Highly Active Manganese-Containing Polyoxometalate as Catalyst for Epoxidation of Alkenes with Hydrogen Peroxide

Ronny Neumann* and Mohammad Gara

Casali Institute of Applied Chemistry
Graduate School of Applied Science
The Hebrew University of Jerusalem
Jerusalem, Israel, 91904

Received January 31, 1994

For more than a decade, intensive efforts have been made in the field of catalytic oxygen transfer. One major goal has been to replace stoichiometric oxidation processes based on effective but toxic reagents such as dichromate with catalytic processes based on the ecologically friendly and inexpensive hydrogen peroxide as oxygen donor. For the activation of hydrogen peroxide, catalytically active intermediates may be classified by the mechanism of their reaction.[1] Thus, heterolytic cleavage is common for electron-poor d^0 complexes of Ti, V, Mo, W, and Re. In the intermediate peroxo complex, the O–O bond is polarized, leading to transfer of an electrophilic oxygen to a nucleophilic substrate as in the epoxidation of alkenes. Inverse polarization may be observed with electron-rich transition complexes of metals such as Rh, Pd, or Pt. On the other hand, peroxo intermediates of biologically relevant metals such as Mn, Fe, Co, and Cu lead to the homolytic cleavage of the O–O bond, formation of radicals, and in the case of alkenes predominantly to allylic oxidation. During this same period, significant research efforts have been invested in the chemistry of iron and manganese porphyrins, these studies being motivated mostly by the desire to mimic and understand the function of the cytochrome P-450 enzyme.[2] In the presence of hydrogen peroxide highly active, high-valent metal–oxo intermediates are formed via the shunt pathway leading to very effective epoxidations of alkenes and hydroxylation of alkanes.[3] Since these reactions could be carried out with high turnovers at ambient temperatures, it has been suggested that the use of synthetic metalloporphyrins could be scaled up for application in an industrial environment. However, the lack of stability of the common porphyrin moieties has prevented these applications. One approach to solve this problem has been to synthesize "robust" metalloporphyrins by polyhalogenation of the porphyrin.[4] A very different approach is to use transition metal substituted polyoxometalates as oxidatively stable "inorganic porphyrin" analogues. In such a scheme, a low-valent transition metal such as Mn(II), Co(II), Fe(III), or Ru(III) is substituted into a deficient or lacunary polyoxotungstate or polyoxomolybdate. Such a system may be envisioned as a transition metal bound by an inorganic ligand, the lacunary polyoxometalate, which can act as a multielectron acceptor. Usually the polyoxometalate has been of the Keggin structure. In some cases, these systems have shown metalloporphyrin like properties such as dioxygen binding,[5] formation of high-valent species with stoichiometric oxygen transfer,[6] and reactions with oxidants such as iodosobenzene, sodium periodate, sodium hypochlorite, and *tert*-butyl hydroperoxide.[7] Catalytic oxidation with hydrogen peroxide has been limited to polyoxometalates containing only electron-poor metals in the d^0 state[8] with one exception where a tetrairon-substituted polyoxometalate,[9] $[Fe^{II}_4(PW_9O_{34})_2]^{10-}$, has been reported to activate hydrogen peroxide for the epoxidation of alkenes at up to 15 turnovers with approximately 90% selectivity. We now report the use of an oxidatively and solvolytically stable disubstituted manganese polyoxometalate,[10] $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$, as catalyst for the epoxidation of alkenes and oxidation of alcohols in a biphasic system at ambient or subambient temperatures, with very high selectivities, >99%, and hundreds to thousands of turnovers with only a small molar excess of 30% hydrogen peroxide.

Polyoxometalates of the general formula $[WMM'_2(XW_9O_{34})_2]^{12-}$, where M and M′ are Zn, Co, Mn, Fe, Ni, or Cu and X is Zn or Co, were synthesized by the reported literature procedure[10] by substitution of the desired transition metal into the $[WZnZn_2(ZnW_9O_{34})_2]^{12-}$ or $[WCoCo_2(CoW_9O_{34})_2]^{12-}$ precursor compound.[11] These are sandwich-type compounds with a WM′MM′ (W, M and M′, M′ opposite each other) ring between two B-XW_9O_{34} units. In the case of X and M = Zn(II) and M′ = Mn(II) these polyoxometalates are catalysts of exceptional activity for the epoxidation of alkenes. Thus, stock solutions of 0.2 mM $[WMM'_2(XW_9O_{34})_2]^{12-}$ were prepared by dissolving 0.02 mmol of $K_{12}[WMM'_2(XW_9O_{34})_2]$ with 0.5 mmol of methyltricaprylammonium chloride in 100 mL of 1,2-dichloroethane and filtering off the precipitated KCl. The reaction was initiated by addition of 1 mmol of substrate and 2 mmol of 30% hydrogen peroxide to 1 mL of the polyoxometalate stock solution under aerobic conditions and stirred in what forms a biphasic reaction system. Typical results for various catalysts using cyclooctene as substrate are summarized in Table 1. One can see from the results that the disubstituted manganese compound was by far the most active. Addition of another reactive (Co, Mn) transition metal into the ring considerably reduced the reactivity ($[WMnMn_2(ZnW_9O_{34})_2]^{12-}$ and $[WCoMn_2(CoW_9O_{34})_2]^{12-}$). Addition of a fourth transition metal into the ring ($[Mn_4(PW_9O_{34})_2]^{10-}$) yielded a totally inactive catalyst. Equally inactive was the more simple monosubstituted Keggin compound ($PMnW_{11}O_{39}{}^{5-}$). Substitution of the completely inactive $[WZnZn_2(ZnW_9O_{34})_2]^{12-}$ with Ni, Fe, or Cu yielded polyoxometalates with only slight catalytic activity. Interestingly the $[Fe_4(PW_9O_{34})_2]^{10-}$ compound shown to have some activity in acetonitrile as solvent[9] was totally inactive in this reaction system. On the other hand the $PW_{11}O_{39}{}^{7-}$ precursor to $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ showed some activity (see also below). The disubstituted manganese compound $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ was also an active catalyst in other biphasic systems, *e.g.*, toluene as solvent (280 turnovers), however, inactive in monophasic reactions with solvents such as acetonitrile or *tert*-butyl alcohol.

