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Title: Oxidation of alkanes by periodate using a Mn(V) nitrido complex as catalyst

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To be cited as: Chem. Asian J. 10.1002/asia.201601027

Link to VoR: <http://dx.doi.org/10.1002/asia.201601027>

A Journal of



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Oxidation of alkanes by periodate using a Mn(V) nitrido complex as catalyst

Li Ma,^[a,b] Lingjing Chen^[b] and Tai-Chu Lau^{*[b]}

Abstract: The design of catalytic systems that can selectively oxidize unactivated C-H bonds under mild conditions is a challenge to chemists. We report here that the manganese(V) nitrido complex, $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$, is a highly efficient catalyst for the oxidation of alkanes by periodate (IO_4^-) at ambient conditions. Excellent yields of alcohols and ketones (>95%) are obtained with a maximum turnover number (TON) of 3000.

The design of catalysts that can efficiently oxidize unactivated C-H bonds under ambient conditions is an important research area.^[1] Although a variety of manganese oxidation catalysts in +2 or +3 oxidation states have been reported, they are generally rather inefficient for the oxidation of alkanes.^[2-8] On the other hand, we recently found that a high-valent manganese complex, $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$, prepared by Wiegardt,^[9] is a highly efficient catalyst for the oxidation of alkanes,^[10] alcohol^[11] and alkenes^[11] at ambient conditions using H_2O_2 as the terminal oxidant. This Mn^VN complex can also catalyze the oxidation of alkanes and water using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ as the oxidant.^[10,12] The active intermediate in these catalytic oxidations is proposed to be $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$.

We report herein the use of $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ as catalyst for the oxidation of alkanes by periodate (IO_4^-). Compared with H_2O_2 or Ce(IV), IO_4^- is a more stable and mild oxidant that can operate under acidic, neutral or basic conditions. Although there are a number of reports on metal-catalysed oxidation of organic substrates with IO_4^- ,^[13] the yields for the oxidation of unactivated C-H bonds are generally <50%. On the other hand, excellent product yields (>95%) are found for the oxidation of alkanes using $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}/\text{IO}_4^-$. Moreover, the maximum turnover number (TON) of 3000 is much higher than that of using H_2O_2 or Ce(IV) as oxidant. The yields were calculated based on IO_4^- reacting as a two-electron oxidant: % yield of alcohol = (mol of alcohol/mol of ${}^n\text{Bu}_4\text{N}[\text{IO}_4] \times 100\%$, % yield of ketone = (mol of ketone/mol of ${}^n\text{Bu}_4\text{N}[\text{IO}_4] \times 2 \times 100\%$, TON = (mol of alcohol + mol of ketone x 2)/mol of catalyst.

The oxidation of alkanes by $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}/\text{IO}_4^-$ was studied using excess alkane in $\text{CF}_3\text{CH}_2\text{OH}$ in the presence of 0.25 M $\text{CH}_3\text{CO}_2\text{H}$ (Table 1). Oxidation occurs readily at ambient conditions within 1–2 h to give the corresponding alcohols and ketones, and the total yields are >95%. When oxidation of cyclohexane was carried out in air, the yield was slightly higher (100%) than under argon (99%) (entry 1 – 2). O_2 is known to

rapidly react with alkyl radicals to give alcohol products.^[14] Addition of BrCCl_3 , an efficient scavenger for carbon-centred radicals, also resulted in only a slight lowering of the yields of alcohol and ketone (by 3%), while 2% of cyclohexyl bromide was produced (entry 3). These results indicate that there are relatively few *freely diffusing* alkyl radicals in these catalytic oxidations. By using more substrate and oxidant ($[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$, 0.025 mM; cyclohexane, 5.0 M; ${}^n\text{Bu}_4\text{N}[\text{IO}_4]$, 0.5 M), a TON of 3000 could be achieved, which is much higher than the TON of 960 using H_2O_2 as oxidant.^[11] Oxidation of linear alkanes occurs exclusively at the secondary C–H bonds (entry 6 – 7). In the oxidation of *trans*- and *cis*-1,2-dimethylcyclohexane, there were <1% of epimerized products (entry 9 – 10), indicating that the oxidation is highly stereospecific.

