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Activation of Nitrous Oxide and Selective Epoxidation of Alkenes Catalyzed by the Manganese-Substituted Polyoxometalate, $[Mn^{III}_2ZnW(Zn_2W_9O_{34})_2]^{10-}$

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Nitrous oxide is usually considered to be inert[1] and a poor ligand toward transition metals.[2] However, there is incentive to use N_2O as an oxygen donor because it contains 36 wt % oxygen, and the byproduct of an oxidation reaction would be N_2. In practice, there are only a few catalytic systems that have been shown to be efficient for the activation of N_2O for selective hydrocarbon oxidation. In the area of heterogeneous catalysis, the most effective catalysts appear to be iron-containing acidic zeolites[3] which at elevated temperatures are thought to yield surface activated iron−oxo species (α-oxygen),[4] which are capable of oxygen transfer to inert hydrocarbons.[5] Iron oxide on basic silica has been shown to catalyze, albeit nonselectively, propene epoxidation.[6] In some organometallic compounds, oxygen transfer from nitrous oxide to alkyl, alkyne, and imido ligands of transition metal complexes has been observed,[7] and metal−oxo species have been formed.[8] In addition, N_2O has been decomposed at subambient temperatures to N_2 and O_2 by a ruthenium complex.[9]

There is ongoing interest in oxidation catalyzed by polyoxometalates (POMs).[10] Here, we describe the activation of N_2O by a Mn(III)-substituted polyoxometalate, $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$ ($Q = (C_8H_{17})_3CH_3N^+$), Figure 1, and subsequent highly selective catalytic epoxidation of alkenes. Previously, it was shown that N_2O reacts at room temperature with a ruthenium porphyrin[11] to give high valent ruthenium−dioxo species[12] capable of epoxidation of alkenes. Somewhat oddly, much more extreme conditions (140 °C, 10 atm N_2O) are necessary for homogeneous catalytic oxidation.[13]

Epoxidation reactions of various alkenes catalyzed by $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$[15] with N_2O as oxygen donor were carried out in glass pressure tubes at 1 atm N_2O and 150 °C in fluorobenzene as solvent. The results presented in Table 1 show that epoxides were formed at very high selectivity (>99.9%). Typically, the reactions were rather slow, TOF $= 0.5-1.4\ h^{-1}$,[16] but proceeded in a linear fashion (Supporting Information), without indication of catalyst decomposition (IR). This is the first report of catalytic epoxidation with N_2O with a Mn-based compound. There were only relatively small differences in the reactivity of the various alkenes; for example, the rather nucleophilic cyclooctene was only twice as reactive as less nucleophilic terminal alkenes such as 1-octene. Interestingly, *trans*-stilbene was slightly more reactive than *cis*-stilbene, and the reaction was stereoselective despite the rather high reaction temperatures. *Cis*- and *trans*-2-hexen-1-ol were similarly reactive. It is worthwhile to note that other transition-metal-substituted POMs of this structure were not active (V(IV), Co(II), Zn(II), Cu(II), Ni(II)) or were not selective (Fe(III) and Ru(III)) (Supporting Information). It is also crucial to note that among the Mn-substituted POMs *only* Mn(III) was active. No epoxidation was observed using similar Mn(II) POMs.

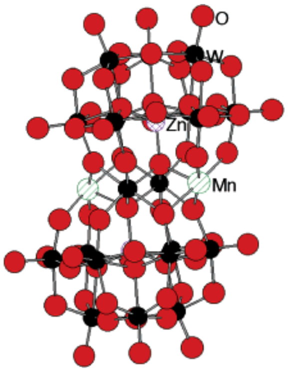

Figure 1. The $[Mn^{III}_2ZnW(Zn_2W_9O_{34})_2]^{10-}$ polyoxometalate.[14]

Table 1. Epoxidation of Alkenes with N_2O Catalyzed by $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]^a$

substrate	product	TTON
1-octene	1-octene oxide	10
trans-2-octene	*trans*-2-octene oxide	14
cyclooctene	cyclooctene oxide	19
1-decene	1-decene oxide	8
cyclohexene	cyclohexene oxide	9
cis-2-hexen-1-ol	2-hexene oxide-1-ol	21
trans-2-hexen-1-ol	2-hexene oxide-1-ol	19
cis-stilbene	*cis*-stilbene oxide	15
trans-stilbene	*trans*-stilbene	25

[a] Reaction conditions: 1 mmol of substrate, 0.01 mmol of $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$, 1 mL of fluorobenzene, 1 atm N_2O, 150 °C, 18 h. TTON is total turnover number (mol product per mol $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$). Epoxides were formed in selectivity >99.9% (GC). Mass balances were verified by addition of an external standard. Also, postreaction acidification of the reaction mixture showed no presence of C−C bond cleavage products such as heptanoic acid.

