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The Manganese-Containing Polyoxometalate, $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$, as a Remarkably Effective Catalyst for Hydrogen Peroxide Mediated Oxidations

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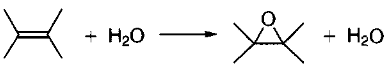
Abstract: The disubstituted manganese polyoxometalate, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, has been used as a catalyst for the epoxidation of alkenes and the oxidation of secondary alcohols to ketones in biphasic (water–organic) reaction media using hydrogen peroxide (30% aqueous H_2O_2) as the oxygen donor. At subambient temperatures, epoxidations are highly selective with little dismutation of hydrogen peroxide by homolysis or formation of side products by allylic oxidation. Thus, cyclohexene was oxidized to cyclohexene oxide at 2 °C with 99% selectivity. At low catalyst loadings and depending on the substrate and reaction temperature, hundreds to thousands of catalytic turnovers were obtained with only a 2-fold excess of hydrogen peroxide over substrate. Kinetic measurements on a model epoxidation of cyclooctene showed that the reaction is first order in cyclooctene, hydrogen peroxide, and $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ catalyst. Magnetic susceptibility measurements along with ESR and atomic absorption spectroscopy reveal that the manganese atom is in a terminal position coordinated by five bridging oxygen atoms and one labile aquo ligand which is disassociated upon transfer of the polyoxometalate anion into an organic phase. Comparison of the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion with other mono-, tri-, or tetrasubstituted manganese polyoxometalates or catalysts having no manganese atoms showed that the catalytic activity of the former was unique. Kinetic evidence exhibited the absence of an induction period for catalyst activation or catalyst deactivation over a period of 12500 turnovers. IR spectra demonstrated that the original catalyst reacted with hydrogen peroxide to form a peroxo intermediate with a typical absorbance at 818 cm^{-1}. After completion of the reaction, the original IR spectrum was measured again. ESR and atomic aborption spectroscopy also revealed that the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion is solvolytically stable to aqueous hydrogen peroxide. Cyclic voltammetry, IR and UV–vis, and a comparative reaction with iodosobenzene as the oxygen donor seem to exclude a high valent manganese–oxo compound as the reactive intermediate. Rather, high reactivity is probably due to a tungsten–peroxo intermediate somehow uniquely activated by an adjacent manganese atom.

Introduction

Environmental concerns have forced the chemical industry to reevaluate many of its processes so as to reduce or eliminate the formation of wastes produced in the synthesis of organic products. This need is especially acute in oxidation technologies often used in the fine chemical industry where the common use of stoichiometric oxidants results in the formation of large amounts of chromium, manganese, and other similarly toxic salts.[1] Consequently, one of the preferred solutions is to use hydrogen peroxide as an oxygen donor in catalytic oxygen transfer reactions as in the epoxidation of alkenes, eq 1. Such



(1)

processes can be technologically viable only if the reactions are highly selective for product formation and of high yield in hydrogen peroxide, *i.e.*, there is minimal formation of molecular oxygen by the dismutation reaction. These conditions often are difficult to realize for metal catalyzed activation[2] generally leads to at least partial homolytic cleavage of the O–O or O–H bond and formation of hydroxy and hydroperoxy radicals, eqs 2 and 3 (TM ≡ transition metal).

$$TM^{n+} + H_2O_2 \rightarrow TM^{(n+1)+} + OH^- + OH^\bullet \qquad (2)$$

$$TM^{(n+1)+} + H_2O_2 \rightarrow TM^{n+} + H^+ + HO_2^\bullet \qquad (3)$$

These radicals may react with each other or hydrogen peroxide to form dioxygen and water (catalytic dismutation) or with organic substrates yielding organic radical intermediates and various products by numerous pathways depending on the substrate. As a rule of thumb, the degree of homolytic cleavage is higher as the oxidation potential of the metal increases. Thus, high selectivity to epoxidation can more easily be obtained by use of electron poor d^0 complexes of Ti, Mo, W, and Re[3] with low $TM^{(n+1)+}/TM^{n+}$ redox potentials and high Lewis acid activity. Use of such compounds enables heterolytic cleavage, where in the intermediate peroxo complex (inorganic peracid), the O–O bond is polarized leading to a transfer of an electrophilic oxygen to a nucleophilic substrate as in the epoxidation of alkenes. Another important prerequisite for a practical process is that the catalyst be stable to oxidation. This problem, for example, has prevented the wide scale use of

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synthetic metalloporphyrins in hydrogen peroxide mediated oxidations,[4] although some attempts have been made to prepare "robust" metalloporphyrins by polyhalogenation of the porphyrin moiety.[5] Over the last few years, it has been found that two types of tungsten and molybdenum based polyanions or polyoxometalates,[6,7] $\{PO_4[M(O)(O_2)_2]_4\}^{3-}$ and $PM_{12}O_{40}^{3-}$ (M = W, Mo), meet the requirements for practical catalysts although there is considerable question and/or dispute whether the latter is simply a precusor to the former compound which is the true catalyst.[8] At any rate, they are selective catalysts for activation of hydrogen peroxide as in epoxidation of alkenes; they do not appreciably dismutate hydrogen peroxide and are oxidatively stable.

We previously reported in a preliminary communication[9] that the manganese(II) disubstituted polyoxometalate,[10,11] $[WZnMn^{II}_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ (**1**), Figure 1, was an oxidatively and solvolytically stable catalyst for the epoxidation of alkenes and oxidation of alcohols with 30% aqueous H_2O_2 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. The manganese polyoxometalate can be viewed as a dimer of a truncated Keggin structure having a "belt" of W, Zn, and Mn cations "sandwiched" between the two $B-XW_9O_{34}$ trivacant Keggin fragments. The Mn cations are assumed to be positioned at terminal M1 positions and are hexacoordinate with one labile aquo ligand although the placement of at least one Mn cation at the M2 bridging position is possible. This compound and other transition metal analogues are structurally similar to the somewhat better known $(TM)_4(PW_9O_{34})_2^{q-}$ (TM = transition metal) species;[12] however, the compound discussed in this paper has truly unique catalytic activity.

