

Catalytic oxidation with hydrogen peroxide catalyzed by ‘sandwich’ type transition metal substituted polyoxometalates

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Abstract

The oxidation of organic substrates catalyzed by ‘sandwich’ type transition metal substituted polyoxometalates of the general formula, $\text{Na}_x\text{M}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$, ($\text{M} = \text{Ru}, \text{Mn}, \text{Zn}, \text{Pd}, \text{Pt}, \text{Co}, \text{Fe}, \text{Rh}$) was examined in three different reaction media. The manganese analog was dissolved in a 1,2-dichloroethane phase using a lipophilic quaternary ammonium counter cation. Various organic substrates were oxidized with 30% aqueous H_2O_2 . Alkenes reactivity increased as a function of the nucleophilicity of the double bond, but decreased as a function of steric crowding in the cyclohexene series. Alkenols with primary hydroxyl groups reacted chemo- and stereoselectively to form the corresponding epoxy alcohols. On the other hand, alkenols with secondary hydroxyl units did not react chemoselectively; both ketones and epoxy alcohols were formed. Diols were oxidized in most cases to ketols, except for 1,4-butanediol which yielded γ -butyrolactone. Secondary amines yielded hydroxyl amines except for piperidine which reacted with the solvent. A manganese containing catalyst supported on a functionalized silica particle was as active and selective as the organic solvent containing biphasic system for the oxidation of alkenes and alkenols. Reactions were also carried out by dissolving $\text{Na}_x\text{M}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ in aqueous solutions of 30% H_2O_2 , 70% *t*-butylhydroperoxide or 0.02 M potassium persulfate in the absence of solvent. Hydrogen peroxide degraded all the TMSP compounds. One degradation product was an effective and chemo- and stereoselective catalyst for the epoxidation of primary alkenols. In alcohol oxidation only the ruthenium precursor was active. For oxidations with 70% *t*-butylhydroperoxide all compounds were stable but only the $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ compound was active. Alcohols were oxidized selectively, however, alkenols yielded a mixture of products. With persulfate, some catalytic effects were observed in double bond oxidation.

1. Introduction

The development of catalysts for the selective and environmentally friendly oxidation of organic compounds is an important research goal designed to replace effective, but ecologically detrimental stoichiometric oxidants. In this context, there is interest in heteropolyoxometalate compounds where either the hetero atom or more usually one or perhaps more of the addenda are substituted by lower valent transition metals. These are also called transition metal substituted polyoxometalates, TMSPs

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[1]. These compounds are attractive as oxidation catalysts because one may view them as having reactive low valent transition metal centers complexed by inorganic oxometalate ligands which have high capacity for electrons. The exclusively inorganic nature of the polyoxometalate ‘ligands’ makes them inherently stable towards decomposition under oxidation conditions as well as themselves having interesting potential catalytic properties in the presence of peroxide oxidants as are typically found for molybdenum and tungsten oxides [2]. Both the stability and potential activity at the transition metal site and polyoxometalate ‘ligand’ is crucial to their future development and industrial application in catalytic oxidations, especially for fine chemicals [3].

The most common class of transition metal substituted heteropolyoxometalates and those also used in most of the earlier catalytic applications are those that are based on the Keggin and Wells–Dawson structures. They have been found to have interesting coordination chemistry including dioxygen

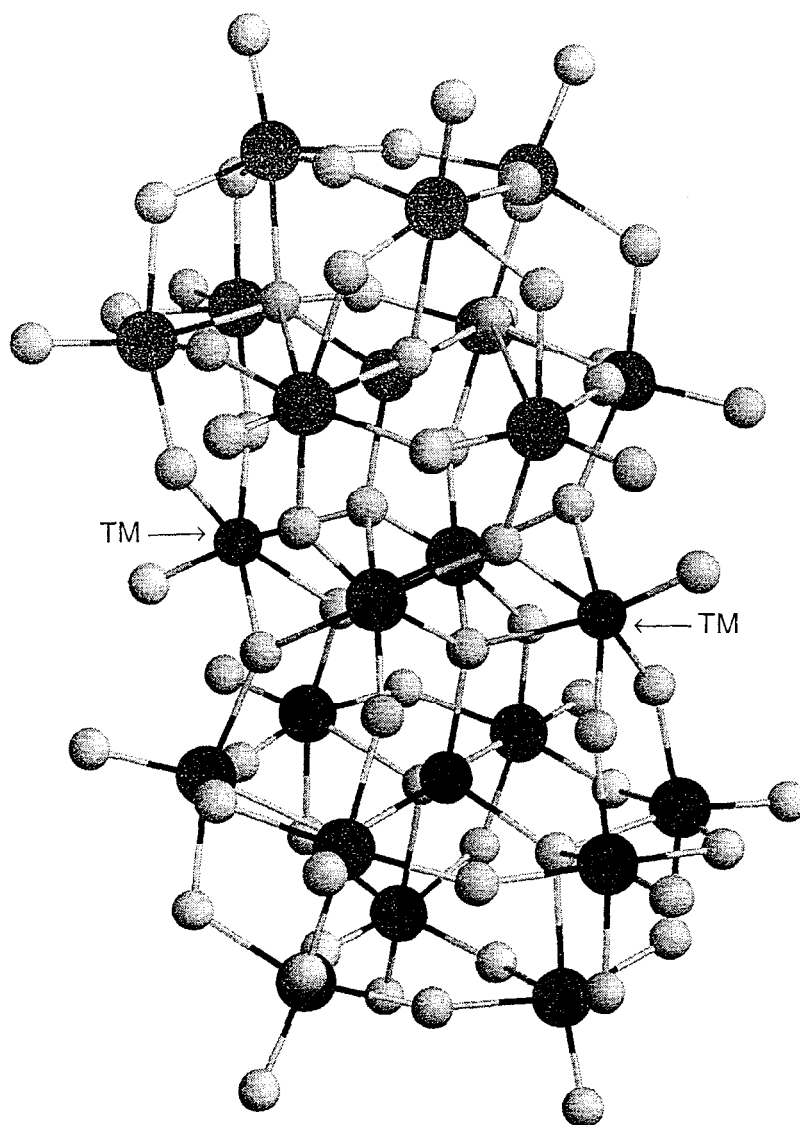


Fig. 1. Representation of the ‘sandwich’ type transition metal substituted polyoxometalates.

ligation [4], formation of high valent intermediates [5] and coordination of substrates [6]. These compounds have been used as catalysts for the epoxidation of alkenes by iodosobenzene [7] and hydroxylation of alkanes by *tert*-butylhydroperoxide [8]. Dioxygen has been used for the oxidation of olefins [9], alkanes, [10] sulfides [11] and hindered phenols [12]. The oxidation of alkanes and alkenes with other oxidants [13,14] has also been reported.