In order to learn more about the scope of the catalytic activity of the disubstituted manganese polyoxometalate and its selectivity,

---

[1] Sheldon, R. A.; Kochi, J. K. *Metal Catalysed Oxidation of Organic Compounds*; Academic Press: New York, 1981. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Strukul, G., Ed.; Kluwer: Dordrecht, The Netherlands, 1992.

[2] *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.

[3] Renaud, J.-P.; Battioni, P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1985,** 888. Battioni, P.; Renaud, J.-P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1986**, 341.

[4] Traylor, T. G.; Byun, Y. S.; Traylor, P. S.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1991**, *113*, 7821. Traylor, T. G.; Tsuchiya, S. *Inorg. Chem.* **1987**, *26*, 1339.

[5] Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

[6] Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186. Khenkin, A. M.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 8178.

[7] Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487. Mansuy, D.; Bartoli, J.-F.; Battioni, P.; Lyon, D. K.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7222. Hill, C. L.; Weeks, M. S.; Khenkin, A. M.; Hou, Y. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1992**, 1093. Neumann, R.; Abu-Gnim, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1324. Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *110*, 6025.

[8] Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587. *Hydrogen Peroxide Oxidation Catalyzed by Heteropoly Acids Combined with Cetylpyridinium Chloride*; Ishii, Y., Ogawa, M., Eds.; MYU: Tokyo, 1990.

[9] Khenkin, A. M.; Hill, C. L. *Mendeleev Commun.* **1993**, 140.

[10] Tourné, C. M.; Tourné, C. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143.

[11] Elemental analysis was performed on the precursor and transition metal substituted compounds. The analysis was not significantly different from those found for the original synthesis (ref 10). For the most important catalyst, $K_{12}[WZnMn^{II}_2(ZnW_9O_{34})_2]$ as a hydrate with 23 water molecules (7.18% by TG). Experimental (theoretical) K, 8.09 (8.13); W, 60.87 (60.53); Zn, 3.30 (3.40); Mn, 2.03 (1.90).

0002-7863/94/1516-5509$04.50/0

Table 1. Oxidation of Cyclooctene with 30% H_2O_2 Catalyzed by Different Polyoxometalates[a]

polyoxometalate	turnovers, mol of product/ mol of catalyst
$[WZnMn_2(ZnW_9O_{34})_2]^{12-}$	2300
$[WMnMn_2(ZnW_9O_{34})_2]^{12-}$	385
$[WCoMn_2(CoW_9O_{34})_2]^{12-}$	0
$[WZnNi_2(ZnW_9O_{34})_2]^{12-}$	88
$[WZnCu_2(ZnW_9O_{34})_2]^{12-}$	100
$[WZnCo_2(ZnW_9O_{34})_2]^{12-}$	195
$[WZnFe_2(ZnW_9O_{34})_2]^{12-}$	45
$[WCoCo_2(CoW_9O_{34})_2]^{12-}$	60
$[WZnZn_2(ZnW_9O_{34})_2]^{12-}$	0
no polyoxometalate	0
$PW_{11}O_{39}^{7-}$ [c]	370
$PMnW_{11}O_{39}^{5-}$	0
$[Fe_4(PW_9O_{34})_2]^{10-}$ [d]	0
$[Mn_4(PW_9O_{34})_2]^{10-}$ [d]	0

[a] Reaction conditions: 0.2 μmol of polyoxometalate, 5 μmol of methyltricaprylammonium chloride, 1 mmol of cyclooctene, 2 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane, time 20 h, temperature 22 °C. [b] The only product observable was cyclooctene oxide, which was quantified by GLC analysis using a 15-m methylsilicone capillary column. [c] This compound is in essence the preferred precursor[8] to the active $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$. [d] Prepared using the literature procedure.[15]

