

## Oxidation of Hydrocarbons Catalyzed by Manganese Carboxylate Complexes

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**Summary:** High-valent manganese carboxylates catalyze the hydroxylation of alkanes and epoxidation of cyclooctene under mild conditions. Up to 21 turnovers of alkane oxidation in 3 hours are observed.

### Introduction

Alkane conversion is an area of great interest.<sup>1a-c</sup> High-valent metal-oxo species, such as [(por)M<sup>V</sup>=O]<sup>+</sup> (por = porphyrinato, M = Cr, Mn, Fe)<sup>2</sup> and non-porphyrin iron acetate complexes<sup>3a-c,4</sup> are known to be active. We studied [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CCPh<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>],<sup>5</sup> **1**, as a model for the O<sub>2</sub>-evolving center of Photosystem II. The recent report of Fish and Christou on alkane oxidation by related clusters<sup>6a,b</sup> prompts us to report our own results on alkane oxidation and alkene epoxidation.

The general procedure we employ involves reaction of oxidant plus substrate (1:1 or 1:10) in the presence of the manganese carboxylate complex (1 or 0.1 mol %) at room temperature for a given time interval. After quenching of excess oxidant with an aqueous iron(II) solution, the organic products were separated and analyzed by gas chromatography. The results are summarized in Table 1.

### Oxidation of Alkanes

Using the triphenylacetate complex **1** in a mixture of cyclooctane and CH<sub>2</sub>Cl<sub>2</sub> (3 mL each) we obtained a total of 4.7 turnovers using TBHP (tert-butylhydroperoxide, entry 1) and 2.3 t.o. using PhIO (iodosylbenzene, entry 2). The greater reactivity of TBHP may be due, in part, to the homogeneity of the reaction conditions: TBHP is employed as a solution in benzene, while PhIO, a polymeric material, is used as a suspension. With both oxidants, the majority of oxidation product formed is cyclooctanone, with minor amounts of cyclooctanol and, in both cases, traces of the alkene epoxidation product cyclooctene oxide. The latter was unexpected; we believe that it may arise from epoxidation (see below) of cyclooctene formed in a radical disproportionation process. However, we were unable to detect bicyclooctyl, the expected radical recombination product.

Oxidation of cyclooctane with TBHP, catalyzed by the trimethylacetate complex [Mn<sup>III</sup><sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(OH)<sub>2</sub>], **2**,<sup>7</sup> in neat alkane gave much higher turnover numbers: after 7 hours at room temperature in neat alkane, we obtained a total of 24.7 turnovers, with a 3.6:1 selectivity for ketone (entry 3). A longer reaction time improved the yield somewhat; after 14 days under otherwise identical conditions, a total of

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30.1 turnovers, with a 2.8:1 selectivity for ketone, were observed (entry 4).

The catalyst is largely deactivated after 3 hours, as shown by entries 5 and 6. In the latter case, the addition of further TBHP after 3 hours led to a small increase in turnovers. Indeed, in all cases, the initially homogeneous brown solutions grew cloudy within a few hours; in the reactions with the triphenylacetate complex **1**, triphenylacetic acid, identified by IR, can be isolated as a by-product. As yet unidentified organic compounds generally were present; 12-30% of starting material could not be accounted for, some of this must be due to loss in workup. Iodosylbenzene gave only a small amount of ketone (entry 7). Blank runs (entry 8, no catalyst; entry 9, 4 mol %  $\text{Mn}(\text{O}_3\text{SCF}_3)_2$  per mol oxidant) with TBHP produced only traces of ketone.

The trimethylacetate complex **2** is also an effective catalyst for the hydroxylation of adamantane in dichloromethane (entry 10), benzene (entry 11), or MeCN (entry 13) by TBHP. The total turnover numbers of 4.9 in  $\text{C}_6\text{H}_6$ , 4.1 in  $\text{CH}_2\text{Cl}_2$  and 9.1 in MeCN are considerably lower than those observed in the oxidation of neat cyclooctane. The reaction shows a strong preference for hydroxylation of tertiary C-H bonds, giving a  $3^\circ/2^\circ$  ratios of 9-14, indicating a high degree of radical character. As noted for the cyclooctane reactions, iodosylbenzene is much less active; under identical conditions, only 1.6 turnovers of ketone were observed (entry 12). For entries 10-14, the reactions were clean, giving only the oxidation products noted. The catalyst began to decompose to insoluble materials within one hour in dichloromethane, while, despite the similar yield, only a faint cloudiness was observed in benzene. The control reaction (entry 14) with no catalyst gave no oxidation products.