A major drawback in the use of transition metal substituted Keggin type compounds is their solvolytic instability towards aqueous hydrogen peroxide [15]. Thus, in the last few years another subclass of transition metal substituted heteropolyoxometalates has been shown by us and others to be both solvolytically stable and to have interesting catalytic properties for oxidation. These compounds can be pictured as having a 'ring' of transition metals 'sandwiched' between two trivacant forms of a parent Keggin structure [16,17], Fig. 1. Thus, $[\text{Fe(II)}_4(\text{PW}_9\text{O}_{34})_2]^{10-}$ has been shown to activate H_2O_2 for alkene epoxidation in monophasic systems [18], whereas $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ and $[\text{WZnRh(III)}_2(\text{ZnW}_9\text{O}_{34})_2]^{10-}$ were found to be highly active in biphasic oxidation with H_2O_2 [19,20]. Other noble metal (Pd(II), Pt(II) and Ru(III)) analogs of the manganese compound were also shown to have significant activity in alkene and alkane oxidation with both hydrogen peroxide and *t*-butylhydroperoxide [21] and the ruthenium analog was active in the highly selective oxidation of adamantane with molecular oxygen [22].

To date, the catalytic activity of the TMSP compounds has only been investigated for a limited number of substrates and substrate types. In this paper, we will present a fuller scope of the synthetic potential of $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ as catalyst using hydrogen peroxide as oxidant. Substrates include, in addition to alkenes, also dienes, alkenols, alcohols, diols and secondary amines. These oxidations of organic compounds by TMSP catalysts were carried out in organic solvents where the solubility of the TMSP catalyst is in the organic phase that was obtained by methathetical exchange of the original alkali cation with quaternary ammonium cations. Regularly, such catalytic oxygen transfer reactions are then carried out in biphasic systems using problematic chlorohydrocarbon solvents or in monophasic systems using polar (difficult to remove from water) solvents such as acetonitrile or *t*-butyl alcohol. The use of ammonium cations and organic solvents in practical processes increase their complexity and require careful solvent recovery. One possible solution is to attach the TMSP catalyst to a functionalized silica particle which may then be dispersed in an aqueous medium [23]. A simpler possible solution is to carry out the reaction in water with alkali salts of TMSP. In this paper we, therefore, also describe our results on the oxidation of organic compounds with aqueous hydrogen peroxide and for comparison *tert*-butyl hydroperoxide and potassium peroxy-monosulfate catalyzed by transition metal substituted sandwich type polyoxometalates, $\text{Na}_x\text{M}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$, (M = Ru, Mn, Pd, Pt, Co, Fe, Rh) in the absence of an organic solvent.

2. Experimental section

2.1. Materials

Sodium 5-zinc-19-tungstate, $\text{Na}_{12}\text{Zn}_3(\text{H}_2\text{O})_2\text{Zn}_2\text{W}_{19}\text{O}_{68} \cdot 46\text{H}_2\text{O}$, and transition metal derivative compounds containing Mn(II), Pd(II), Pt(II), Co(II), and Fe(II) synthesized by the reported literature procedure [16] and the Ru(III) and Rh(III) analogs were prepared by our procedure [20,21]. Organic compounds used as substrates in the oxidation reaction were reagent grade (> 99% purity) from Fluka and Aldrich and were used without additional purification. Aqueous 30% hydrogen peroxide (Merck), 70% *tert*-butylhydroperoxide (Fluka) and Oxone (triple salt containing KHSO_5 , Aldrich) were of reagent grade and used as is.

2.2. Instrumentation

Oxidation reaction products were characterized and quantified using reference compounds when available by use of GLC (Hewlett-Packard 5890 gas chromatograph) with a flame ionization detector and a 15 m × 0.3 mm 5% phenylmethylsilicone (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. The oxidation of benzyl alcohol was monitored by HPLC (Merck-Hitachi 6200) equipped with a UV absorption detector using a 25 cm × 4 mm C-18 reversed column with 9:1 methanol/water as eluent. UV–vis spectra were measured on a Hewlett-Packard 8452A diode array spectrometer.

2.3. Catalytic oxidation in biphasic media

Stock solutions of 1.0 mM $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ were prepared by mixing 0.10 mmol $\text{K}_{12}[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2] \cdot 23\text{H}_2\text{O}$ with 2.5 mmol methyltricaprylammonium chloride in 100 ml 1,2-dichloroethane and filtering off the precipitated KCl. Reactions were carried out in 3 ml vials equipped with stirring bars. In a typical reaction, substrate (1 mmol) was dissolved in 1 ml of the stock solution and the reaction brought to the desired temperature. The reaction was initiated by addition of 2 mmol 30% hydrogen peroxide to the stock solution under atmospheric conditions and stirred in what forms a biphasic reaction system. The reaction was monitored by withdrawing aliquots from the organic phase of the reaction medium and directly injecting the sample into the gas chromatograph.