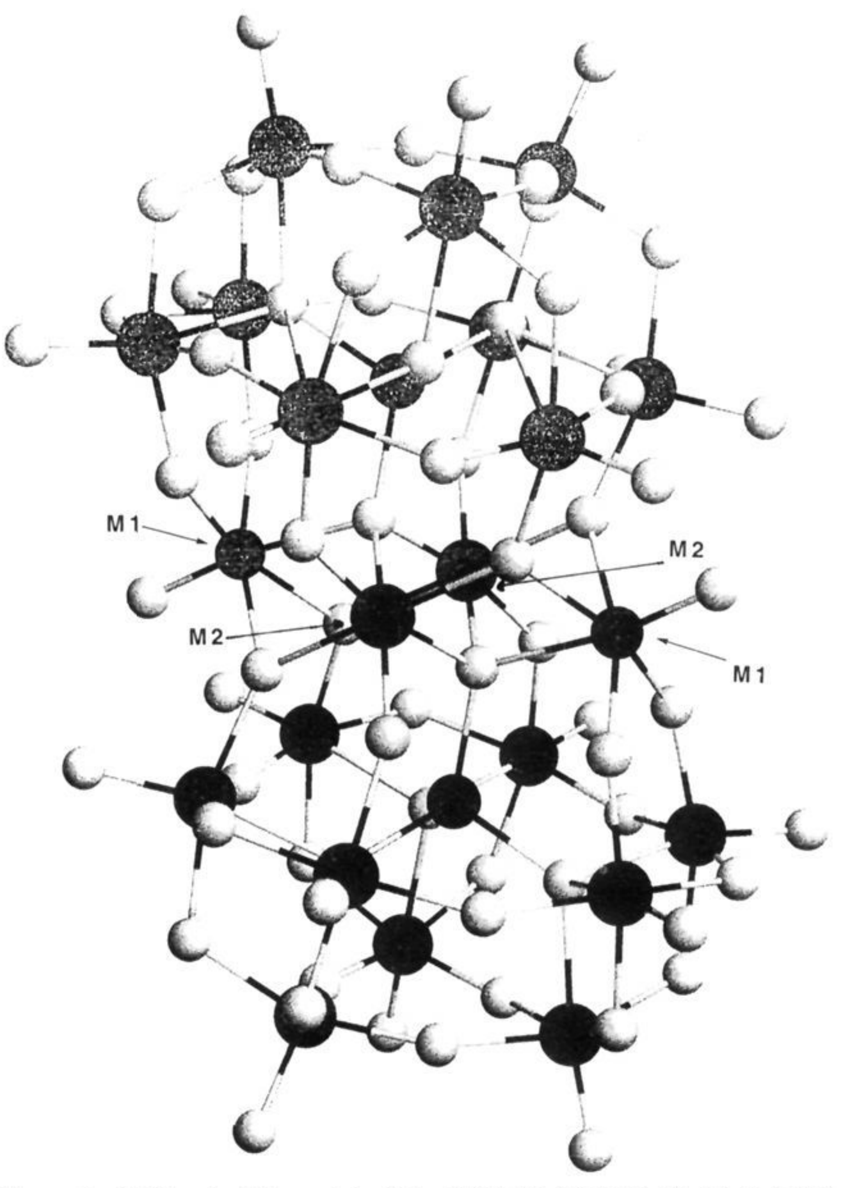

Figure 1. Ball and stick model of the $[WZnMn^{II}_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate.

In this paper, we present our complete results on the activity of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ as a catalyst for the aqueous hydrogen peroxide mediated epoxidation of alkenes and the oxidation of alcohols to ketones. Using magnetic susceptibility measurements and ESR and atomic absorption spectroscopy we show that the Mn cations are indeed at the terminal M1 positions. Using kinetic measurements on a model substrate such as cyclooctene, and IR, ESR, and atomic absorption spectroscopy we show that the catalyst is oxidatively and hydrolytically stable over a range of at least 12500 turnovers in the epoxidation of cyclooctene. Further use of the mentioned methods together with cyclic voltammetry and UV−vis and IR spectroscopy and use of other oxidants and catalysts led us to exclude the possibility of the formation of a high valent manganese−oxo species as an active intermediate. Instead, we suggest a reaction pathway based upon a tungsten−peroxo intermediate. We suspect that in the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ catalyst one of the oxygen peroxo atoms co-interacts with an adjacent manganese center to form a highly active peroxo intermediate which is both a highly reactive and a selective epoxidation catalyst.

Experimental Section

General Methods, Materials, and Instrumentation. The polyoxometalates $Na_{12}WZnTM_2(L)_2(ZnW_9O_{34})_2{\cdot}nH_2O$, $K_{12}WZnTM_2(L)_2(ZnW_9O_{34})_2{\cdot}nH_2O$, $Na_{12}WTM_3(L)_2(ZnW_9O_{34})_2{\cdot}nH_2O$, $Na_{12}WCoTM_2(L)_2(CoW_9O_{34})_2{\cdot}nH_2O$, $K_{10}TM_4L_2(PW_9O_{34})_2{\cdot}nH_2O$, $K_7PW_{11}O_{39}{\cdot}nH_2O$, and $K_5Mn^{II}PW_{11}O_{39}{\cdot}nH_2O$ where TM is Mn(II), Mn(III), Ni(II), Cu(II), Co(II), or Fe(III) and L is H_2O or OH^-, were all prepared and purified by literature procedures.[10,12,13] The amount of water was determined by thermogravimetric analysis (Mettler TG 50 thermoanalytical balance). Elementary analysis was performed by alkaline

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(11) In general, the substituted transition metal, in this case manganese, is thought to be coordinated in one position by a labile aquo or hydroxy ligand. While this is true for the sodium salt as synthesized and in water, it will be shown below that in organic media, this aquo ligand is disassociated and the preferred representation is $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$.

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digestion of the polyoxometalate followed by atomic absorption measurements (GBC 903 single beam spectrometer) with an acetylene–air or acetylene–nitrous oxide flame oven for Na, K, Zn, and TM, whereas W was determined gravimetrically with 8-hydroxyquinoline.[14] The analyses were not significantly different from those found for the original syntheses. 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). The methyltricaprylammonium salt of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, mostly $((C_8H_{17})_3CH_3N)_3PO_4[W(O)(O_2)_2]_4$, was prepared[15] by dissolving 10 g of tungstic acid in 14 mL of 30% H_2O_2 and mixing at 50 °C for 40 min. Solid impurities were removed by centrifugation and 343 μL of 85% H_3PO_4 were added. To a part of this solution, 3.5 mL, was added 900 mg of Aliquat 336 (methyltricaprylammonium chloride) dissolved in 10 mL of benzene. The phases were mixed for 10 min and separated, and the organic phase was dried with Na_2SO_4. After evaporation $((C_8H_{17})_3CH_3N)_3PO_4[W(O)(O_2)_2]_4$ was obtained as a colorless oil, yield 95%. Solvents used were of analytical grade and they were used without further purification. The alkenes and alcohols used as substrates were of the highest purity commerically available from Aldrich or Fluka. Alkenes were purified prior to reaction by passing them over an alumina column. H_2O_2 was a 30% aqueous solution (Merck). The amount of hydrogen peroxide was measured by use of the common iodometric titration. Reaction products were characterized and quantitized using reference compounds when available by use of GLC (Hewlett-Packard 5890 gas chromatograph) with a flame ionization detector and a 15 m x 0.32 mm methylsilcone (0.25 μm coating) capillary column and helium carrier gas. Products whose initial identity was questionable were unambiguously identified using a gas chromatograph equipped with a mass selective detector (GC-MS Hewlett-Packard 5970A) equipped with the same column described above. IR spectra as KBr pellets or neat after evaporation of the solvent on the KBr plate were recorded on a Nicolet 510M FTIR instrument. UV–vis spectra were measured on a Hewlett-Packard 8452A diode array spectrometer. Cyclic voltammetry was measured on a BAS CV-1B instrument using a glassy carbon working electrode, a Ag/AgNO$_3$ reference electrode, and 0.5 M NaCl as the supporting electrolyte in aqueous solutions at pH = 7. ESR spectra (X-band) were taken with a Varian E-12 spectrometer at room temperature or at 120 K with a liquid nitrogen cyrostat. Magnetic susceptibilities were recorded at 5 to 100 K at a magnetic field of 20 G using a Squid Magnetometer Model MPMS-2 from Quantum Design.

Procedure for Catalytic Oxidations. Stock solutions of 0.2 mM polyoxometalate were prepared by mixing 0.02 mmol polyoxometalate sodium or potassium salt with 0.5 mmol methyltricaprylammonium chloride in 100 mL of 1,2-dichloroethane and filtering off the precipitated KCl. Reactions were carried out in 3 mL vials equiped with stirring bars. In a typical reaction, substrate (1 mmol) was dissolved in 1 mL of stock solution polyoxometalate and the reaction brought to the desired temperature. The reaction was initiated by addition of 2 mmol of 30% hydrogen peroxide to the stock solution under atmospheric conditions and with stirring; in a biphasic reaction system forms. The reaction was monitored by withdrawing aliquots from the organic phase of the reaction medium and directly injecting the sample into the gas chromatograph. Hydrogen peroxide consumption was measured by iodometric titration of an aliquot of the remaining oxidant in the aqueous phase. Kinetics of cyclooctene epoxidation were carried out by using identical procedures and varying the required amounts of the relevant compounds. Thus, the reaction order in cyclooctene (see also Figure 5 below) was determined using the following conditions: 1.0 μmol $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium cation, 1 mmol of cyclooctene, 2 mmol of 30% hydrogen peroxide, and 1 mL of 1,2-dichloroethane. The reaction orders in $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ and hydrogen peroxide were computed at 2 °C from log *vs* log plots of concentration in both compounds and observed rate constants. The amount of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ was varied from 0.5 to 10 μmol (6 points) and the amount of 30% hydrogen peroxide was varied over the range 2–10 mmol (5 points). Values for the reaction order were calculated from two replicate experiments in each case.