Table 2. Oxidation of Various Substrates with 30% H_2O_2 Catalyzed by $[WZnMn_2(ZnW_9O_{34})_2]^{12}$ [a]

substrate	products	turnovers,[b] 2 °C (70 °C)
cyclohexene	cyclohexene oxide	1450 (10)
	cyclohexen-2-ol	0 (430)
	cyclohexen-2-one	5 (1340)
cyclooctene	cyclooctene oxide	2040
1-octene	1-octene oxide	25 (500)
2-methyl-1-heptene	2-methyl-1-heptene oxide	190 (630)
trans-2-octene	*trans*-2-octene oxide	340 (1400)
	trans 2-octen-4-one	0 (400)
2-methyl-2-heptene	2-methyl-2-heptene oxide	1465
2,3-dimethyl-2-butene	2,3-dimethyl-2-butene oxide	4335
cyclohexanol	cyclohexanone	510 (4275)
2-octanol	2-octanone	675 (4630)
1-phenylethanol	acetophenone	1855

[a] Reaction conditions: 0.2 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium chloride, 1 mmol of substrate, 2 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane, time 24 h. [b] Turnovers are given as mol of product/mol of catalyst at 2 °C and 70 °C where relevant. The products were all identified and quantified by GLC analysis using appropriate references and when necessary GC–MS using a 15-m methylsilicone capillary column.

epoxidations and oxidations of alcohols were carried out with a variety of substrates, Table 2. At a reaction temperature of 2 °C, amazingly high selectivities were obtained: in all cases, >99%. This is especially clear in the oxidation of cyclohexene known to be highly sensitive to allylic oxidation. Reactivity of the substrate is observed to be a function of the nucleophilicity of the carbon–carbon double bond, with increased substitution leading to higher yields. At 2 °C, the reaction is incomplete after 24 h (little hydrogen peroxide dismutation). Longer reaction periods and/or increased amounts of oxidant increase alkene yields. At higher temperatures of 70 °C, reaction turnovers to product are significantly increased; however, the higher temperatures also lead to lower hydrogen peroxide yields due to the dismutation reaction and often to reduced selectivity. Thus, cyclohexene is only epoxidized at 2 °C whereas at 70 °C only allylic oxidation is observed. One may presume that at low temperatures *only* oxygen transfer is occurring, but at higher temperatures homolytic cleavage is more dominant.

Finally, it is important to add some preliminary comments on the solvolytic stability of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate and the identity of the active catalyst. In general polyoxometalates are thermodynamically and oxidatively stable compounds; however, they are often degraded by aqueous hydrogen peroxide. This is especially well-known for Keggin type compounds with a phosphorus heteroatom[12] which degrade to the more simple and catalytically active $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$. In this case we have good reason to believe that the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ anion is the active catalyst. First, the manganese metal in the ring is crucial to the activity of the catalyst. Thus, with only substitution by zinc no catalytic activity is observed even though the compounds should have similar solvolytic stability. This rules out a purely tungsten and/or zinc based compound as the active catalyst or an isolated tungsten center as the active catalyst site.[13] Second, the IR spectrum of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ [peaks at 1055 (w), 919 (s), 868 (s), 768 (s), and 723 (s) cm^{-1}] is unchanged after being treated with hydrogen peroxide.[14] Third, the UV–vis spectrum after reaction shows only the original $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ oxidized to $[WZnMn^{III}_2(ZnW_9O_{34})_2]^{10-}$ (distinctive peak at 530 nm). The spectrum is identical to the spectrum of a separately prepared authentic sample[10] of $[WZnMn^{III}_2(ZnW_9O_{34})_2]^{10-}$. Lastly, a possible degradation of the catalyst should have an effect on the kinetic profile of the reaction either by appearance of an induction period or by deceleration of the rate by loss of active species. Neither phenomenon is observed in this case. A kinetic profile of the oxidation of cyclooctene at 2 °C (see conditions in Table 1) shows that the reaction is cleanly first order in cyclooctene over a wide range of 0–4500 turnovers (0–90% yield).

A disubstituted manganese polyoxometalate, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, has been found as an excellent catalyst for the epoxidation of alkenes at ambient and subambient temperatures with very high selectivities and hydrogen peroxide yield.

Acknowledgment. This research was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities.

---

(12) Aubry, C.; Chottard, G.; Platzner, N.; Brégault, J.-M.; Thouvenout, R.; Chaveau, F.; Huet, C.; Ledon, H. *Inorg. Chem.* **1991**, *30*, 4409.

(13) It may be noted that the absence of a phosphorus heteroatom precludes the formation of the commonly active degradation product, $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, found in other systems. Of course, it could be argued that the original $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ anion instead degrades to a more simple as yet unknown active compound. Such a scenario is also unlikely because a similar degradation could be expected for the isostructural trisubstituted manganese compound which, however, is considerably less active.

(14) Two millimoles of 30% H_2O_2 was added to 1 mL of a 0.2 mM $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ stock solution and stirred for 8 h. The excess H_2O_2 was decomposed by aqueous KI, and the phases were separated. The IR spectrum was then taken after evaporation of the 1,2-dichloroethane solvent and compared to the original IR spectrum of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$.

(15) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.