2.4. Oxidation with supported catalysts

$(\text{MeO})_3\text{SiPhCH}_2\text{N} + (\text{CH}_3)_2(\text{CH}_2)_7\text{CH}_3\text{Cl}^-$ was prepared by reacting 10 ml (0.4 mol) $(\text{MeO})_3\text{SiPhCH}_2\text{Cl}$ with an equimolar amount of octyldimethylamine dissolved in 60 ml of petroleum ether (100–120) at reflux overnight. After cooling the product was filtered off (yield 40–70%) and used as is. The silicate particles were synthesized containing 2 mol% of the quaternary ammonium derivative by mixing together 132 mmol of $\text{Si}(\text{OEt})_4$, 0.34 mmol $\text{PhSi}(\text{OEt})_3$ and 2.6 mmol of $(\text{MeO})_3\text{SiPhCH}_2\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_7\text{CH}_3\text{Cl}^-$ in 75 ml EtOH; 20 ml of water and 0.7 ml dibutyltindilaurate (polymerization catalyst) were added and the mixture was held at 60°C for three hours. The solution was cooled and 0.17 mmol $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ was added as an aqueous solution. The solvents were slowly evaporated off (24–48 h) and dried at 50°C overnight. In this manner catalytic silicate particles containing 0.133 mol% $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ were obtained. Reactions were carried out by mixing 1 mmol of substrate, and 2 mmol of 30% aqueous H_2O_2 were mixed at room temperature for 24 h with the silicate xerogel. The substrate/ $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ ratio was 500/1.

2.5. Catalytic oxidation in aqueous media

Most reactions were carried out in 5 mL vials equipped with cap and a stirring bar. Using hydrogen peroxide as oxidant a typical procedure consisted of adding the substrate (0.2 mmol) to a solution of the alkali salt of the polyoxometalate catalyst (0.5 μmol) in 1 ml of 30% aqueous H_2O_2 (9 mmol). For *t*-butylhydroperoxide as oxidant a similar procedure involved substrate (0.2 mmol) and catalyst

(0.5 μmol) dissolved in 1 ml of 70% aqueous *t*-butylhydroperoxide (7.3 mmol). Reactions with potassium monopersulphate were performed using substrate (0.1 mmol) and catalyst (0.2 μmol) dissolved in 5 ml of a phosphate buffer (pH = 7) containing KHSO_5 (0.1 mmol). The mixture was stirred for a few hours at ambient temperature and sampled. Except for the oxidation of benzyl alcohol which was monitored by HPLC, the progress of the reactions was followed by GC. GLC analysis was performed on aliquots withdrawn directly from the reaction mixture and extraction of organic products into ether. The most effective GC conditions for the rapid quantification of products for the reactions of the various substrates involved the use of a 5% phenyl methyl silicone fused-silica capillary column, helium as the carrier gas, and temperature programming. The concentrations of peroxidic oxidants (hydrogen peroxide, *t*-butylhydroperoxide (TBHP) and monoperoxosulfate) were monitored by iodometric titration. The stability of the polyoxometalate catalysts was determined by their UV absorption intensity at 300 nm versus their initial optical density (A_t/A_0). For the hydrogen peroxide oxidation reaction, this measurement was carried out by HPLC separation of the H_2O_2 and polyoxometalate using the conditions mentioned above. This was necessary for commercial hydrogen peroxide has significant absorption at 300 nm. For the other oxidants where this problem does not exist the stability measurement was carried out directly.

3. Results and discussion

3.1. Biphase oxidation with 30% H_2O_2 catalyzed by $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$

Reactions in biphasic media were carried out by transferring the anionic $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ into an organic 1,2-dichloroethane (DCE) via metathesis of the potassium salt with tricaprylmethylammonium chloride (Aliquat 336). The original research [19] showed that the epoxidation of alkenes was highly selective with very little or no allylic oxidation at ambient or lower temperatures. Turnover numbers were also very high with only 0.02 mol% catalyst being required. From a synthesis point of view highest (up to quantitative) yields were obtained by performing the reactions in continuous cycles. Therefore, spent aqueous hydrogen peroxide solutions were separated and removed followed by addition of another portion of hydrogen peroxide. The number of required cycles is inversely proportional to the reactivity of the substrate. Two scales of substrate reactivity were observed. First, the alkene reactivity was a function of the nucleophilicity of the double bond so that the order of reactivity corresponded to the degree of substitution at the double bond and was 2,3-dimethyl-2-butene > 2-methyl-2-heptene > 1-methyl-2-heptene > 2-octene > 1-octene. Relative reactivities were 450/180/40/30/1. Additionally, cyclic alkenes such as cyclooctene were more active than acyclic analogs such as 2-octene. Second, the reactivity was strongly influenced by steric factors. Thus, it was found that for a cyclohexene series increased substitution at the double bond did not lead to increased reactivity but the opposite was found, i.e. cyclohexene > 1-methylcyclohexene \sim 2-carene \gg α -pinene. The relative reactivities were 350/280/270/1. These relative reactivities as borne out by substitution versus steric effects were investigated by using the oxidation of dienes as a probe. Thus, 4-vinylcyclohexene and limonene were exceptionally similarly reactive, however, the former reacted exclusively at the *endo* double bond whereas in limonene reactivity was similar for both double bonds. This result is especially atypical for limonene were epoxidation at the ring carbon is always preferred.

Further investigations into the catalytic utility of $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ in biphasic reaction media were carried out by studying the oxidation of alkenols. In this case, both chemoselectivity and

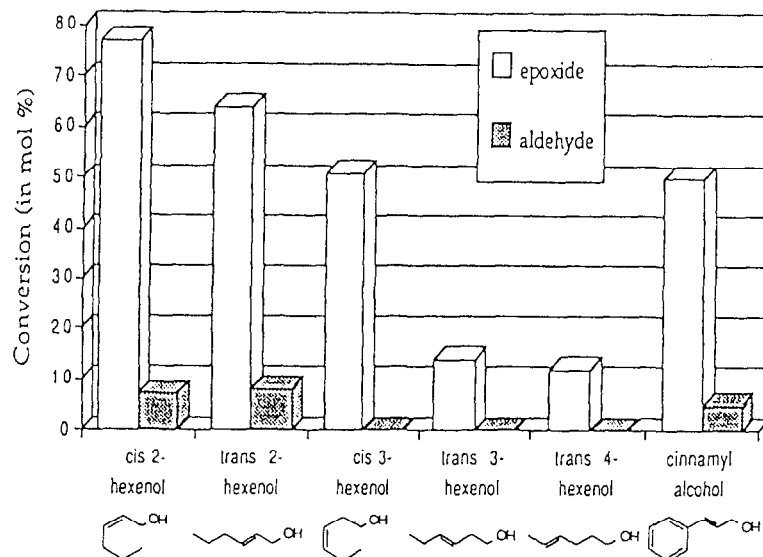


Fig. 2. Oxidation of alkenols with primary hydroxyl groups in a biphasic medium. Reaction conditions: 1 mmol substrate, 1 μ mol $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, 2 mmol 30% aqueous H_2O_2 at room temperature for 18 h.

