

## Manganese(II) based Oxidation of Alkanes: Generation of a High Valent Binuclear Catalyst *in situ*

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The efficiently Mn<sup>2+</sup>-catalysed oxidation of saturated hydrocarbons by alkylhydroperoxides or iodosylbenzene in the presence of 2,2'-bipyridine in acetonitrile follows the following pathway: Mn<sup>2+</sup> + bipy → [Mn(bipy)<sub>3</sub>]<sup>2+</sup> → [Mn<sub>2</sub>O<sub>2</sub>(bipy)<sub>4</sub>]<sup>3+</sup>, the latter being identified as the catalytic species; it affords cyclohexanol and cyclohexanone in equal amounts and the remarkable robustness of the active complex, under oxidative conditions, is noted.

Homogeneous catalytic C–H activation of alkanes still represents an important challenge.<sup>1</sup> A biomimetic approach, based on models of cytochrome P450-dependent monooxygenases, has been very successful.<sup>2</sup> Recently, modeling of such biological metal sites has, however, been achieved by a tremendous sophistication.<sup>3</sup> Cost may handicap its use in industrial processes and the search for cheaper, less sophisticated active complexes is still under investigation. Non-haem complexes then may supply such requirements.<sup>4</sup> While efficient non-haem polynuclear iron catalysts have recently emerged,<sup>5</sup> very few containing manganese have been described.<sup>6</sup> We have previously shown that manganese-containing catalysts were much more stable than the iron analogues during oxidation of alkanes by alkylhydroperoxides.<sup>7</sup> Here we report an original oxidizing system consisting of a manganous salt, a simple bidentate nitrogen ligand and an alkylhydroperoxide. The catalytic species, a high valent dinuclear manganese complex, is generated *in situ* and is very robust during multiple turnovers.

The manganous salt, Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, in the presence of *tert*-butyl hydroperoxide (TBHP) as an oxidant, is not able to catalyse the oxidation of cyclohexane in acetonitrile at room temp. under an argon atmosphere. Mixing 0.7 mmol dm<sup>-3</sup> of this salt with increased amounts of 2,2'-bipyridine (bipy) in the presence of 140 equiv. TBHP and 1100 equiv. of cyclohexane afforded cyclohexanol and cyclohexanone in equal amounts and *tert*-butylcyclohexyl hydroperoxide as a minor product as analysed by GC (Table 1). The yield based on the reaction depends on the bipy/Mn ratio (*R*) with a maximum of *R* ≥ 2. Above this value, the oxidation yield, based on the oxidant, remains at ca. 35% after 90 min; at this time all the TBHP was consumed. The selectivity in alcohol + ketone is about 90%.

**Table 1** Oxidation of cyclohexane by alkyl peroxide or iodosylbenzene catalysed by Mn complexes.

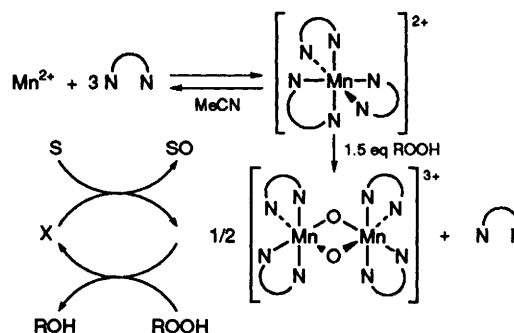
Catalyst <sup>a</sup>	[cat]/mM	Oxidant	CyOH <sup>b</sup>	CyONE <sup>b</sup>	Yield <sup>c</sup> (%)
Mn <sup>2+</sup> /bipy	0.7	TBHP	7	9	18
Mn <sup>2+</sup> /2 bipy	0.7	TBHP	15	15	35
Mn <sup>2+</sup> /3 bipy	0.7	TBHP	16	15	36
1	0.7	TBHP	14	16	37
2	0.35	TBHP	33	40	43
3	0.7	TBHP	1	1	2
4	0.35	TBHP	33	40	40
1	0.7	PhIO	1.8	1.5	25
4	0.35	CHP	18	20	21

