moreover, the catalytic activity of MnT(4-OCH<sub>3</sub>P)PBr<sub>4</sub>(x) with different counter anions in the oxidation of cyclooctene was studied and the complex with acetate showed the highest catalytic activity (Table 3). However, little difference was found between the catalytic activity of MnT(4-OCH<sub>3</sub>P)PBr<sub>4</sub>(x) with OAc counter anion and that of the manganese porphyrin with Br, IO<sub>3</sub>, N<sub>3</sub>, and SCN one. The presence of counter anions with better leaving ability including OAc, Br, IO<sub>3</sub>, N<sub>3</sub>, and SCN led to higher catalytic activity of the manganese porphyrin. This behavior may be due to the necessity of cleavage of the Mn-counter anion bond in the catalytic cycle.<sup>7,18</sup>

Interestingly, while little difference has been found between the catalytic efficiency of the manganese porphyrins with phenyl- and 4-methoxyphenyl at the meso positions of nonbrominated *meso*-tetraphenylporphyrins,<sup>16</sup> large differences have been observed between the catalytic efficiency of the tetra-brominated counterparts.

### 3. Experimental

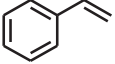
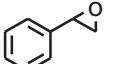
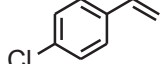
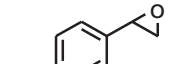
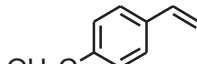
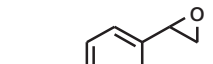
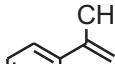
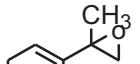




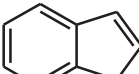
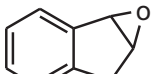




Synthesis and purification of H<sub>2</sub>T(4-OCH<sub>3</sub>)PP and H<sub>2</sub>TPP (Figure) were carried out according to the literature.<sup>17</sup> Freshly distilled pyrrole (56 mL, 0.8 mol) and benzaldehyde (or 4-methoxy benzaldehyde) were added to 3 L of refluxing reagent grade propionic acid. After refluxing for 30 min, the solution was cooled to room temperature and filtered, and the filter cake was washed thoroughly with methanol. After a hot water wash, the resulting purple crystals were air dried and finally dried in a vacuum to remove adsorbed acid. H<sub>2</sub>TPPBr<sub>4</sub> and H<sub>2</sub>T(4-OCH<sub>3</sub>)PBr<sub>4</sub> (Figure) were prepared according to the literature.<sup>19,20</sup> Free base porphyrin (0.49 mmol) was dissolved in CHCl<sub>3</sub> (80 mL). To this solution was added freshly recrystallized NBS (360 mg, 1.96 mmol) (recrystallized from hot water and dried at 80 °C under vacuum). The reaction mixture was stirred for 24 h and then CHCl<sub>3</sub> was evaporated to dryness. The residue was washed with methanol (2 × 20 mL) to remove any soluble succinimide impurities. The products, H<sub>2</sub>TPPBr<sub>4</sub> and H<sub>2</sub>T(4-OCH<sub>3</sub>)PBr<sub>4</sub>, were recrystallized from CHCl<sub>3</sub>/n-hexane (3:1, v/v) and dried under vacuum.

UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>) (H<sub>2</sub>T(4-OCH<sub>3</sub>)PBr<sub>4</sub>):  $\lambda_{max}$  (nm): 445, 544, 708 nm. <sup>1</sup>H NMR (250 MHz CDCl<sub>3</sub>, TMS) ( $\delta$  ppm): -2.72 (2H, s, NH); 4.09 (12H, s, -OCH<sub>3</sub>); 7.31–7.34 (8H, d, <sup>3</sup>J (HH)= 7.5 Hz, H<sub>m</sub>); 8.09–8.12 (8H, d, <sup>3</sup>J (HH)= 7.5 Hz, H<sub>o</sub>); 8.69 (4H, s, H <sub>$\beta$</sub> ). The absorption bands of MnTPPBr<sub>4</sub>(OAc) prepared using the method of Adler et al. appear at 492 ( $\lambda_{max}$ ), 604, and 656 nm. UV-Vis and <sup>1</sup>H NMR spectral data of H<sub>2</sub>TPPBr<sub>4</sub> and the manganese complex have been reported previously.<sup>19</sup> Moreover, the  $\lambda_{max}$  of MnT(4-CH<sub>3</sub>P)PBr<sub>4</sub>(X) with X = F, Cl, Br, N<sub>3</sub>, IO<sub>3</sub>, and SCN prepared by the method of Oghoshi et al.<sup>20</sup> was found at 486, 489, 502, 502, 499, and 499 nm, respectively.