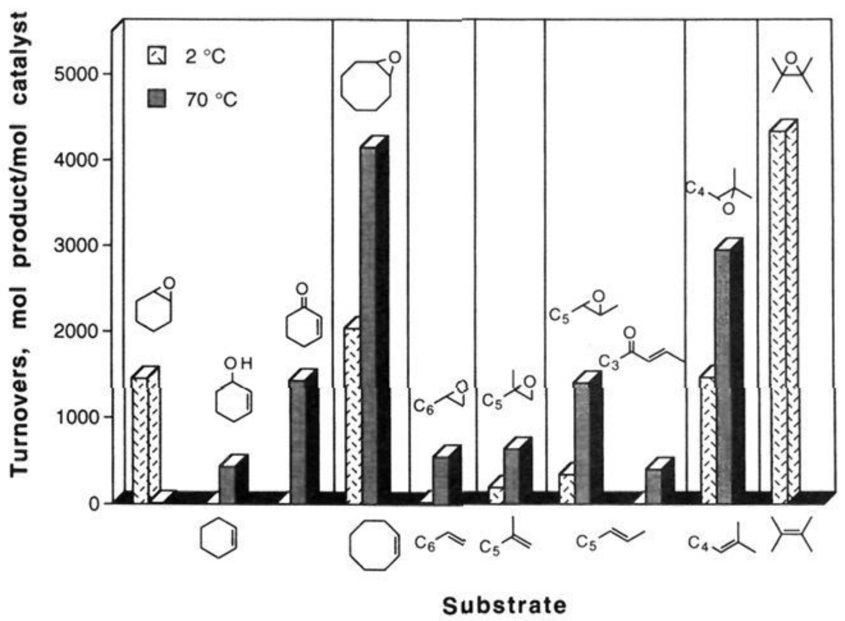

Figure 2. Epoxidation of alkenes with 30% H_22O_2 catalyzed by $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$. Reaction conditions: 0.2 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium cation, 1 mmol of alkene, 2 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane, time 24 h.

ESR Spectra. The spectrum of the polycrystalline powder of $Na_{12}WZnMn^{II}_2(ZnW_9O_{34})_2$ was measured at 120 K, microwave power 10 mW, 9.103 GHz microwave frequency, modualtion amplitude 5 G, and time constant 0.3 s. The spectrum of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ in an organic solution was taken after preparing a 3 mM solution in 1,2-dichloroethane and drying the solution with Na_2SO_4 for 3 h. The ESR spectra were acquired under the same conditions described for the polycrystalline sample. Likewise, a spectrum of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ was taken after mixing 5 mL of a 3 mM solution in 1,2-dichloroethane with 3 mL of 30% H_2O_2.

Infrared Spectra. The spectrum of the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion was taken by evaporating the stock solution from a KBr plate. Similarly, the spectrum of the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion upon interaction with hydrogen peroxide was obtained by adding 2 mmol of 30% H_2O_2 to 1 mL of a 0.2 mM $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ stock solution and stirring for 30 min. Finally, the IR spectrum of the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion after reaction was taken by again adding 2 mmol of 30% H_2O_2 to 1 mL of a 0.2 mM $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ solution, stirring for 8 h, decomposing the excess H_2O_2 with aqueous KI, and seperating the phases separated. The IR spectrum was then taken after evaporation of the 1,2-dicloroethane solvent and compared to the original IR spectrum of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$.

Analysis of $WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ by Atomic Absorption Spectroscopy after Interaction with 30% H_2O_2. $Na_{12}WZnMn_2(H_2O)_2(ZnW_9O_{34})_2$ (0.2 g) was mixed with 0.1 g of methyltricaprylammonium chloride in 10 mL of 1,2-dichloroethane The solution was divided into two equal parts, and 10 mL of distilled water and 30% H_2O_2 were added to the first and second parts, respectively. The solutions were stirred for 5 h at room temperature, the phases were separated, and the aqueous phase was analyzed for the presence of Mn and Zn cations by atomic absorption spectroscopy.

Results and Discussion

Catalytic Oxidations with Hydrogen Peroxide. The scope of the catalytic activity of the disubstituted manganese polyoxometalate $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ and its selectivity were investigated for several types of hydrocarbon substrates including alcohols, alkenes, and alkanes with hydrogen peroxide as the oxygen donor. In reactions performed by the procedure as described in the Experimental Section, epoxidation of alkenes and oxidation of secondary alcohols to ketones was very effective, whereas in the oxidation of primary alcohols and alkanes there was no reaction, Figures 2 and 3. For alkene oxidation, especially impressive was the fact that at lower reaction temperatures, *e.g.*, 2 °C, amazingly high selectivities were obtained—in all cases, >99%. This is most clear in the oxidation of cyclohexene where high selectivity to cyclohexene

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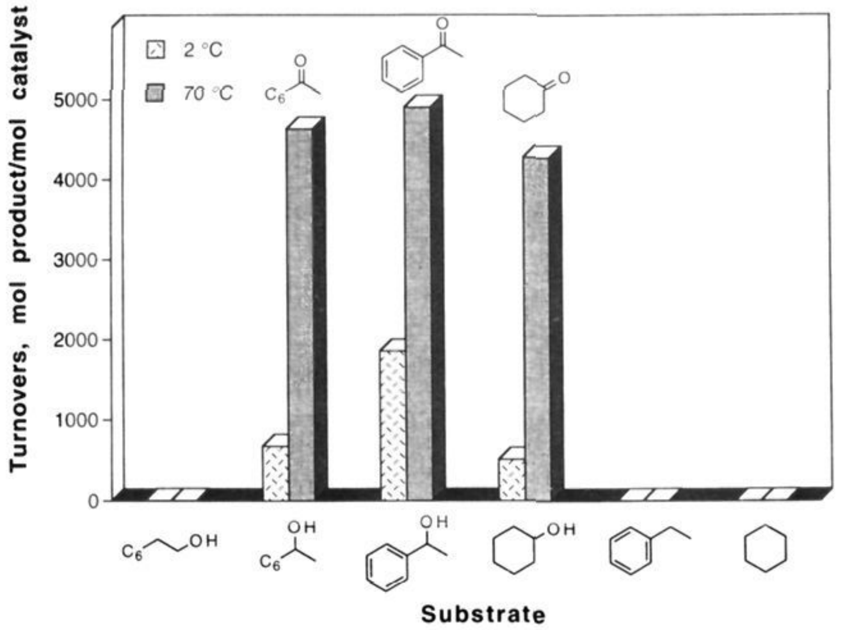

Figure 3. Oxidation of alcohols and alkanes with 30% H_22O_2 catalyzed by $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$. Reaction conditions: 0.2 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium cation, 1 mmol of alcohol or alkane, 2 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane; time 24 h.

oxide was observed despite the known sensitivity of this substrate to allylic oxidation which yields cyclohexen-2-ol and cyclohexen-2-one as major products. At higher temperatures, turnovers were much higher; however, in some cases as when using cyclohexene or *trans*-2-octene as substrates, the increased reactivity comes at the expense of lower selectivity. Thus, cyclohexene was 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 by heterolysis, but at higher temperatures homolytic cleavage is more likely. 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 with the notable exception of styrene which was practically inert. The oxidation of alcohols proceeded in the expected following order of relative activity: benzylic > cyclic ~ secondary acyclic ≫ primary acyclic.