Table 1. Oxidation of various alkanes by $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]/{}^n\text{Bu}_4\text{N}[\text{IO}_4]$ ^[a]

Entry	Substrate	Products (% yield)	Total yield (%)
1	cyclohexane	cyclohexanol (68), cyclohexanone (31)	99
2 ^[b]	cyclohexane	cyclohexanol (69), cyclohexanone (31)	100
3 ^[c]	cyclohexane	cyclohexanol (66), cyclohexanone (30), cyclohexyl bromide (2)	98
4	cycloheptane	cycloheptanol (65), cycloheptanone (34)	99
5	cyclooctane	cyclooctanol (66), cyclooctanone (34)	100
6	n-heptane	2-heptanol (27), 3-heptanol (26), 4-heptanol (14), 2-heptanone (25), 3-heptanone (5), 4-heptanone (2)	99
7	n-octane	2-octanol (20), 3-octanol (18), 4-octanol (18), 2-octanone (16), 3-octanone (14), 4-octanone (14)	100
8	2,3-dimethylbutane	2,3-dimethyl-2-butanol (95)	95
9	<i>trans</i> -1,2-dimethylcyclohexane	<i>trans</i> -1,2-dimethylcyclohexanol (36), <i>cis</i> -1,2-dimethylcyclohexanol (1), 2,3-dimethylcyclohexanol (17), 3,4-dimethylcyclohexanol (19), 2,3- and 3,4-dimethylcyclohexanone (25)	98
10	<i>cis</i> -1,2-dimethylcyclohexane	<i>cis</i> -1,2-dimethylcyclohexanol (84), 2,3-dimethylcyclohexanol (4), 3,4-dimethylcyclohexanol (8), 2,3- and 3,4-dimethylcyclohexanone (3)	99

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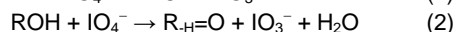
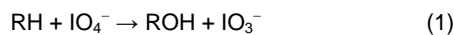
[a] Reaction conditions: $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$, 2.5 mM; substrate, 1.2 M; ${}^n\text{Bu}_4\text{N}[\text{IO}_4]$, 0.25 M; HOAc, 0.25 M; solvent, $\text{CF}_3\text{CH}_2\text{OH}$. All reactions were carried out at 23 °C under argon. Time = 2 h.

[b] The reaction was carried out in air.

[c] The reaction was carried out in the presence of 0.25 M CCl_3Br .

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Analysis of the iodine-containing product by ion chromatography showed that 97% of IO_3^- were formed from cyclohexane oxidation (Table S1), indicating that IO_4^- functions as a two-electron oxidant. Hence the Mn(V) catalysed oxidation of alkanes by IO_4^- can be represented by equations (1) and (2). Alcohols are first formed, which may be further oxidized to the corresponding ketones.



In cyclohexane oxidation, a kinetic isotope effect (KIE) of 4.7 ± 0.3 was determined by a competition method using an equimolar mixture of cyclohexane ($\text{c-C}_6\text{H}_{12}$) and d_{12} -cyclohexane ($\text{c-C}_6\text{D}_{12}$) as substrate. Deuterium isotope effects were also investigated using either $\text{c-C}_6\text{H}_{12}$ or $\text{c-C}_6\text{D}_{12}$ as single substrate. Pseudo-first-order kinetics were observed and the rate constants (k_{obs}) for the catalytic oxidation of $\text{c-C}_6\text{H}_{12}$ and $\text{c-C}_6\text{D}_{12}$ are $(2.08 \pm 0.12) \times 10^{-2}$ and $(2.02 \pm 0.14) \times 10^{-2} \text{ min}^{-1}$, respectively at 23 °C (Figure 1). The fact that these rate constants are the same but a KIE of 4.7 was observed from competition experiments suggests that the formation of the active oxidant between $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ and IO_4^- is the rate-determining step, which does not involve the alkane.