stereoselectivity of the catalysts were measured. Comparison of the reactivity of alkenols with primary hydroxyl units, Fig. 2, shows a reactivity trend of allyl alcohols > homoallyl alcohols \sim ω -alkenols and *cis* > *trans*. The higher reactivity of *cis*- versus *trans*-substrates is typical for epoxidation reactions. The epoxides were all formed with 100% stereospecificity. The more reactive allyl alcohols such as 2-hexen-1-ol and cinnamyl alcohol showed less chemoselectivity and \sim 5–10% aldehyde was formed. This oxidation at the primary alcohol was somewhat unexpected since simple alcohols such as 1-octanol are inert. On the other hand, homoallyl alcohols and ω -alkenols were 100% chemoselective to epoxidation. For oxidation of alkenols with secondary hydroxyl groups, (Fig. 3) chemoselectivity was low so that both epoxy-ones and en-ones were formed in large quantities.

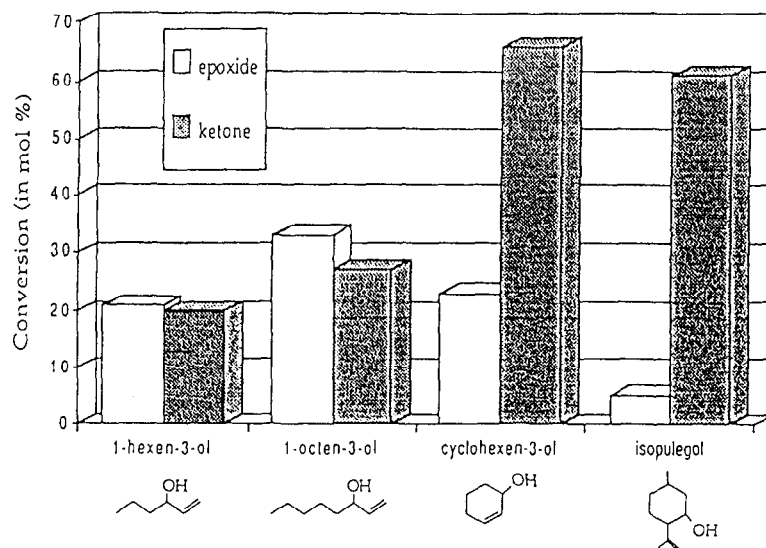
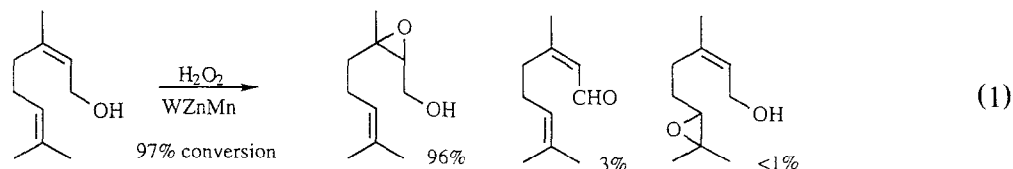
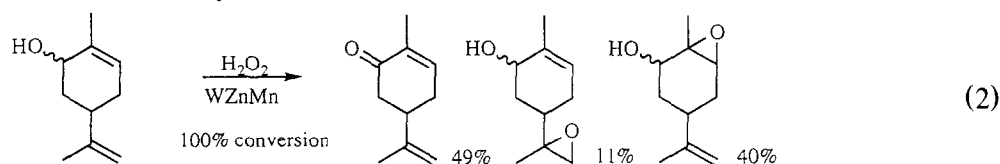


Fig. 3. Oxidation of alkenols with secondary hydroxyl groups in a biphasic medium. Reaction conditions: 1 mmol substrate, 1 μ mol $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, 2 mmol 30% aqueous H_2O_2 at room temperature for 18 h.

Thus, both cyclohexen-2-ol and isopulegol gave mostly the ketone as product, whereas 1-octene-3-ol and 1-hexen-3-ol gave equivalent amounts of ketone and epoxide. The high reactivity and selectivity for the oxidation of alkenols was then utilized for the oxidation of functionalized dienes. For example, geraniol was oxidized with high chemoselectivity to the allylic epoxide at 97% yield (Eq. (1)). This result is in line with the efficient oxidation of 2-hexen-1-ol versus the sluggish reaction of simple alkenes.



On the other hand the oxidation of carveol (Eq. (2)) was not selective. This result is compatible for what was found in the reaction of cyclohexen-2-ol and limonene.



Diols were the next substrates considered in the study of the catalytic activity of $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ in biphasic reaction media. In the past we reported that benzylic alcohols were more reactive than secondary acyclic and cyclic alcohols with ketones being formed as the sole product. Primary alcohols were not oxidized. The new results for the oxidation of diols is given in Table 1. The vicinal diols, 1,2-butanediol, 2,3-butanediol and 1-phenyl-1,2-ethanediol, yielded the α -ketols and in the later case also some benzaldehyde as a result of carbon–carbon bond cleavage. These results show that this system is relatively mild for vicinal diol oxidation. For 1,3-diols such as 1,3-butanediol and 2,5-pentanediol, the β -ketols were the exclusive products. Finally 1,4-butanediol was oxidized to γ -butyrolactone.