The effectivity of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyst was also tested in terms of hydrogen peroxide yields using cyclooctene as the standard substrate, Figure 4. At 2 °C, even after 24 h, the yield in hydrogen peroxide was only marginally lower than the conversion of cyclooctene to cyclooctene oxide, indicating that there was little hydrogen peroxide dismutation. Only after 72 h was the reaction essentially complete. At 27 °C and presumably even more obviously at the higher temperature of 70 °C the reaction was considerably accelerated; however, the yield of the reaction in hydrogen peroxide was also somewhat lower. Only in cases where allylic oxidation pathways are significantly energetically more favorable, notably with cyclohexene, do lower hydrogen peroxide yields go hand in hand with reduced reaction selectivity. Substrates not especially susceptible to allylic oxidation, *e.g.* cyclooctene, show no reduction in reaction selectivity (100% epoxide) and only formation of molecular oxygen. Experiments using $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyst and cyclooctene or cyclohexene as substrates with dioxygen as oxidant at up to 70 °C showed *no* reaction, indicating that formation of allylic oxidation products in reactions with hydrogen peroxide in the case of cyclohexene is by reaction between cyclohexene and hydroperoxy and hydroxy radicals formed by homolytic cleavage of hydrogen peroxide. Autooxidations under these conditions *are not initiated* by formation of cyclohexenyl radicals by interaction with the catalyst and propagation by reaction with triplet molecular oxygen. Furthermore, it may be noted that radical

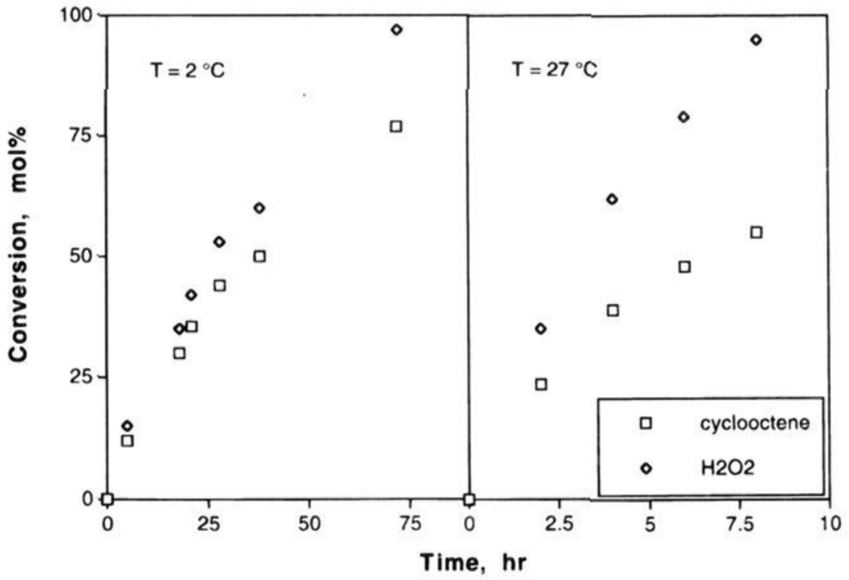

Figure 4. Effectivity of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ as a catalyst in terms of hydrogen peroxide yields in epoxidation of cyclooctene. Reaction conditions: 0.2 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium cation, 1 mmol of cyclooctene, 1.5 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane. Conversions of H_2O_2 and cyclooctene are given as mol % of initial quantity of each compound introduced. Thus, the effective final yield of H_2O_2 (mol % of H_2O_2 per mol of cyclooctene oxide product) is 55% at 2 °C and 41% at 27 °C.

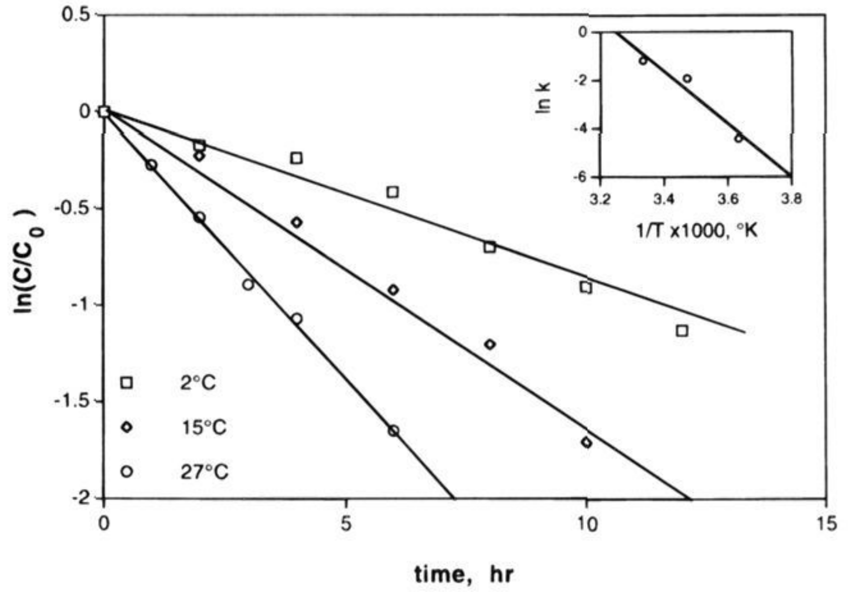

Figure 5. Kinetic profiles of cycooctene epoxidation as a first-order plot and as a function of temperature. Reaction conditions: 1.0 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium cation, 1 mmol of cyclooctene, 2 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane. The insert is a plot of the measured rate constants (slopes) as a function of temperature in an Arrhenius plot.

chain reactions are in general not readily propagated in these systems for oxidation of fairly reactive ethylbenzene failed in the presence of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ and hydrogen peroxide.

Again using cycloctene as a probe, however at ten times higher catalyst concentrations, kinetic measurements of the conversion as a function of temperature showed the reaction to be first order in cyclooctene, Figure 5. Computed initial rates, r_0, from the reaction profiles are in a range of 0.0035 to 0.014 mol/s per mol of catalyst at temperatures between 2 and 27 °C. The activation parameters for the cyclooctene epoxidation were computed by use of the Arrhenius equation from the observed rate constants, Figure 5 (insert). The activation energy was 10.9 ± 0.3 kcal/mol ($\Delta H^{\ddagger}_{298} = 10.2 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger}_{298} = -34.5 \pm 1.6$ eu). The activation energy although low for catalytic reactions in general is quite typical for biphasic oxidation reactions and/or oxygen transfer reactions.[16] The reaction was found to be first order at 2 °C in both hydrogen peroxide and

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[16] Dobson, J. C.; Seek, W. K.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1513.

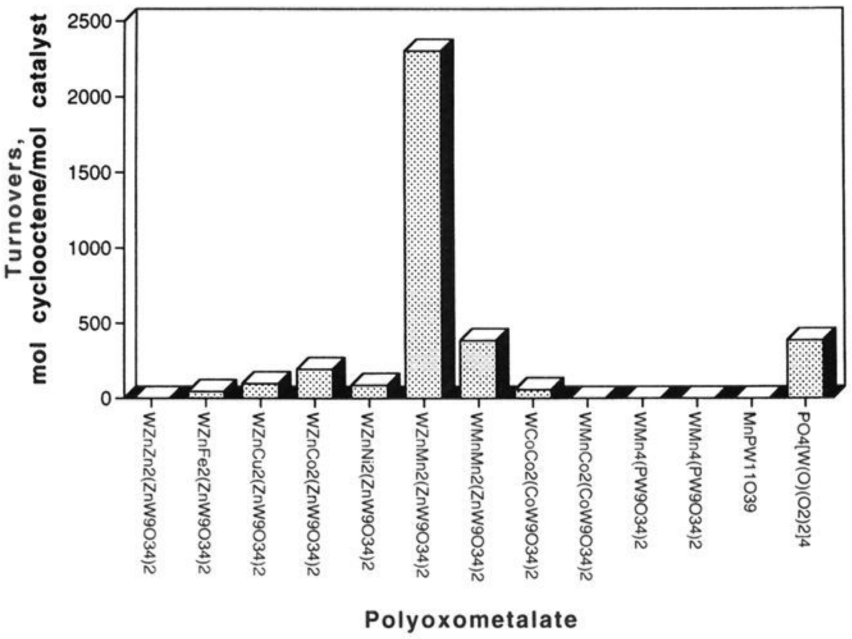

Figure 6. Epoxidation of cyclooctene as a funtion of polyoxometalate catalyst. Reaction conditions: 0.2 μmol of polyoxometalate, 5 μmol of methyltricaprylammonium cation, 1 mmol of cyclooctene, 2 mmol of 30% hydrogen peroxide, 1 mL of 1,2-dichloroethane; time 22 h.

$[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyst concentration. The reaction orders were computed from the slope of a log concentration *vs* log observed rate constant in both compounds by measuring initial rates at various initial hydrogen peroxide and $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ concentrations.[17] The results of the kinetic measurements for the epoxidation of cyclooctene are summarized in eq 4.

$$\text{rate} = k[[\text{catalyst}]^1[\text{c-C}_8\text{H}_{16}]^1[\text{H}_2\text{O}_2]^1 \qquad (4)$$

where $k = (1.02 \times 10^6)\ e^{-10900/RT}$.