### Oxidation of Cyclooctene

Oxidation of cyclooctene with PhIO catalyzed by **1** in  $\text{CH}_2\text{Cl}_2$  at 25 °C gave 4-11 t.o. of the epoxide. Increasing the reaction time from three to 24 hours (entries 15 and 16) increased the yield of epoxide substantially, but also increased the amount of byproducts, including the ketone. Under reflux (entry 17), turnovers increased at the expense of selectivity. The hydroperoxide proved to be a much less satisfactory oxidant; reaction in  $\text{CH}_2\text{Cl}_2$  gave only 1 t.o. (entry 18), while in benzene (entry 19) more epoxide was formed but also substantial amounts of alcohol and ketone. With iodosylbenzene as the source of oxygen atoms, a clean 3.1 turnovers of epoxide were obtained (24 h, entry 20), less than observed with **1** (entry 16). TBHP gave the epoxide in a yield and selectivity (entry 22) similar to that observed with **1**. Only traces of epoxide were obtained with PhIO in the absence of catalyst (entry 22), or with manganese triflate (4 mol % per mol TBHP, entry 24), although reaction of iodosylbenzene with manganese triflate produced substantial amounts of alcohol and epoxide (entry 23). In general, PhIO gave fewer unidentified organic byproducts than did TBHP; GC analysis showed the by-products to be substantially different for PhIO and TBHP oxidations. In the case of entry 20, GC/MS showed no evidence for the presence of Cl in any of the by-products. Fragmentation patterns of some of the by-products were consistent with their being unsaturated alcohols and ketones. Interestingly, **1** gave fewer by-products than **2**.

### Conclusion

Not only can alkanes be efficiently oxidized, but cyclooctene undergoes selective and clean epoxidation. The usefulness of complexes **1** and **2** seems to be limited by deactivation under the reaction conditions. While our study was in progress, Fish et al. reported alkane oxidation with TBHP in acetonitrile using similar tri- and

tetranuclear manganese complexes.<sup>6a</sup> They observe up to 127 turnovers<sup>8</sup> of cyclohexane oxidation, with little selectivity for alcohol or ketone. Although this system system epoxidizes cyclohexene, considerable amounts of allylic oxidation byproducts are formed.<sup>6b</sup> A radical route seems likely for both systems. Fish et al. propose a mechanism<sup>6a</sup> similar to that suggested for cytochrome P450.<sup>2</sup>