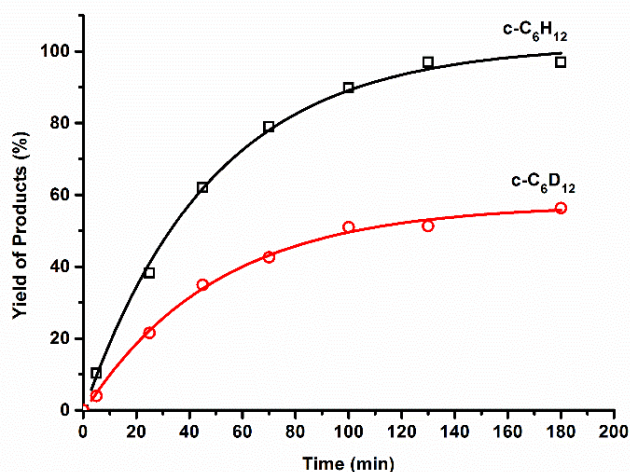


Figure 1. Pseudo-first-order fit of % yield vs time for $\text{c-C}_6\text{H}_{12}$ (1.2 M) and $\text{c-C}_6\text{D}_{12}$ (1.2 M) oxidation by $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ (2.5 mM) and ${}^n\text{Bu}_4\text{N}[\text{IO}_4]$ (0.25 M) in $\text{CF}_3\text{CH}_2\text{OH}$ in the presence of $\text{CH}_3\text{CO}_2\text{H}$ (0.25 M) at 23 °C.

Electrospray ionization mass spectrometry (ESI/MS) was employed to detect any intermediates formed in catalytic oxidation. The MS of $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ in $\text{CF}_3\text{CH}_2\text{OH}$ shows a predominant peak at m/z 512.2, which is assigned to $\{(\text{PPh}_4)[\text{Mn}(\text{N})(\text{CN})_4]\}^-$ (Figure S1).^[10] When 1 equiv. of ${}^n\text{Bu}_4\text{N}[\text{IO}_4]$ was added, two new peaks at m/z 531.1 and 628.0 appeared (Figure 2, S2 – 3), these are assigned as the solvated nitrido oxo species, $\{({}^n\text{Bu}_4\text{N})[\text{Mn}(\text{N})(\text{O})(\text{CN})_4]\}^- \cdot \text{CF}_3\text{CH}_2\text{OH}$ and $\{(\text{PPh}_4)[\text{Mn}(\text{N})(\text{O})(\text{CN})_4]\}^- \cdot \text{CF}_3\text{CH}_2\text{OH}$, respectively. Mn=O is known to undergo oxygen exchange with H_2O .^[10,15] Accordingly when $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2^{18}\text{O}$ (90% ^{18}O -labelled, 9:1 v/v) was used as

solvent, two new peaks at m/z 533.2 and 630.0 appeared, consistent with the ^{18}O -labelled species $\{({}^n\text{Bu}_4\text{N})[\text{Mn}(\text{N})(^{18}\text{O})(\text{CN})_4]\}^- \cdot \text{CF}_3\text{CH}_2\text{OH}$ and $\{(\text{PPh}_4)[\text{Mn}(\text{N})(^{18}\text{O})(\text{CN})_4]\}^- \cdot \text{CF}_3\text{CH}_2\text{OH}$, respectively (Figure 2, inset b).

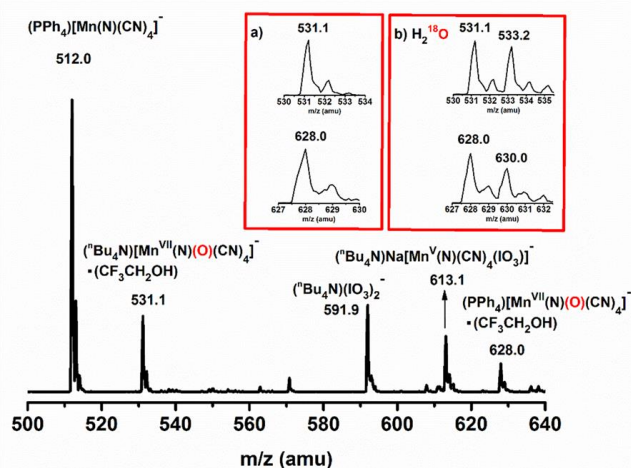


Figure 2. MS of a solution of $(\text{PPh}_4)_2[\text{Mn}(\text{N})(\text{CN})_4]$ (4.5 mM) and ${}^n\text{Bu}_4\text{N}[\text{IO}_4]$ (4.5 mM) in $\text{CF}_3\text{CH}_2\text{OH}$ after a reaction time of 3 min. Insets show the expanded spectra of the m/z 531.1 and 628.0 peaks when a) $\text{CF}_3\text{CH}_2\text{OH}$ was used as solvent; b) $\text{CF}_3\text{CH}_2\text{OH}/\text{H}_2^{18}\text{O}$ (90% ^{18}O -labelled) (9:1 v/v) was used as solvent.