Another important outlook on the use of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate was to compare its catalytic activity with other (a) transition metal substituted polyoxometalates of the same or similar structure, (b) manganese substituted polyoxometalates and (c) common polyoxometalates catalysts. The results, as can be found in Figure 6, show that the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ anion is unique in its catalytic activity. The "parent" zinc substituted compound, $[WZnZn_2(ZnW_9O_{34})_2]^{12-}$, showed no catalytic activity. The presence of three or more transition metals "sandwiched" between truncated Keggin fragemnts as in $[WMnMn_2(ZnW_9O_{34})_2]^{12-}$, $[WCoMn_2(CoW_9O_{34})_2]^{12-}$, $[WCoCo_2(CoW_9O_{34})_2]^{12-}$, $[Mn_4(PW_9O_{34})_2]^{10-}$, and $[Fe_4(PW_9O_{34})_2]^{10-}$ yielded only slightly active or even totally inactive catalysts.[18] The disubstituted compounds $[WZnTM_2(ZnW_9O_{34})_2]^{12-}$ with different transition metals (TM = Ni, Fe, Co, and Cu) prepared by the literature procedure[10] showed only minimal or no catalytic activity. Equally inactive was the more simple monosubstituted Keggin compound $PMnW_{11}O_{39}{}^{5-}$. Substantial activity was also found with the well-known $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ peroxometalate which was, however, found to be less active than the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ compound.[19] Interestingly, epoxidations carried out in monophasic reaction systems using solvents such as acetonitrile, *tert*-butyl alcohol, or acetone invariably failed. On the other hand, reactions could be carried out in a variety of solvents which yielded a biphasic system such as 1,2-dichloroethane, toluene, methyl *tert*-butyl ether, and ethyl acetate although the former showed by far the highest activity—2080, 280, 190, and 65 turnovers, respectivly, for selective epoxidation of cyclooctene to cyclooctene oxide under the conditions of Fig 2 at 2 °C. We have no firm explanation for this observation except to conclude that the presence of water as a strongly coordinating solvent in the organic reactive phase is detrimental to catalytic activity. Presumably, unfavorable competition in coordination to the catalytic active site between water and hydrogen peroxide shuts down the reaction in monophasic systems.[2] In biphasic systems hydrogen peroxide can effectively be transferred to the organic phase by the quaternary cation.[20,21]

Identification, Properties, and Stability of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ Polyoxometalate as the Catalytically Active Species. Although $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ is one in a family of isostructural compounds which have been analyzed by X-ray crystallography and by ^{183}W NMR for diamagnetic analogues, few other properties of this compound have been studied. After learning about the high catalytic activity of these compounds, we sought to further investigate the spectroscopic, electrochemical, and magnetic properties of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ in pure form, solution, and under reaction conditions. These measurements are important in testing the oxidative and solvolytic stability of the catalyst and in trying to suggest a mechanism for the hydrogen peroxide mediated oxidations.

It can be tacitly assumed from the literature procedure[10] for the preparation of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ from $[WZnZn^{II}_2(ZnW_9O_{34})_2]^{12-}$ that the manganese(II) cations may replace the zinc(II) cation either in the terminal position (M1, Figure 1) surrounded by five oxygens belonging to the $(ZnW_9O_{34})^{12-}$ fragments and a sixth labile aquo ligand or in a bridging position (M2, Figure 1) surrounded by six oxygens belonging to the $(ZnW_9O_{34})^{12-}$ fragments. Since by X-ray crystallography one cannot unambiguously locate the manganese and zinc cations because of their similar electron density coupled with the possibility of various mixtures and since the presence of paramagnetic manganese(II) precluded the identification of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ by ^{183}W NMR, we sought other methods to define the manganese(II) positions. Magnetic susceptibility measurements as pictured by the Curie plot are shown in Figure 7. The deviation from linearity indicates either weak antiferromagentic interaction between two Mn(II) centers or the presence of a paramagnetic impurity.[22] If there is indeed an antiferromagnetic interaction between manganese centers, then it is most likely that at least one manganese center is in the M2 bridging position and the other is in the M1 terminal

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[17] The measured slopes (orders) were 0.96 ± 0.04 ($r^2 = 0.97$) for $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ and 1.11 ± 0.05 ($r^2 = 0.92$) for 30% H_2O^2. Errors are given at a 90% confidence interval and *t*-values showed significance at a 99.99% significance level.

[18] It is very conceivable that the activity observed for the $[WMnMn_2(ZnW_9O_{34})_2]^{12-}$ compound is in fact due to the presence as an impurity of the disubstituted $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$.

[19] For the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate, the catalyst was often effective to very high turnovers, whereas for $[(C_8H_{17})_4N]_3PO_4[W(O)(O_2)_2]_4$ reactions *always* stopped after 350–850 turnovers for all substrates (perhaps poisoned?). Others (Dengel, A. W.; Griffith, W. P.; Parkin, B. C. *J. Chem. Soc., Dalton Trans.* **1993**, 2683) have observed up to 1080 turnovers using a different cation $[(C_6H_{13})_4N]_3PO_4[W(O)(O_2)_2]_4$. It seems that $\{PO4[W(O)(O_2)_2]_4\}^{3-}$ has higher *initial* catalytic activity in the more difficult epoxidation of terminal alkenes such as 1-octene, whereas $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ is more effective for easier to oxidize cyclooctene. It would therefore appear that while the activity of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ is more sensitive to the substrate it has a significantly larger catalytic capacity. A full comparison of catalytic activity and selectivity (for cyclooctene selectivity is quantitave to the epoxide) of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ and $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ is beyond the scope of this paper, but it is certainly desirable.

[20] Dehmlow, E. V.; Slopianka, M. *Chem. Ber.* **1979**, *112*, 2765.

[21] The effect of the identity of the quaternary ammonium salt on transition metal catalyzed oxidations with aqueous hydrogen peroxide in biphasic media is an important subject. Neumann, R.; Khenkin, A. M. *J. Org. Chem.* **1994**, *59*, 7577.

[22] Carlin, R. L.; van Duyneveldt, A. J. *Magnetic Properties of Transition Metal Compounds*; Springer-Verlag: Berlin, Heidelberg, 1977.

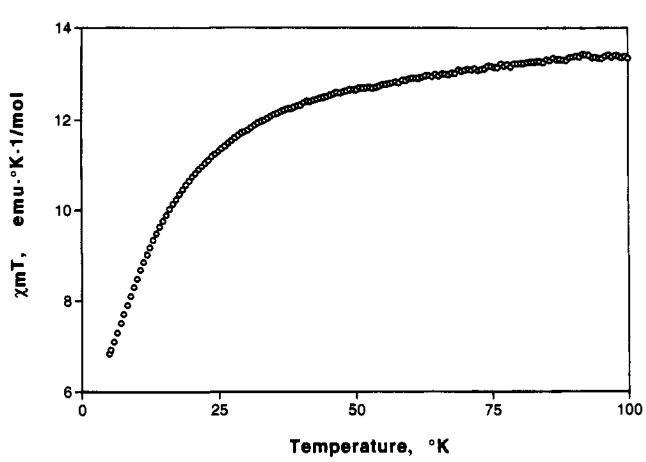

Figure 7. Plot of molar susceptibility (χ_m) as a function of temperature for $Na_{12}WZnMn_2(ZnW_9O_{34})_2$.

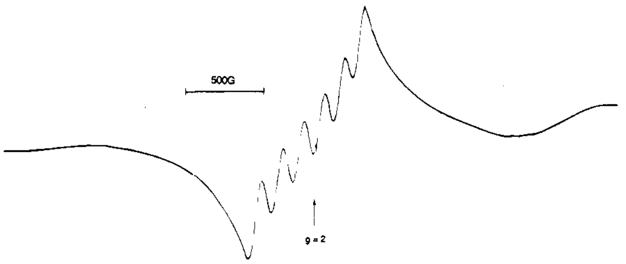

Figure 8. ESR spectrum of $Na_{12}WZnMn_2(ZnW_9O_{34})_2$ as a polycrystalline solid at 120 K.