**Table 1:** Catalytic Oxidations with Manganese Carboxylates **1** and **2**

Entry	Cata.	Substrate	Oxidant	Time <sup>a</sup>	Ketone	2° Alcohol	3° Alcohol	Products <sup>b</sup>	
								Epoxide	% Recov. <sup>c</sup>
1	<b>1</b>	cyclooctane	TBHP	9 h	2.8	1.6	-	0.3	78
2	<b>1</b>	"	PhIO	11 h	1.8	0.3	-	0.2	86
3	<b>2</b>	"	TBHP	7 h <sup>d</sup>	19.3	5.4	-	-	89
4	<b>2</b>	"	TBHP	14 d <sup>d</sup>	22.2	7.9	-	0.1	70
5	<b>2</b>	"	TBHP	3 h <sup>d</sup>	20.7	-	-	-	88
6	<b>2</b>	"	TBHP	6 h <sup>d,e</sup>	22.3	5.0	-	0.3	87
7	<b>2</b>	"	PhIO	24 h <sup>d</sup>	1.8	-	-	-	90
8	none	"	TBHP	24 h <sup>f</sup>	0.5%	-	-	-	84
9	Mn(OTf) <sub>2</sub>	"	TBHP	24 h <sup>f</sup>	0.4%	-	-	-	54
10	<b>2</b>	adamantane	TBHP	6 h	0.5	0.3	3.3	-	97
11	<b>2</b>	"	TBHP	6 h <sup>g</sup>	0.8	0.4	3.7	-	82
12	<b>2</b>	"	PhIO	6 h	-	-	1.6	-	84
13	<b>2</b>	"	TBHP	26 h <sup>h</sup>	1.5	0.5	7.1	-	78
14	none	"	TBHP	6 h	-	-	-	-	80
15	<b>1</b>	cyclooctene	PhIO	3 h	-	-	-	4.0	61
16	<b>1</b>	"	PhIO	24 h	0.7	-	-	11.0	56
17	<b>1</b>	"	PhIO	3 h <sup>j</sup>	0.6	-	-	6.4	56
18	<b>1</b>	"	TBHP	6 h	-	-	-	1.0	57
19	<b>1</b>	"	TBHP	24 h <sup>g</sup>	0.2	0.6	-	2.3	52
20	<b>2</b>	"	PhIO	24 h	-	-	-	3.1	70
21	<b>2</b>	"	TBHP	3 h	0.2	-	-	1.7	69
22	none	"	PhIO	10 h <sup>f</sup>	-	-	-	0.4%	79
23	Mn(OTf) <sub>2</sub>	"	PhIO	24 h <sup>f</sup>	0.4%	4.0%	-	1.2%	67
24	Mn(OTf) <sub>2</sub>	"	TBHP	7 h <sup>f</sup>	-	-	-	0.1%	64

<sup>a</sup>Reaction times denoted in hours (h) or days (d). <sup>b</sup>Product yields given in turnovers (1 turnover = 1 mol product/mol catalyst), except for blanks, in which case, in percent. <sup>c</sup>Total mols. of identifiable products and starting material recovered per mols. substrate employed. <sup>d</sup>Reaction performed in neat substrate. <sup>e</sup>A second 100 equiv. oxidant added after first 3 h; see text. <sup>f</sup>For blank reaction the percentage shown is based on the mols. of product observed per mol of oxidant. <sup>g</sup>in benzene. <sup>h</sup>in acetonitrile <sup>j</sup>Reaction performed at reflux.

## Experimental Procedure

**Synthesis of **2**:** To a suspension of manganese(II) trifluoromethanesulfonate (1.00 g, 2.83 mmol) and potassium trimethylacetate (1.00 g, 7.13 mmol) in a Schlenk flask under N<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added a solution of [Bu<sub>4</sub>N]MnO<sub>4</sub> (0.68 g, 1.89 mmol)<sup>11</sup> in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) dropwise over 30 min. The resulting brown suspension was stirred at room temperature for 4 h, evaporated, and extracted with pentane (2x30 mL). The dark-brown extracts were filtered through a column of Celite and evaporated. The resulting brown residue was dried in vacuo at 50 °C and used without further purification. Yield 0.77 g (73%). Analytical, spectroscopic and redox titration data<sup>7</sup> are consistent with a tetramer of the formula [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(OH)<sub>2</sub>], similar to **1**.<sup>7</sup>

Catalytic Oxidation of Adamantane: TBHP Oxidation: The manganese carboxylate complex **2** (40 mg, 44.9  $\mu\text{mol}$ ) and adamantane (612 mg, 4.49 mmol) were dissolved in the solvent (25 mL) in a Schlenk tube under  $\text{N}_2$ . TBHP in benzene (3.3 mL, 4.56 mmol) was added, and the resulting solution was stirred at room temperature for 6 hours. The reaction was quenched with a 0.36 M  $\text{FeSO}_4$ -tartaric acid solution, the organics separated and analyzed by GC. PhIO Oxidation: The manganese carboxylate complex **2** (20 mg, 22.5  $\mu\text{mol}$ ) and adamantane (306 mg, 2.25 mmol) were dissolved in 20 mL  $\text{CH}_2\text{Cl}_2$  in a 50 mL round-bottom flask. Solid iodosylbenzene (493 mg, 2.25 mmol) was added, and the resulting suspension was stirred open to air at room temperature for 6 hours. The mixture was worked up and analyzed as described above.

## References

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- (8) In this report, turnover numbers are based on TBHP consumed, counting each mole of ketone twice.

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