Based on our experimental results a mechanism for the catalytic alkane oxidation is proposed (Figure 3). O-atom transfer from IO_4^- to $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ occurs in the first step which is rate-determining. The resulting $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$ then oxidizes the alkane (RH) via a H-atom abstraction/O-rebound mechanism to give ROH.^[16] The lack of significant effects of O_2 or BrCCl_3 means that the alkyl radicals are efficiently trapped in the solvent cage. ROH can be further oxidized to the corresponding ketone by the active Mn(VII) species.

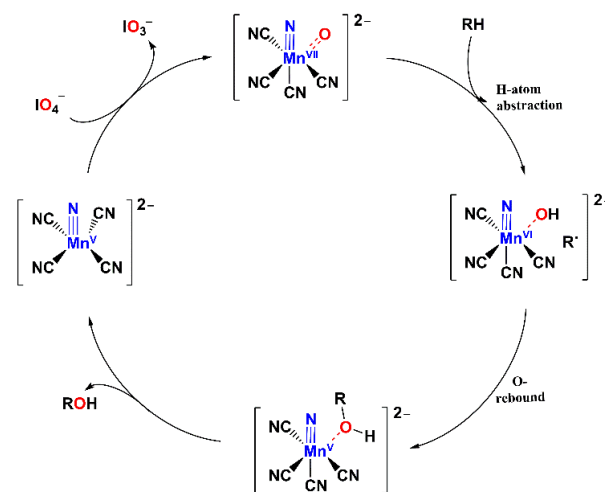


Figure 3. Proposed mechanism for catalytic oxidation of alkane.

In conclusion, the $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}/\text{IO}_4^-$ catalytic system is unusually efficient in the oxidation of various alkanes. Excellent yields of >95 % and TON of 3000 are obtained. The active intermediate is proposed to be the Mn(VII) nitrido oxo species, $[\text{Mn}^{\text{VII}}(\text{N})(\text{O})(\text{CN})_4]^{2-}$, which can also be generated using H_2O_2 or Ce(IV) as oxidant. The observed higher product yields and TONs than using H_2O_2 is probably because IO_4^- is thermally more stable and less susceptible to decomposition by trace metals. This work further demonstrates that $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$ is a versatile catalyst that can utilize a variety of oxidants for the efficient functionalization of unactivated C-H bonds under mild conditions.

Acknowledgements

The work described in this paper was supported by Hong Kong University Grants Committee Area of Excellence Scheme (AoE/P-03-08), the Research Grants Council of Hong Kong (CityU 101713), the Shenzhen Science and Technology Research Grant (JCYJ20150601102053067) and the Shenzhen Research Institute, City University of Hong Kong.

Keywords: alkane oxidation • C-H activation • periodate • catalysis • manganese nitrido complex

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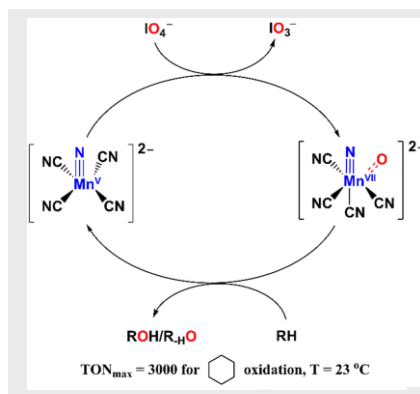
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Layout 1:

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Highly efficient alkane oxidation:

The oxidation of various alkanes catalyzed by $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$ using periodate (IO_4^-) as terminal oxidant at room temperature has been investigated. Excellent yields of alcohols and ketones (>95%) are obtained with a maximum turnover number (TON) of 3000.



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Oxidation of alkanes by periodate using a Mn(V) nitrido complex as catalyst

Layout 2:

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