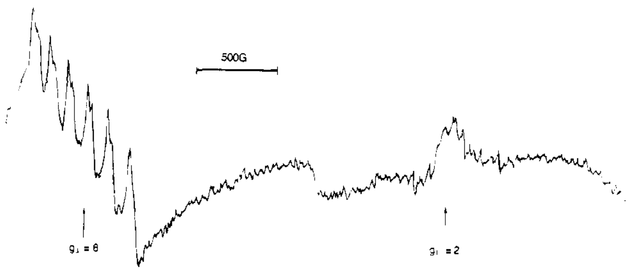

Figure 9. ESR spectrum of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ in 1,2-dichloroethane at 120 K.

position[23] since it is not likely that two manganese atoms in the terminal position would magnetically interact considering an interatomic distance of at least 5 Å. Other evidence to be presented below, however, indicates the likelihood of a paramagnetic impurity on the scale of 1−3% as the cause of deviation from linearity in the Curie plot.

The polycrystalline powder ESR spectrum of $Na_{12}WZnMn_2(ZnW_9O_{34})_2$ in shown in Figure 8. The six-line isotropic spectrum centered at $g = 2$ is typical and as expected for a manganese(II) ($I = {}^5/_2$) d^5 compound in a high-spin octahedral field.[24] The ESR spectrum of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ in an organic phase is very different. Thus, a well-dried 3 mM solution of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ in 1,2-dichloroethane yields an ESR spectrum as shown in Figure 9. This anisotropic spectrum[25] has a weak absorption at $g_{\parallel} = 2$ and a strong absorption with a six-line hyperfine at $g_{\perp} = 6$. Such an anisotropic spectrum is attributed to a manganese(II) d^5 compound in a high field tetragonal or square pyrimidal field.[24] Our interpretation of this result is that in the organic solvent the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ anion has lost the more labile aquo ligand thus changing coordination at the manganese center from octahedral to tetragonal pyramidal. This loss of an aquo ligand from the transition metal center upon extraction into an apolar organic phase has been observed in monosubstituted manganese and other Keggin compounds in the past.[26] This ESR spectrum therefore clearly indicates that the manganese atoms may be located at the M1 terminal positions only.

In a third experiment as described in the Experimental Section, $Na_{12}WZnMn_2(ZnW_9O_{34})_2$ was extracted into 1,2-dichloroethane using methyltricaprylammonium chloride as extractant. The organic phase was then washed with distilled water and the aqueous phase was analyzed by atomic absorption spectroscopy for the presence of manganese. The analysis showed that 2.1 wt % of the total possible manganese was washed into water.[27] Since only anionic manganese polyoxometalate species are expected to remain in the organic phase due to the presence of an excess of a highly hydrophobic counter cation, the sourse of manganese in the aqueous phase must be from a cationic manganese impurity. Thus, the magnetic susceptibility, ESR, and atomic absorption experiments and the higher intrinsic lability of the terminal position lead to the conclusion that the catalyst can be best described as in Figure 1 with the manganese atoms at the M1 terminal position bound by a aquo ligand. There are probably some manganese impurities in the $Na_{12}WZnMn_2(ZnW_9O_{34})_2$ polyoxometalate.

Having identified the catalyst precursor, the next phase of the research was to investigate the stabilty of the compound under reaction conditions. This study is especially important since it has been observed that more simple Keggin type compounds although oxidatively and thermally stable are solvolytically degraded in the presence of aqueous hydrogen peroxide. One may qualify this statement, however, by saying that although this degradation is very fast in aqueous phases, in organic solvents the degradation of the Keggin polyoxometalate may be largely inhibited.[8] Thus, transfer of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate into an organic phase prior to addition of hydrogen peroxide as carried out in this research *a priori* would tend to reduce the susceptibility to solvolytic hydrogen peroxide degradation. Additionally, under conditions that the Keggin compounds, $XM_{12}O_{40}{}^{q-}$ (X = P, Si, Ge, etc.; M = Mo, W), do degrade, reasonably active catalysts have been identified only for X = P. A third mute point is that the original $[WZnZn_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate synthesis[10] was performed by aging solutions of $[Zn(H_2O)(ZnW_{11}O_{39})]^{8-}$ monosubstituted Keggin type structures showing that the "sandwich" type compound is thermodynamically more stable.

By comparing the catalytic activity of the structurely similar compounds, $[WZnZn_2(ZnW_9O_{34})_2]^{12-}$, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, $[WMnMn_2(ZnW_9O_{34})_2]^{12-}$, and $[Mn_4(PW_9O_{34})_2]^{10-}$, Figure 6, and by assuming similar solvolytic stability toward hydrogen peroxide it is clear that the presence of manganase is required for catalytic activity, but only the disubstituted compound has very high catalytic activity. Formation of simpler peroxotungstates not containing manganese is thus a highly unlikely explanation for catalytic activity. This is especially obvious since the only phosphorus-containing compound, $[Mn_4(PW_9O_{34})_2]^{10-}$, where formation of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, a proven oxidation catalyst, is possible had no catalytic activity. The same line of reasoning excludes a more simple manganese

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[23] Gómez-Garcia, C. J.; Coronado, E.; Borrás-Almenar, J. J. *Inorg. Chem.* **1992**, *31*, 1667. Gómez-Garcia, C. J.; Coronado, E.; Gómez-Romero, P.; Casañ-Pastor, N. *Inorg. Chem.* **1993**, *32*, 3378.

[24] Wertz, J. E.; Bolton, J. R. *Electron Spin Resonanace: Elementary Theory and Practical Applications*; McGraw Hill: New York, 1972.

[25] Such ESR spectra are common for mono-axially bound iron and managanese porphyrins. An early example can be found in: Ehrenberg, A. *Ark. Kemi* **1962**, *19*, 119.

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

[27] This translates to 1.1 mg of Mn impurity per 6000 mg of polyoxometalate.

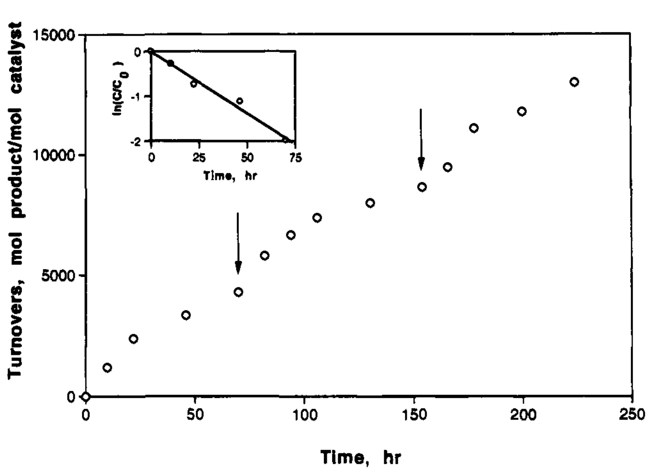

Figure 10. Kinetic profile of cyclooctene epoxidation with addition of additional substrate and oxidant at 2 °C. Reaction conditions: 0.2 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium cation, 1 mmol of cyclooctene, 2 mmol of 30% H_2O_2, 1 mL of 1,2-dichloroethane. At the times marked with arrows the aqueous phase was decanted and addtional portions of 1 mmol ccyclooctene and 2 mmol 3% H_2O_2 were added. Insert: kinetic profile of the first 72 h as a first order plot.

compound as the active catalytic species. In such a situation $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, $[WMnMn_2(ZnW_9O_{34})_2]^{12-}$, and $[Mn_4(PW_9O_{34})_2]^{10-}$ should have similar activity. The possible degradation of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyst should also have an effect on the kinetic profile of the reaction either by appearance of an induction period or deceleration of the rate by loss of active species. Neither phenomena is observed in this case. A kinetic profile of the oxidation of cyclooctene at 2 °C at a low catalyst loading of 1:5000 catalyst:substrate ratio, Figure 10, shows that the reaction is cleanly first order in cyclooctene over a wide range of 0 to 4300 turnovers (0–86% yield). Even addition of two more portions of 30% H_2O_2 and cyclooctene after 4300 and 8650 turnovers shows no change in the kinetic profile. Degradation of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ by hydrogen peroxide could also form simple water soluble cationic species. In order to test for such a scenario, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ dissolved in 1,2-dichloroethane was mixed with hydrogen peroxide and with water as a control for 6 h. The aqueous phase was then analyzed for zinc and manganese by atomic absorption. The weight percent of zinc or manganese found in the aqueous phase was 2.1% (H_2O) and 2.3% (H_2O_2) for manganese and 2.3% (H_2O) and 1.9% (H_2O_2) for zinc.[28] Thus, there was no significant difference between $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ treated with hydrogen peroxide or with water. Additionally, the catalytic activity of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ treated with water or peroxide was unchanged relative to the original untreated catalyst.