Secondary amines were also oxidized in the biphasic media (Table 2). Using *N,N*-dialkyl,

Table 1
Oxidation of diols with 30% H_2O_2 by $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ in a biphasic medium ^a

Substrate	Products ^b	Conversion (mol%) ^c
1,2-butanediol	2-keto-1-butanol	34
2,3-butanediol	2-keto-3-butanol	41
1,3-butanediol	3-keto-1-butanol	26
2,4-pentanediol	2-keto-4-pentanol	35
1-phenyl-1,2-ethanediol	2-hydroxyacetophenone 40, benzaldehyde 60	50
1,4-butanediol	γ -butyrolactone	17

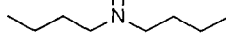
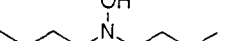
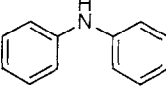
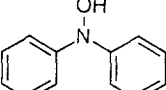
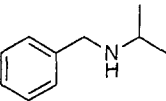
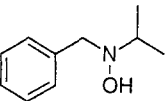
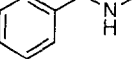
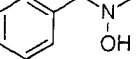
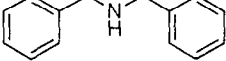
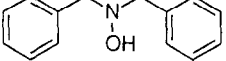

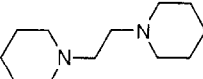
^a Reaction conditions: 1 mmol substrate, 1 μmol $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, 2 mmol 30% aqueous H_2O_2 , 1 mL 1,2-dichloroethane at room temperature for 18 h.

^b The amount of product is given as mol% of all products.

^c Conversion to all products.

Table 2

Oxidation of secondary amines with 30% H₂O₂ by [WZnMn(II)₂(ZnW₉O₃₄)₂]¹²⁻ in a biphasic medium

Substrate	Products ^b	Conversion, mol% ^c
		5
		5
		14
		15
		45
	benzaldehyde	33
		67
		66 ^d

^a Reaction conditions: 1 mmol substrate, 1 μmol [WZnMn(II)₂(ZnW₉O₃₄)₂]¹²⁻, 2 mmol 30% aqueous H₂O₂, 1 mL 1,2-dichloroethane at room temperature for 18 h.

^b The amount of product is given as mol% of all products.

^c Conversion to all products.

^d With 1,2-dibromoethane and 1,3-dichloropropane as solvent 45 and 51 mol% conversion, respectively.

N,N-diphenyl and mixed amines as substrates showed low yields of hydroxyl amines as products. Selectivity, however, was very high for *N,N*-dibutylamine, *N,N*-diphenylamine, *N,N*-methylbenzylamine and *N,N*-isopropylbenzylamine. For *N,N*-dibenzylamine the cleavage product, benzaldehyde became significant. Interestingly piperidine reacted completely differently. The only product was formed by a coupling reaction involving the solvent 1,2-dichloroethane and the substrate. Use of 1,2-dibromoethane as solvent gave the same product at lower yields. This result as well as the lack of product in the absence of peroxide and catalysts indicates that the reaction is not a typical nucleophilic substitution between the substrate and solvent. Use of 1,3-dichloropropane as solvent gave a similar coupled product. Piperidine was inert in dichloromethane or chloroform as solvent; no hydroxyl amine was formed at all.

One may conclude in saying that the use of the manganese substituted polyoxometalate, [WZnMn(II)₂(ZnW₉O₃₄)₂]¹²⁻, as catalyst for activation of aqueous hydrogen peroxide for oxidation in biphasic media is valuable for a variety of substrates. For non-functionalized alkenes, reactivity is based on a combination of two effects, the nucleophilicity of the carbon–carbon double bond and steric effects. Combination of different double bonds in a single molecule can lead to high regioselectivity depending on the relative reactivity at each alkene unit. Alkenols with primary hydroxy groups may be epoxidized with very high chemoselectivity and stereospecificity. On the other hand, alkenols with secondary hydroxy groups are oxidized with poor chemoselectivity. The system is a mild oxidant for diols, ketols being the major and in most cases only product. In the

oxidation of secondary amines, high selectivity of oxidation to hydroxyl amines could be achieved albeit at low yields. Piperidine did not reactive in the usual manner. With reactive solvents a coupling product was formed.

3.2. Aqueous phase oxidation with supported catalysts

As stated above the elimination of the use of an organic solvent in oxidation reactions with 30% hydrogen peroxide is a highly desirable synthetic aim. In order to meet this goal we have devised a catalytic assembly where a known catalyst active for example in epoxidation reactions is attached to a functionalized silica particle [23]. The functionalization includes an ammonium cation pendant to attach an anionic polyoxometalate and various percentages of hydrophobic phenyl groups. Optimal systems may be found by balancing the hydrophilicity and hydrophobicity of the catalytic surface so that both the hydrophobic organic substrate, for example, an alkene, and the hydrophilic oxidant will have similar adsorption to the silica particle surface leading to maximum effective oxidation.

The catalytic usefulness of this approach can be illustrated by attaching $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ to a silica particle having 20% pendant phenyl units and 3% pendant benzyldimethyloctylammonium cations as described in the experimental part. In Fig. 4, the results for the oxidation of both alkene and alkenol substrates at 25°C is shown. The results are comparable in terms of reactivity and selectivity to the results presented above for liquid–liquid solvent containing biphasic media. Clearly one may be able to dispense of the organic solvent. In addition, catalyst recovery is simplified by use of filtration of the silica particle.

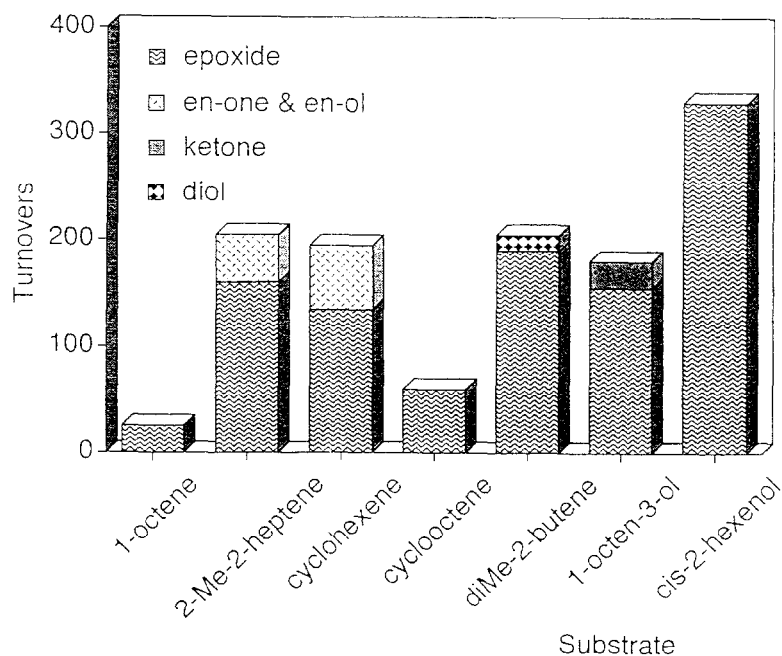


Fig. 4. Oxidation using a supported $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ catalyst. Reaction conditions: 1 mmol substrate, 2 μmol supported $[\text{WZnMn}(\text{II})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, 2 mmol 30% aqueous H_2O_2 at room temperature for 18 h.