<sup>a</sup> 1 = [Mn(bipy)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>; 2 = [Mn<sub>2</sub>O<sub>2</sub>(bipy)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>; 3 = [Mn(phen)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>; 4 = [Mn<sub>2</sub>O<sub>2</sub>(phen)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>. <sup>b</sup> Turnover number in mmole of cyclohexanol or cyclohexanone per mmole of catalyst. In a typical experiment, to 3.5 μmol of mononuclear catalysts or 1.75 μmoles of dinuclear catalysts in 4.5 ml acetonitrile was added 1100 equiv. of cyclohexane followed by 140 equiv. of the oxidant. Time of reaction = 90 min. <sup>c</sup> Total yield (alcohol + ketone + dialkylperoxide) based on the oxidant taking in account the fact that 2 equiv. of oxidant are required to make 1 equiv. of ketone. <sup>d</sup> 20 equiv. of iodosylbenzene for 90 min time reaction.

Before any addition of TBHP, the bipy/Mn mixture solution turned gradually pale yellow as *R* increased. Its UV–VIS spectrum exhibited a shoulder near 350 nm, similar to the one of [Mn(bipy)<sub>3</sub>]<sup>2+</sup> 1, suggesting that 1 was formed in MeCN. This prompted us to investigate the oxidizing properties of complex 1,<sup>8</sup> under standard conditions. We then found the same oxidation yields as those obtained with the bipy/Mn mixture (with *R* ≥ 2).

Upon addition of 140 equiv. of TBHP, the bipy/Mn mixture immediately turned green, which persisted, owing to the presence of the well-known bis (μ-oxo) mixed valence complex, [Mn<sub>2</sub>O<sub>2</sub>(bipy)<sub>4</sub>]<sup>3+</sup> 2, formed in quantitative yield, as clearly shown by EPR, UV–VIS spectroscopies and cyclic voltammetry experiments.<sup>9</sup> Formation of complex 2 was not dependent on the presence and the nature of the substrate. TBHP titration by electronic spectroscopy attests that 1.5 equiv. are required to generate complex 2 quantitatively from bipy/Mn (*R* = 2) mixture or complex 1 in 45 min. Similar results were obtained when cumene hydroperoxide (CHP) or iodosylbenzene, a single oxygen atom donor, was substituted for TBHP. It has been previously demonstrated that oxidation of complex 1 into 2 in MeCN can be also accomplished by an electrochemical route.<sup>8</sup>

Again, independently prepared<sup>10</sup> complex 2 had the same catalytic activity as the bipy/Mn system during cyclohexane oxidation. No changes in the UV–VIS, <sup>1</sup>H NMR and the EPR spectra have been noticed during the reaction. We then propose that the real catalyst is complex 2, in agreement with the fact that the maximum oxidation yield was obtained with *R* = 2. This is also supported by the comparison of the catalytic activities of complexes 3 and 4, [Mn(phen)<sub>3</sub>]<sup>2+</sup> and [Mn<sub>2</sub>O<sub>2</sub>(phen)<sub>4</sub>]<sup>3+</sup>, respectively.<sup>8,10</sup> While only traces of oxidation products were detected with 3, complex 4 afforded similar yields to 2 (Table 1). This is consistent with the observation that complex 3 was slowly transformed into complex 4 under standard reaction conditions, reaching only 35% yield after 90 min, and shows that the catalytic activity of the system is driven by its ability to form the mixed valence species.† 1,10-Phenanthroline ligand is more rigid than 2,2'-bipyridine and seems slower to exchange during the conversion of 3 into 4.