The preferred method for studying the stabilty of the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ anion under reaction conditions would be to compare the ^{183}W NMR spectrum before and after an oxidation reaction. Unfortunately, the presence of the paramagentic manganese center prevented the aquisition of meaningful spectra. Alternatively, we studied the IR and ESR spectra of the $WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyst before and after reaction. Comparison of the ESR spectra of $WZnMn_2(ZnW_9O_{34})_2]^{12-}$ in the organic phase before and after stirring with 30% H_2O_2 for 6 h revealed that the spectrum attributable to five-coordinate manganese(II), Figure 9, was virtually unchanged. The IR spectra of $WZnMn_2(ZnW_9O_{34})_2]^{12-}$ is shown in Figure 11a. The IR spectrum has peaks attributable to W–O and Zn–O vibrations at 1060 (w) (Zn–O); 954 (sh); 919 (s) (W–O$_t$); 868 (s) (W–O$_c$–W); 793 (sh); 768 (s) (W–O$_e$–W); and 723 (s) cm^{-1} (W–O$_b$–W) (t, terminal; c, corner sharing; e, edge sharing; b, sandwich bound). After addition of hydrogen peroxide a somewhat different IR spectrum, Figure 11b, (peaks at 1060 (w), 952 (sh), 920 (s), 869 (s), 818 (m), 793 (m), 722 (s) cm^{-1}) is observed. The major change is the almost complete disappearance of the peak at 768 cm^{-1} coupled with the appearance of a new peak at 818 cm^{-1} typically attributable to formation of a peroxo species. One may observe that a peak at 793 cm^{-1} also appears. Careful examination of the spectrum shows that this could be either a new peak, perhaps also attributable to a peroxo vibration, or more likely a more clearly visible peak, previously only a shoulder peak, now more clearly observable upon addition of H_2O_2 due to the disappearance of the peak at 768 cm^{-1}. After decomposition of the excess H_2O_2 by aqueous KI, the IR spectrum is then almost again identical to that of $[WZnMn_2(ZnW_9O_{34})_2]^{12}$ prior to the addition of hydrogen peroxide, Figure 11c. Considering, therefore, the spectroscopic results (atomic absorption, ESR, and IR), the kinetic evidence, and the unique activity of the disubstituted manganese polyoxometalate, we believe that the catalyst precusor, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, is stable over a long period of catalytic activity.[29]

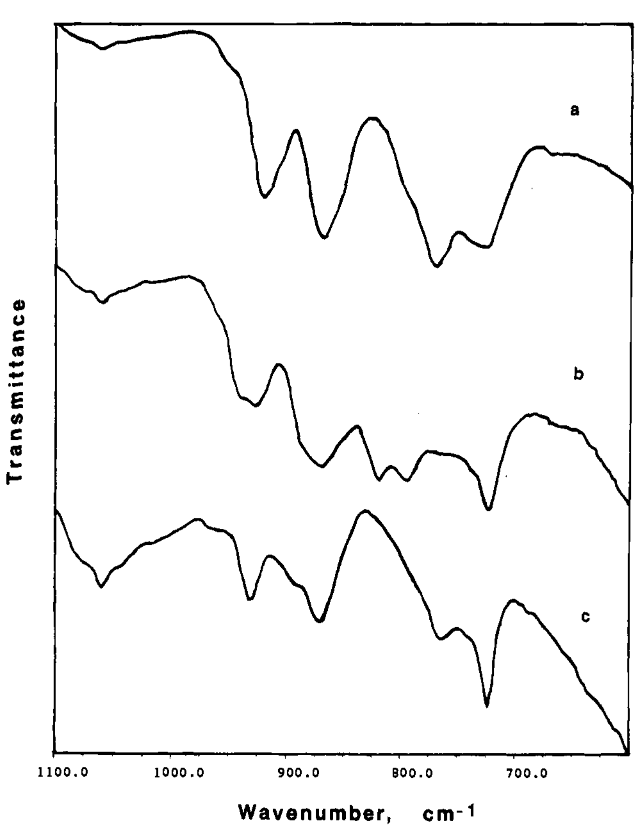

Figure 11. IR spectra of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ before during and after reaction. (a) before reaction, (b) after addition of 30% H_2O_2 and (c) after demposition of excess 30% H_2O_2 with aqueous 10% KI.

After providing reasonable evidence that the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion is the active catalyst precursor, there remains the question of the exact mechanism of catalytic action

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[28] These are in fact very minor impurities as they translate into manganese and zinc impurities on the scale of 0.02 wt % (~1 mg of impurity per 6000 mg of polyanion) based one the weight of the entire $Na_{12}WZnMn_2(ZnW_9O_{34})_2$ polyoxometalate.

[29] One might add that although one could argue that the small impurities of manganese and zinc could be somehow the source of high catalytic activity, we feel that such a possiblity is very remote considering that simple compounds such as $Mn(OOCCH_3)_2$ and $Zn(OOCCH_3)_2$ show no catalytic activity.

which first and foremost must plausibly explain the unique activity of the specific $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ anion. From a fundamental point of view at least two basically different explanations can be forwarded. The first approach could be to picture the catalyst as an "inorganic porphyrin". In such a scheme, the low-valent transition metal, Mn(II), is considered bound by an inorganic ligand, the lacunary polyoxometalate, which can act as a multielectron acceptor. Addition of an oxygen donor brings about formation of a very reactive high-valent manganese−oxo intermediate, capable of alkene epoxidation. In the past, such a representation has been used to explain metalloporphyrin-like properties such as dioxygen binding,[26] formation of high valent species with stoichiometric oxygen transfer,[30] and reactions with oxidants such as iodosobenzene, sodium periodate, sodium hypochlorite, and *tert*-butyl hydroperoxide.[31] Thus, using for example iodosobenzene as oxygen donor the formation of active high-valent Mn(IV) or Mn(V) oxo species could be the basis for high catalytic activity. However, a parallel oxidation of cyclooctene with iodosobenzene and hydrogen peroxide (0.2 μmol of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, 5 μmol of methyltricaprylammonium chloride, 1 mmol of substrate, 2 mmol of oxidant, 1 mL of 1,2-dichloroethane; time 24 h) showed for iodosobenzene there were 28 turnovers whereas for hydrogen peroxide there were 4100 turnovers. This result showing such a large difference in catalytic activity seems to be incompatible (see also data below) with an "inorganic porphyrin" type oxidation by a high-valent manganese−oxo species.

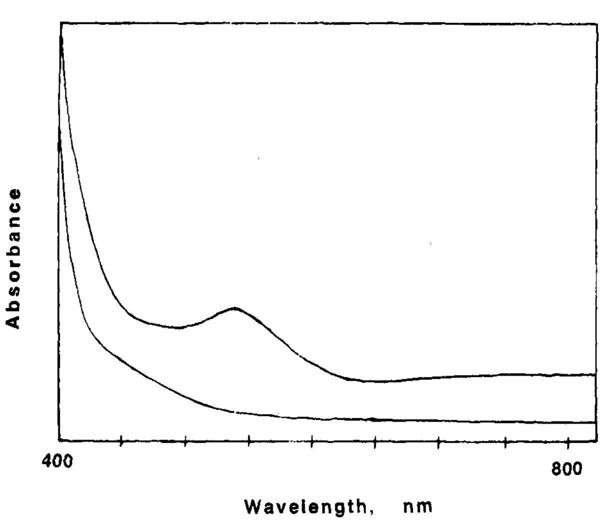

Figure 12. UV spectra of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$. (Bottom) Spectrum of $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ in 1,2-dichloroethane before addition of 30% H_2O_2. (Top) Spectrum of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ in 1,2-dichloroethane 2 h after addition of 30% H_2O.