Table 3
Oxidation of alcohols in 30% H₂O₂ catalyzed by Na₁₁Ru₂Zn₃W₁₉O₆₈^a

Substrate	Products ^b	mol%	Conversion ^c	Turnovers ^d
Benzyl alcohol	benzaldehyde	50	78	312
	benzoic acid	50		
1-phenylethanol	acetophenone	40	22	88
	1-phenyl-1,2-ethanediol	15		
	benzoic acid	45		
Cyclohexanol	cyclohexanone	100	5	20
2-heptanol	2-heptanone	100	18	72
2-propanol	acetone	100	16	64
1-heptanol	1-heptanal	100	1	4

^a Reaction conditions: 1 mL 30% H₂O₂ (10 mmol), 0.2 mmol of substrate, Na₁₁Ru₂Zn₃W₁₉O₆₈ (0.5 μmol) at 25°C, reaction time 2 h. During the course of the reaction ~ 50% of the oxidant is used up.

^b The amount of product is given as mol% of all products.

^c Conversion of substrate to all products (mol%).

^d Amount of total product formed per mol catalyst in 2 h.

3.3. Aqueous phase oxidation with 30% H₂O₂ catalyzed by Na_xM₂Zn₃W₁₉O₆₈

Eight different ‘sandwich type’ polyoxometalates of the general formula Na_xM₂Zn₃W₁₉O₆₈ (M = Ru, Mn, Pd, Pt, Co, Fe, Rh and Zn) were tested as catalysts for the oxidation of various organic substrate types using 30% aqueous hydrogen peroxide as the reaction medium. For highly hydrophobic non-functionalized alkenes such as cyclooctene, cyclohexene, styrene and 1-octene having practically no water solubility no oxidation of the substrate could be detected. On the other hand for the oxidation of alcohols (Table 3), of all the tested transition metal substituted polyoxometalates only the ruthenium (III) compound, Na₁₁Ru₂Zn₃W₁₉O₆₈, showed catalytic activity. The relative activity, 1-phenylethanol > benzyl alcohol > cyclohexanol > 2-heptanol > 1-heptanol, clearly showed the benzylic oxidation to be most facile. Secondary alcohols are more reactive than primary analogs and cyclic compounds are more reactive than acyclic ones. Examination of the oxidation of an allylic primary alcohol such as *cis*-2-hexenol having two reactive groups and slight water solubility revealed practically only epoxidation at the carbon–carbon double bond. In this case, however, all of the tested polyoxometalates had very similar catalytic activity. In the absence of TMSP compounds no reaction took place. Further investigations into this oxidation by 30% hydrogen peroxide using HPLC as a method for study of the catalyst stability showed that the ‘sandwich’ polyoxometalates are not stable under reaction conditions and are degraded. A pertinent example is shown in Fig. 5, where the concentration of hydrogen peroxide, Na₁₁Ru₂Zn₃W₁₉O₆₈, and epoxide product were followed for the oxidation of *cis*-2-hexenol. Significantly, the apparent concentration of Na₁₁Ru₂Zn₃W₁₉O₆₈ as measured by UV absorption at 300 nm drops by 50% in less than ten minutes¹. This decrease is accompanied by a very large consumption of 3 mmol hydrogen peroxide (6000 mol H₂O₂ per mol TMSP). The decreased absorption at 300 nm strongly indicates the formation of a new catalytic species with a lower molar extinction coefficient at 300 nm. This presumption of formation of the new catalytic species is strengthened by the observation of an induction period in the formation of *cis*-epoxide from *cis*-2-hexenol. Such induction periods are not observed in ‘sandwich’ TMSP

¹ It is interesting to point out that at low, 3 wt%, hydrogen peroxide concentrations neither the hydrogen peroxide nor the TMSP catalysts were decomposed, however, no oxidation was observed.

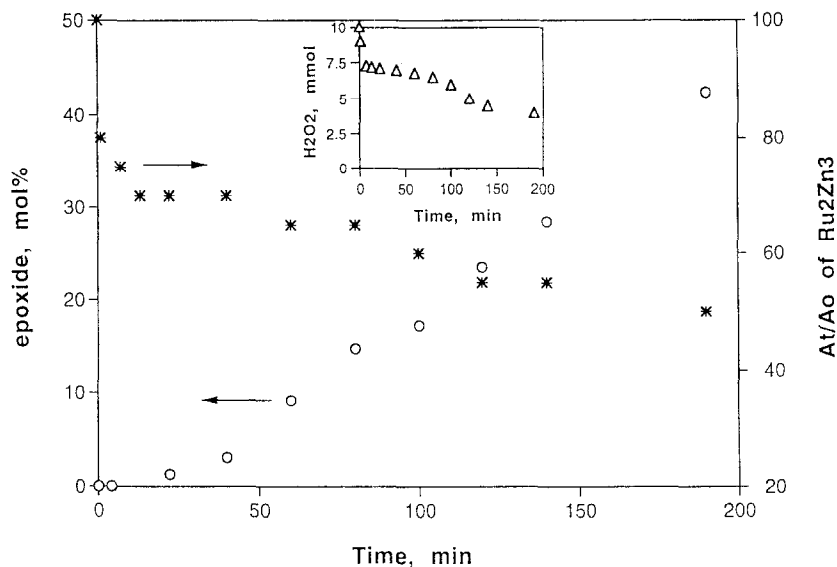


Fig. 5. Concentration versus time profiles of reaction components in *cis*-2-hexenol oxidation. Reaction conditions: 0.2 mmol *cis*-2-hexenol, 0.5 μ mol $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$, 10 mmol 30% aqueous H_2O_2 . The concentration of the epoxide was determined by GLC, the decomposition of H_2O_2 was measured by iodometric titration and the amount of catalyst was calculated from absorption measurements.

catalyzed oxidations in organic media described above. There is also a continued decrease in the optical density after the initial reaction period which leads us to conclude that there is an on-going slow degradation of the catalytically active species. The yield in hydrogen peroxide is rather low as it is decomposed at a rate of 5 mmol per mmol epoxide formed.