**Fig. 1** TBHP-dependent activation of the bipy/Mn catalyst. X represents the unidentified active oxidizing species

This bipy/Mn system also oxidized adamantane to adamantan-1-ol as a major product with traces of secondary alcohol and ketone, thus leading to a high  $C_3/C_2$  value (yield up to 20% with a substrate: catalyst ratio of 400). Alcohols were also oxidized with very good yields; over 55% in the case of benzylalcohol with the production of benzaldehyde. Oxidation by TBHP on n-heptane was also performed, with complex **1** or **2** as a catalyst. The reaction yielded heptan-2-, -3-, -4-ols and the corresponding ketones with a good overall yield of 33% based on the oxidant. Heptan-1-ol and heptanal could not be detected. As shown from the products ratios (2-ol: 8%, 3-ol: 6%, 4-ol: 1%, 2-one: 41%, 3-one: 28%, 4-one: 16%), the system **1** or **2**/TBHP was not regioselective and interestingly, afforded ketones in large proportions.

The catalytic activity of **2** was remarkably conserved during oxidation of cyclohexane. Repeated addition of TBHP led to similar oxidation yields. However, the alcohol/ketone ratio decreased owing to the oxidation of alcohol formed during the preceding runs. This stability may be correlated to the ability of the catalyst to be continuously regenerated by alkylhydroperoxides.†

Fig. 1 summarizes a plausible pathway for the formation of the active catalyst. The mixed valence species may be formed by two routes: (i) by condensation of two  $Mn^{IV}$  species issued from a two-electron oxidation of the manganous species by the alkylperoxide. No such species has been identified in our reaction solution whatever the conditions were but an authentic sample of the  $\mu$ -oxo dimanganese(IV),  $[Mn_2O_2(bipy)_4]^{4+}$ , prepared electrochemically, was instantaneously reduced to the mixed valence species **2** in the presence of TBHP; (ii) by a one-electron oxidation of the manganous complex followed by a disproportionation of the resultant manganic species as suggested by Sawyer *et al.* for the electrochemical conversion of **1** to **2**.<sup>8</sup>

Complexes **1** and **2** catalysed the dismutation of TBHP in the absence of substrate as checked by dioxygen formation. Addition of substrate greatly inhibited the reaction. The fact that oxidation of adamantane by complex **2** gave the same yields whether the reaction mixture was vigorously bubbled with argon or pure oxygen strongly suggested that TBHP-derived  $O_2$  was not involved in the oxidations. Moreover, the alcohol/ketone ratio was the same under both conditions. The involvement of peroxy radicals can be ruled out on the basis that iodobenzene could replace alkylhydroperoxides and gave comparable cyclohexanol/cyclohexanone ratio and  $C_3/C_2$  ratio. On the other hand, the catalyst efficiency depended also on the nature of the alkylperoxide (Table 1). We then suggest that the mechanism might involve the formation of a Mn-OOR intermediate followed by a O-O cleavage to provide high valent oxo-manganese species, responsible for the oxidations. We are currently trying to identify the putative intermediates. The fact that an authentic sample of the di-

$\mu$ -oxo dimanganese(IV),  $[Mn_2O_2(bipy)_4]^{4+}$ , in the absence of oxidant, was not able to oxidize cyclohexane indicates that such a species can be ruled out as one of these intermediates.

This new approach is very promising since it combines both simplicity and stability of the catalyst system, as well as mild conditions. Simple modifications of the ligand may afford better catalyst efficiency. We are currently using substituted bidentate nitrogen ligands as well as different manganese salts in order to modulate alkane oxidation activities. Also, this work shows that alkylhydroperoxides, instead of  $KMnO_4$  or  $H_2O_2$ , provide a promising new route to the synthesis of high valent polynuclear manganese clusters.

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### Footnotes

† Complex **3** can give similar oxidation yields to complex **4** but after a few hours.

‡ We have observed that inactivation of our iron containing catalysts is due to the formation of inert ferrous complexes.<sup>5c</sup> Such a reaction is avoided in the present case.

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