An a priori logical supposition concerning the mode of activation of N_2O in this system would be that the Mn(III) center reacted with N_2O to yield a Mn(V)−oxo species and N_2. This would be followed by epoxidation, Scheme 1, with the Mn(V)−oxo species as the latter are often viewed as active oxygen transfer agents capable of selective alkene epoxidation.[17] It has already been shown that Mn(IV)−oxo polyoxometalate species are inactive in epoxidation reactions.[18]

Possible intermediates were investigated by ESR spectroscopy. In general, peaks for Mn(III) species ($g = 8$), and also for $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$, cannot be observed under usual X-band ESR conditions.[19] However, when $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$ was mixed at 150 °C for 4 h in a pressurized tube under 1 atm N_2O in fluorobenzene, very surprisingly, an ESR spec-

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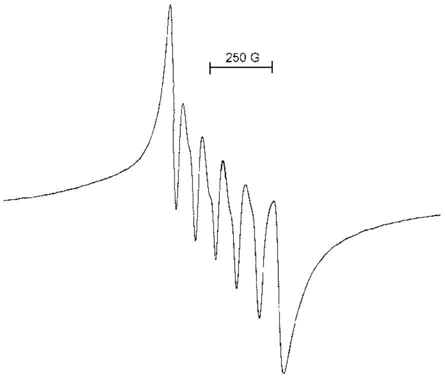
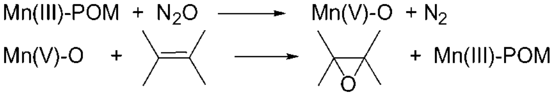


Figure 2. X-band ESR spectrum of species obtained by reaction of $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$ with N_2O in fluorobenzene at 120 K.

Scheme 1. A Direct Activation of N_2O by Mn(III)−POM



Scheme 2. A Disproportionation Mechanism for Activation of N_2O

$$\begin{array}{lcl}
2\,Mn^{III} + N_2O & \longrightarrow & Mn^{IV} + Mn^{IV}{=}O + N_2 \\
Mn^{IV}{=}O + Mn^{III} & \longrightarrow & Mn^{V}{=}O + Mn^{II} \\
Mn^{V}{=}O + \text{alkene} & \longrightarrow & Mn^{III} + \text{epoxide} \\
\hline
2\,Mn^{III} + \text{alkene} + N_2O & \longrightarrow & Mn^{IV} + Mn^{II} + N_2 + \text{epoxide}
\end{array}$$

trum ($g = 2.002$), Figure 2, very typical of a Mn(II) octahedral species was obtained,[20] which was also identical to the spectrum of authentic $K_{12}[Mn^{II}_2(H_2O)_2ZnW(ZnW_9O_{34})_2]$.[21] No other peaks, for example, at $g = \sim 4$, attributable to a Mn(IV) POM were observed. The Mn(II) concentration was *significant* and was estimated to be at least 70 ± 10% of the total Mn by comparison with aqueous solutions of authentic $Mn(II)(OAc)_2$. In the absence of N_2O, no ESR active species were obtained. The formation of this spectrum, however, was reversible. Thus, upon allowing the N_2O to evaporate off, the ESR spectrum disappeared, and subsequent repressurization and heating again gave the observed spectrum.

To explain the formation of a Mn(II)−POM species, a disproportionation mechanism could be suggested, Scheme 2.

There are four experimental observations that appear to be incompatible with such a mechanism: (a) The formation of Mn(II) in such a scheme would not be reversible upon removal of N_2O as observed. (b) There would be an immediate accumulation of Mn(II) in the system, but Mn(II)POM by itself was not catalytically active, and turnover would not be possible. (c) No Mn(IV) species were observed by ESR. (d) Vanadium(V)-containing POMs also form a monoreduced V(IV) species that, however, do not lead to epoxidation. In such a case, disproportionation is not possible.