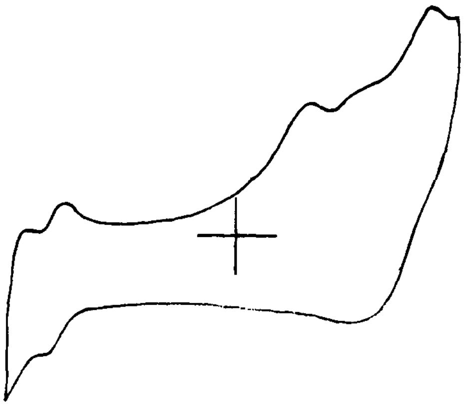

Figure 13. Cyclic voltagram of $Na_{12}WZnMn_2(ZnW_9O_{34})_2$ in 0.5 M NaCl at pH = 7.

A more favorable and alternative approach useful in explaining the high activity of the hydrogen peroxide $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyzed oxidation would be to surmise that the oxidation proceeds by the common peroxotungstate intermediate.[2] In such an approach, one must forward a line of reasoning to explain the unique but uncertain function of the manganese center. One may speculate that some synergestic intramolecular interaction between a tungsten peroxo species with a manganese center could explain catalytic activity. In fact, this type of synergism may explain the high activity of the $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ peroxometalate where one of the two peroxo oxygen atoms is simultaneously bound to two W(VI) atoms,[32] increasing the electrophilicty of the oxygen by polarization of electron density and therefore its reactivity to nucleophilic substrates. The change in the IR spectra, Figure 11, upon addition of H_2O_2, specifically the appearance of a typical peroxo absorbance at 818 cm^{-1}, indicates that the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ catalyst precusor indeed can form a stable peroxometalate intermediate which is probably the catalytically active species in this reaction system. The possible function of the manganese center and more specifically the steady state oxidation state was studied further. Examination of the UV−vis spectrum, Figure 12, of $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ in 1,2-dichloroethane after addition of aqueous hydrogen peroxide and mixing for 2 h shows the formation of a distinctive peak at 530 nm attributable to the partially oxidized species[10,33] $[WZnMn^{II}_{2-x}Mn^{III}_x(ZnW_9O_{34})_2]^{(12-x)-}$, where $1 \leq x \leq 2$. The oxidation of manganese with hydrogen peroxide is not complete as Mn(II) residues remain as can be observed by taking the ESR spectrum which is always the same observed in Figure 9. Cyclic voltammetric measurements, Figure 13, indicate two different Mn^{2+}/Mn^{3+} oxidation potentials for the $Na_{12}WZnMn^{II}_2(ZnW_9O_{34})_2$ compound at pH = 7: first, an electrochemically irreversible Mn^{2+}/Mn^{3+} oxidation at *ca.* 0.2 V for one of the two manganese cations and then a reversible Mn^{2+}/Mn^{3+} oxidation at *ca.* 0.45 V for the other (second) manganese cation. These redox potentials are not especially unusual for a manganese-substituted polyoxometalate. For example, the potential at 0.45V is almost identical to that of the mono-manganese-substituted Dawson compound, $P_2MnW_{17}O_{61}{}^{8-}$, reported in the literature,[34] but somewhat lower than that reported for the manganese Keggin compound.[35] Finally, a comparison of the catalytic activity of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ with the activity of an authentic "$[WZnMn^{III}_2(ZnW_9O_{34})_2]^{10-}$" polyoxometalate, better visualized

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(30) 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.

(31) 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.

(32) From the published crystal structure of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ [ref 15] certain peroxo oxygen atoms are bound to two W(VI) centers wheras others are not.

(33) It is virtually impossible to prepare a pure $[WZnMn^{III}_2(ZnW_9O_{34})_2]^{10-}$ ($x = 2$) compound. Thus using the literature procedure[10] where the relevant $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ anion is oxidized by permanganate, residues of non-oxidized Mn(II) species always remain as is easily observed by measuring the ESR spectrum of the polycrystalline powder.

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(35) Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875.

as $[WZnMn^{II}_{2-x}Mn^{III}_x(ZnW_9O_{34})_2]^{(12-x)-}$ $(1 < x < 2)$ was made. The epoxidation of cyclooctene under standard conditions showed that no significant difference in the catalytic activity of the two compounds could be observed. It would therefore appear from both a electrochemical and a chemical standpoint that the active catalytic intermediate could be best described as a tungsten peroxo compound where the polyoxometalate has mixed valency as concerns the manganese transition metal (Mn^{3+}/Mn^{2+}). It is tempting to state, however at this stage still only somewhat more of a working hypothesis, that the interaction of one of the manganese cations is the key to the unique activity of the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate. This property could for example be manifested in an epoxidation reaction by a peroxo → Mn^{3+} electronic interaction which would tend to make the peroxo oxygen a better electrophilic agent. On the other hand, an inverse Mn^{2+} → peroxo interaction would increase the nucleophilicity of the oxygen donor. The relative activity, *e.g.* 2,3-dimethyl-2-butene > cyclooctene > 1-octene, of the alkene substrates tends to support the former scenario. The picture is naturally clouded by the fact that a manganese center may always be oxidized or reduced directly by hydrogen peroxide by homolysis, eqs 2 and 3 (Figure 4). However, the unique activity of the disubstituted manganese compound in relation to a simple monosubstituted Keggin compound or the tri- or tetrasubstituted sandwich polyoxometalate indicates that steric or spacial effects probably also could play an important part in the unique activity of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$. There are ten different types of tungsten atoms[10] (one in the "belt", M2, six bridged to the transition metals in the "belt", and three more distant atoms) as is observable in the ^{183}W NMR of the diamagnetic analogue $[WZnZn^{II}_2(ZnW_9O_{34})_2]^{12-}$. It is thinkable, therefore, that interaction of hydrogen peroxide with the singular tungsten M2 center to form a tungsten peroxo intermediate, Figure 1 (only possible with the disubstituted compound[18]), leads to a unique manganese–peroxo–tungsten interaction that is responsible for potent catalytic activity since other structural analogues such as $[WZnZn^{II}_2(ZnW_9O_{34})_2]^{12-}$or $[WMnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ are inactive even though IR spectra in the presence of hydrogen peroxide indicate formation of peroxo species (peaks at 810–830 cm^{-1}). In the formation of tungsten peroxo intermediates at other tungsten atoms one can picture spacial interactions with adjacent manganese centers that could be duplicated in other *inactive* manganese polyoxometalates such as $PMnW_{11}O_{39}^{5-}$ or $Mn_4(PW_9O_{34})_2^{10-}$. Finally, it must be noted that the presence of a zinc atom at the M2 position could also be relevant to catalytic activity although there is no precedent for zinc oxo or peroxo species as active catalysts.

Conclusion

A polyoxometalate disubstituted with a manganese(II) transition metal, $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$, dissolved in an organic solvent by a quaternary ammonium counter cation, was used as a highly effective catalyst for the epoxidation of alkenes and the oxidation alcohols to ketones using 30% aqueous hydrogen peroxide as oxygen donor. Hundreds to thousands of turnovers were acheived with very high selectivity, >99%, to the epoxide product at high hydrogen peroxide yields and at ambient or subambient temperatures. Kinetic measurements on a typical epoxidation of cyclooctene showed the reaction to be first order in cyclooctene, hydrogen peroxide, and $WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate with an activation energy of 10.9 kcal/mol. Magnetic susceptibility measurements and ESR and atomic absorption spectroscopy showed that the Mn cations are at the terminal M1 positions with the labile aquo ligand removed in the organic phase. Kinetic measurements and IR, ESR, and atomic absorption spectroscopy indicated that the catalyst is oxidatively and hydrolytically stable over a range of at least 12500 turnovers of substrate. Cyclic voltammetry, UV–vis and IR spectroscopy, and comparison of activity with iodosobenzene as oxygen donor and other analogous catalysts lead us to propose a reaction pathway based upon a tungsten–peroxo intermediate. A unique tungsten peroxo intermediate placed at the M2 bridging tungsten, possible only for the disubstituted $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate, and its interaction with an adjacent manganese atom at M1 to form a highly reactive peroxo intermediate is hypothesized to be the reason that $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ is both a very reactive and a remarkably selective epoxidation catalyst. Further research such as attempts to isolate the postulated peroxo intermediate will be carried out in order substantiate the reaction pathway.

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