The product selectivity for the oxidation of a series of alkenols is presented in Table 4. For alkenols with primary hydroxy groups, the predominant reaction is the stereoselective epoxidation

Table 4
Oxidation of alkenols in 30% H_2O_2 catalyzed by $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ ^a

Substrate	Products ^b		Conversion ^c	Turnovers ^d
Cyclohexen-2-ol	cyclohexen-2-one	100	49	196
<i>Cis</i> -2-hexen-1-ol	<i>cis</i> -epoxide	91	96	384
	<i>trans</i> -epoxide	1		
<i>Cis</i> -3-hexen-1-ol	2-hexenal	8	20	80
	<i>cis</i> -epoxide	98		
<i>Trans</i> -2-hexen-1-ol	3-hexenal	2	87	348
	<i>trans</i> -epoxide	97		
4-hexen-1-ol	2-hexenal	3	19	76
	epoxide	89		
1-octen-3-ol	2-hexenal	11	12	48
	1-octen-3-one	50		
Carveol	1,2-epoxyoctan-3-ol	50	20	80
	carvone	15		
	2-3-epoxycarveol	85		

^a Reaction conditions: 1 mL 30% H_2O_2 (10 mmol), 0.2 mmol of substrate, $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ (0.5 μ mol) at 25°C, reaction time 2 h. During the course of the reaction ~ 50 % of the oxidant is used up.

^b The amount of product is given as mol% of all products.

^c Conversion of substrate to all products (mol %).

^d Amount of total product formed per mol catalyst in 2 h.

with little alcohol oxidation to aldehyde or ketone. Allyl alcohols are more reactive and chemoselective than homoallylic alcohols which are in turn more reactive and chemoselective than ω -hydroxy alkenes. For alkenols with secondary hydroxy units, the chemoselectivity was varied. For cyclohexen-2-ol, only the ketone was formed. Carveol on the other hand gave mostly epoxide, whereas, 1-octen-3-ol gave intermediate results. Interestingly, comparison of the product selectivity using the aqueous system described in Table 4 was similar to reactions carried out using $\text{Na}_2\text{WO}_4/30\% \text{H}_2\text{O}_2$ or tungstic acid/ H_2O_2 in water–methanol media as a solvent [24].

The fact that all the TMSP compounds showed similar reactivity in the oxidation of alkenols, combined with the kinetic results as presented in Fig. 5, clearly indicates that the active species in the alkenol oxidation is most likely an unidentified peroxotungstate intermediate devoid of a transition metal. This unknown peroxotungstate does not oxidize simple alkenes under the given reaction conditions. Although all the tested TMSP compounds were reactive in alkenol oxidation, the fact that only the ruthenium derivative was active in alcohol oxidation requires explanation. Our hypothesis is to assume that the ‘sandwich’ type polyoxometalates decomposed to a peroxotungstate and another more simple transition metal containing compound, which only in the case of ruthenium was reactive. This uncharacterized ruthenium complex is uniquely capable (as compared to the other transition metal analogs) in alcohol oxidation, perhaps by ruthenium mediated abstraction of hydrogen at the secondary carbon atom.

3.4. Aqueous phase oxidation by 70% *tert*-butyl hydroperoxide catalyzed by $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$

In contradiction to what was observed in the oxidation of organic substrates with hydrogen peroxide, we have found that *only* $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ catalyzes the oxidation of organic com-

Table 5
Oxidation of organic compounds in 70% *t*-butyl hydroperoxide catalyzed $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ ^a

Substrate	Products ^b		Conversion ^c	Turnovers ^d
Benzyl alcohol	benzaldehyde	87	89	356
	benzoic acid	13		
1-phenylethanol	acetophenone	100	64	256
Cyclohexanol	cyclohexanone	100	60	240
2-heptanol	2-heptanone	100	42	168
1-heptanol	1-heptanal	100	9	36
Cyclohexen-2-ol	cyclohexen-2-one	100	50	200
	<i>cis</i> -epoxide	25		
<i>Cis</i> -2-hexen-1-ol	<i>trans</i> -epoxide	26	66	264
	2-hexenal	25		
	other ^e	24		
	<i>cis</i> -epoxide	27		
<i>Cis</i> -3-hexen-1-ol	<i>trans</i> -epoxide	35	32	128
	3-hexenal	20		
	other ^e	18		
	<i>trans</i> -epoxide	26		
<i>Trans</i> -2-hexen-1-ol	2-hexenal	25	54	216
	other ^e	49		

^a Reaction conditions: 1 mL 70% *t*-BuOOH (7.3 mmol), 0.2 mmol of substrate, $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ (0.5 μmol) at 25°C, reaction time 3 h. During the course of the reaction 15–20% of the oxidant is used up.

^b The amount of product is given as mol% of all products.

^c Conversion of substrate to all products (mol%).

^d Amount of total product formed per mol catalyst in 3 h.

^e Allylic oxidation products.

pounds, alcohols and alkenols, using 70% aqueous TBHP as oxidant. Other TMSP compounds, $\text{Na}_x\text{M}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ ($\text{M} = \text{Mn}, \text{Pd}, \text{Pt}, \text{Co}, \text{Fe}, \text{Rh}$ and Zn), and less soluble and reactive alkenes are completely inactive. In Table 5 we have summarized the results for such oxidation for some representative substrates. In the case of alcohol oxidation, the relative reactivity is somewhat higher than that found in the hydrogen peroxide mediated oxidations. For alkenol oxidation, slightly higher reactivities were observed but selectivities were significantly different. While the hydrogen peroxide oxidation of primary allylic and homoallylic alcohols yielded epoxides in high stereospecificity and chemoselectivity, reactions in the presence of *t*-butylhydroperoxide were not stereoselective or chemoselective.