It would therefore appear that a Mn(V)−O species is not formed in this reaction system and that N_2O reacts with a Mn(III) center of the polyoxometalate to *reduce* the polyoxometalate, while N_2O is oxidized. Such a reaction is rather surprising considering the high ionization potential, ∼12.8 eV of N_2O,[22] but may conceivably be explained by an outer sphere electron transfer, wherein the polyanionic nature of polyoxometalates energetically increases the favorability of such D−A interactions and formation of D−A complexes.[23] An understanding of the exact nature of the activation of N_2O by the Mn(III)−polyoxometalate and an explanation for the subsequent highly selective epoxidation are at this time still somewhat premature and will be the focus of future research.

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Supporting Information Available: Description of reactivity with other transition-metal-substituted POMs (Table) and reaction profile (Figure) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc. A* **1968**, 2886−2889.
(2) Bottomly, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5238−5342.
(3) Panov, G. I. *CATTECH* **2000**, *4*, 18−32. Panov, G. I.; Uriate, A.; Rodkin, M. A.; Sobolev, V. I. *Catal. Today* **1998**, *41*, 365−385.
(4) Notte, N. P. *Top. Catal.* **2000**, *13*, 387−394.
(5) Rhodkin, M. A.; Sobolev, V. I.; Dubkov, K. A.; Watkins, N. H.; Panov, G. I. *Stud. Surf. Sci. Catal.* **2000**, *130A*, 881−886.
(6) Duma, V.; Hönicke, D. *J. Catal.* **2000**, *191*, 93−204.
(7) Mansunaga, P.; Hillhouse, G. L.; Rheinhold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 2075−2077. Vaughan, G. A.; Chadwick, D.; Hillhouse, G. L.; Rheinhold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491−5493. Baranger, A. M.; Hanna, T. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 10041−10046.
(8) Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862−4867. Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606−615.
(9) Pamplin, C. B.; Ma, E. S. F.; Safari, N.; Rettig, S. J.; James, B. R. *J. Am. Chem. Soc.* **2001**, *123*, 8596−8597.
(10) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 171−199. Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407−455. Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171−198. Neumann, R. *Prog. Inorg. Chem.* **1998**, *47*, 317−370.
(11) Groves, J. T.; Roman, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5594−5595.
(12) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790−5791.
(13) Yamada, T.; Hashimoto, K.; Kitaichi, Y.; Suzuki, K.; Ikeno, T. *Chem. Lett.* **2001**, 268−269. Hashimoto, K.; Kitaichi, Y.; Tanaka, H.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2001**, 922−923.
(14) As formed in water, the transition-metal-substituted polyoxometalates are hexacoordinate (octahedral) around the transition metal with five oxo ligands and one aqua ligand. Upon extraction to apolar solvents, the labile aqua ligand is removed, and the metal center becomes pentacoordinate (tetragonal). Neumann, R.; Gara, M. *J. Am. Chem. Soc.* **1995**, *117*, 5066−5074 and references therein.
(15) $Q_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]$ was prepared by metathical exchange of $Na_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]\cdot xH_2O$ with 10 equiv of Aliquot 336 (approximately $(C_8H_{17})_3CH_3N^+Cl^-$). $Na_{10}[Mn^{III}_2ZnW(ZnW_9O_{34})_2]\cdot xH_2O$ was prepared according to Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143−155.
(16) The activity of the polyoxometalate is, however, comparable per gram catalyst to that of iron oxide-basic silica (ref 6) with much improved selectivity and at much lower temperatures.
(17) Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269−6273.
(18) Zhang, X. Y.; Pope, M. T. *J. Mol. Catal. A Chem.* **1996**, *114*, 201−208.
(19) Campbell, K. A.; Lashley, M. R.; Wyatt, J. K.; Nantz, M. H.; Britt, R. D. *J. Am. Chem. Soc.* **2001**, *123*, 5710−5719.
(20) This includes the modest features between the six main peaks arising from semi-forbidden transitions ($\Delta m_I = \pm 1$), cf.: Morrissey, S. R.; Horton, T. E.; DeRose, V. Y. *J. Am. Chem. Soc.* **2000**, *122*, 3473−3481.
(21) Neumann, R.; Gara, M. *J. Am. Chem. Soc.* **1995**, *117*, 5066−5074. It was shown that there is *no* magnetic coupling between the two Mn(II) centers leading to distortion of the ESR spectrum.
(22) There is no exact correlation between the gas-phase ionization potential and the solution oxidation potential, which is the more relevant, but unknown, parameter.
(23) Weinstock, I. A. *Chem. Rev.* **1998**, *98*, 113−170. Khenkin, A. M.; Weiner, L.; Wang, Y.; Neumann, R. *J. Am. Chem. Soc.* **2001**, *123*, 8531−8542.

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