In a general oxidation procedure, stock solutions of the catalyst (0.003 M) and nitrogenous bases (0.5 M) were prepared in CH<sub>2</sub>Cl<sub>2</sub>. In a 10-mL round-bottom flask the reagents were added in the following order: alkene (0.25 mmol), catalyst (0.003 mmol, 1.0 mL), and imidazole (0.03 mmol, 60  $\mu$ L). Tetrabutylammonium oxone

(0.5 mmol, 0.206 g) was then added to the reaction solutions at 25 °C. The mixture was stirred thoroughly for 2 min at ambient temperature. Formation of epoxide was detected by GC analysis. All reactions were repeated at least 3 times, analyzed by GC, and averaged.

**Table 2.** Oxidation of different olefins with  $n\text{-Bu}_4\text{NHSO}_5$  catalyzed by  $\text{MnT}(4\text{-OCH}_3\text{P})\text{PBr}_4(\text{OAc})$  and  $\text{MnTPPBr}_4(\text{OAc})$  (the data in parentheses) in ethanol.<sup>a</sup>

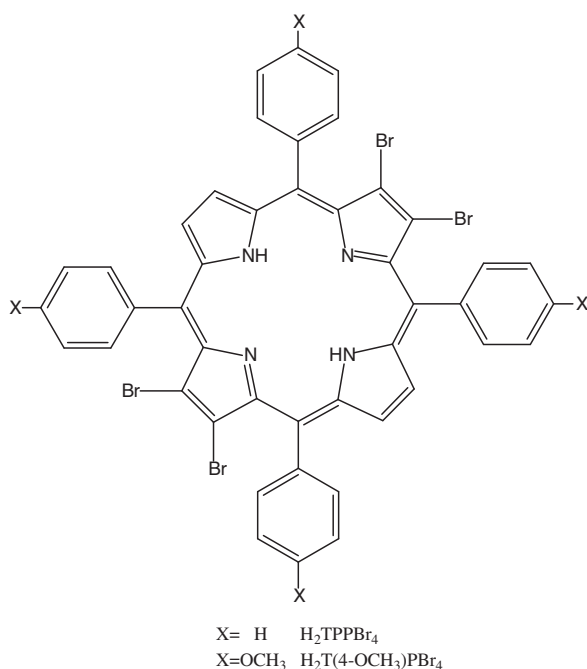
Olefins	Conversion(%)	Epoxide	Epoxide selectivity (%)
	70 (100)		100
	80 (100)		100
	86 (100)		100
	88 (100)		24 (75) <sup>b</sup>
	66 (95)		100
	47 (92)		100 (83) <sup>b</sup>
	84 (97)		100
	5 (51)		35
	30 (24) <sup>d</sup>		100

<sup>a</sup> See the footnotes of Table 1. <sup>b</sup> Acetophenone was the other product. <sup>c</sup> The products of allylic oxidation. <sup>d</sup> Exo or endo

**Table 3.** Effect of counteranion on the catalytic activity of  $\text{MnT}(4\text{-OCH}_3\text{P})\text{PBr}_4(\text{X})$  in oxidation of cyclooctene with  $n\text{-Bu}_4\text{NHSO}_5$  in ethanol at room temperature.<sup>a</sup>

X	OAc	F	Cl	Br	IO <sub>3</sub>	N <sub>3</sub>	SCN
Conversion (%) <sup>b</sup>	66.0	47.0	55.0	60.0	64.0	62.0	61.0

<sup>a,b</sup>See the footnotes of Table 1.



**Figure.** The porphyrins used in this study.

#### 4. Conclusions

In summary, the catalytic activity of  $\text{MnT}(4\text{-CH}_3\text{P})\text{PBr}_4(\text{X})$  ( $\text{X} = \text{OAc}, \text{F}, \text{Cl}, \text{Br}, \text{N}_3, \text{IO}_3, \text{and SCN}$ ) and  $\text{MnTPPPBr}_4(\text{OAc})$  in oxidation of alkanes and olefins with  $n\text{-Bu}_4\text{NHSO}_5$  in ethanol as the best solvent of the oxidation reaction was studied and compared. In spite of the better catalytic activity of the latter relative to the former, there was no large difference between the catalytic performances of the 2 catalysts in the oxidation of most of the olefins used. However, the catalytic activity of  $\text{MnTPPPBr}_4(\text{OAc})$  was significantly greater than that of  $\text{MnT}(4\text{-CH}_3\text{P})\text{PBr}_4(\text{OAc})$  in the oxidation of alkanes. Furthermore, the oxidative degradation of the former was smaller than that of the latter.

#### Acknowledgment

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