As in the case of use of hydrogen peroxide as oxidant, the stability of catalysts to 70% aqueous *t*-butylhydroperoxide were determined by measuring the UV absorption of the TMSP at 300 nm before and after reaction. Neither the reactive $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ polyoxometalate nor the other non-reactive analogs showed any decrease in the optical density indicating high stability. The uniqueness of the catalytic activity of the ruthenium compound, together with the stability of all the TMSP compounds under the reaction conditions and the non-stereospecificity of the epoxidation would seem to indicate that the reaction does not take place via formation of a peroxotungstate intermediate which always yields stereospecific epoxidation [25]. Rather, the reactions may take place via a variety of mechanisms including (a) ruthenium mediated hydrogen atom or electron abstraction followed by reaction with the oxidant or (b) attack of a *t*-butylalkoxy radical at the carbon–carbon double bond leading to the non-stereospecific epoxide formation. Finally, it is well worth pointing out that as in the case of the hydrogen peroxide mediated reactions, the reactivity of substrates to *t*-butylhydroperoxide in the present research is significantly different to that observed when using biphasic systems where the catalysts were dissolved in the organic phase [21].

3.5. Aqueous phase oxidation by potassium peroxymonosulfate

Potassium peroxymonosulfate, commercially available as the triple salt $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (Oxone), is an inorganic peroxide which is a significantly stronger oxidant compared to both hydrogen peroxide and *t*-butylhydroperoxide [26]. In the past, it has been shown that water soluble manganese porphyrins catalyze the oxidation of organic compounds using Oxone, but the catalyst is

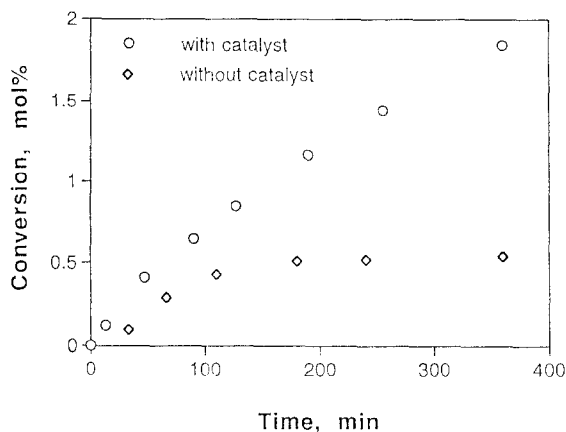
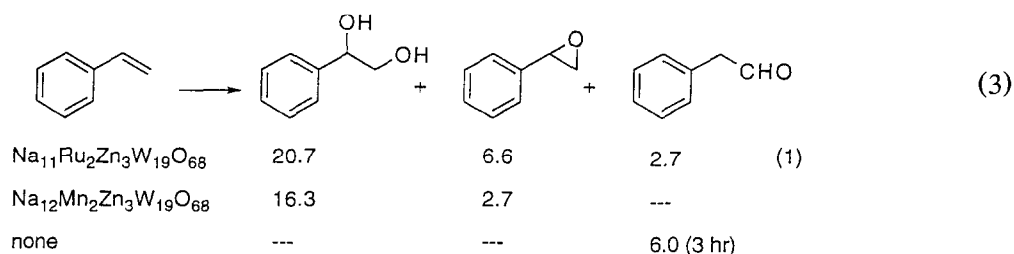


Fig. 6. Reaction profile of the oxidation of cyclooctene with Oxone. Reaction conditions: cyclooctene (0.1 mmol), potassium persulfate (0.1 mmol) in 5 mL of phosphate buffer (pH 7) at 25°C without and with catalyst $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ (0.5 μmol).

rapidly destroyed [27]. As concerns polyoxometalates, the organic phase dissolved ruthenium substituted Keggin type heteropolyanion was active as a catalyst in hydrocarbon oxidation by Oxone under biphasic conditions [13].

First, we tested the catalytic activity of the various TMSP compounds in the activation of persulfate to olefin oxidation at neutral pH. For the oxidation of 1-octene, there was no reaction with any polyoxometalate. The more nucleophilic cyclooctene known to react well with peroxy-tungstate intermediates also reacted only very sluggishly (Fig. 6) with only slight catalytic activation observed, for example, with the ruthenium analog, $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$. The slight catalytic activity is however complimented by a slow degradation of the original TMSP compound as is noted by a 50% decrease in the optical density over a period of 6 h. Therefore, it is most conceivable that the active species as in the case of the hydrogen peroxide reaction is not the original polyoxometalate, but a simpler intermediate. It would seem that such a peroxosulfate intermediate has only very marginal activity (4 turnovers/6 h) compared to a similar hydroperoxy intermediate formed in hydrogen peroxide induced reaction where there was no catalytic activity which is inactive. Interestingly, styrene is significantly *more* reactive than cyclooctene, a reversal of what is found in biphasic systems where the TMSP catalyst is in the organic phase [19,20]. Thus, styrene yields a mixture of products under the reaction conditions described in the experimental part with up to 30 mol% conversions after one hour using the ruthenium catalyst as the most active polyoxometalate (Eq. (3)). Interestingly, the addition of catalysts changes the product selectivity from formation of phenylacetaldehyde without catalyst to epoxide and vicinal diol with catalyst.



The use of transition metal substituted polyoxometalates of the ‘sandwich’ type dissolved in water as active catalysts for the oxidation of alkenols and alcohols may be summarized as follows. The most active and in some cases (*t*-butylhydroperoxide) the only active catalyst was the ruthenium analog, $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$. Using hydrogen peroxide and potassium persulfate as oxidant the ruthenium polyoxometalate appeared to be degraded to another ruthenium containing compound capable of catalyzing alcohol oxidation. Another degradation compound common to all the tested polyoxometalates was responsible for the catalytic alkenol oxidation with hydrogen peroxide. In the oxidation of primary alkenols, oxidation was highly chemo- and stereoselective, the epoxides being the major product. For secondary alkenols a mixture of products was obtained. The $\text{Na}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{19}\text{O}_{68}$ compound in water was stable towards *t*-butylhydroperoxide. With *t*-butylhydroperoxide as oxidant effective and selective oxidation of alcohols was possible. On the other hand in the oxidation of alkenols reactions were non-selective.

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