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A Bismuth Substituted “Sandwich” Type Polyoxometalate Catalyst for Activation of Peroxide – Umpolung of the Peroxo Intermediate and Change of Chemoselectivity

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ABSTRACT: The epoxidation of alkenes with peroxides by W^{VI} , Mo^{VI} , V^V , and Ti^{IV} compounds is well established and it is well accepted that the active intermediate peroxo species are electrophilic towards nucleophilic substrates. Polyoxotungstates, for example those of the “sandwich” structure, $[WZn(TM-L)_2(ZnW_9O_{34})_2]^{4-}$, where TM = transition metal and L = H_2O , have in the past been found to be excellent epoxidation catalysts. It has now been found that by substituting the Lewis basic Bi^{III} into the terminal position of the “sandwich” polyoxometalate structure to yield $[Zn_2Bi^{III}_2(ZnW_9O_{34})_2]^{4-}$, leads to an apparent umpolung of the peroxo species and formation of a nucleophilic peroxo intermediate. There are two lines of evidence that support the formation of a reactive nucleophilic peroxo intermediate. (1) More electrophilic sulfoxides are more reactive than more nucleophilic sulfides and (2) non-functionalized aliphatic alkenes and dienes showed ene type reactivity rather than epoxidation pointing towards “dark” formation of singlet oxygen from the nucleophilic intermediate peroxo species. Allylic alcohols reacted much faster than alkenes but showed chemoselectivity towards C-H bond activation of the alcohol and formation of aldehydes or ketones rather than epoxidation. This explained via alkoxide formation at the Bi^{III} center followed by oxidative β -elimination.

Keywords: Homogeneous Catalysis, Peroxide, Singlet Oxygen, Polyoxometalate, Bismuth

Introduction

The use of peroxides as the terminal oxidant for catalytic transformations such as alkenes to epoxides and sulfides to sulfoxides, originally studied in the early 20th century,¹ has been extensively investigated over the last several decades. The investigation of the use of hydrogen peroxide has been especially intensive related also its advantage in the context of green chemistry and low waste reaction processing.²⁻⁶ As a result, catalytic reactions have been considerably optimized with attention being focused on turnover, rate, and catalyst stability and recovery. In the area of H_2O_2 activation and a broad spectrum of non-redox transformations, tungsten based complexes have played a central role where the Lewis acidity of the W^{VI} atoms logically leads to electrophilic peroxo intermediates. In this context, especially catalysts with more than one tungsten atom, polyoxotungstates, have been shown to be very active and selective. Three families of polyoxotungstate catalysts appear to be the most reactive; the so-called Venturello complex,⁵⁻⁶ $\{PO_4[W(O_2)_2]_4\}^{3-}$ that is also accessible from phosphotungstic acid,⁷⁻¹³ γ -Keggin-type decatungstates,¹⁴⁻¹⁹ and the Tourné “sandwich” type polyoxometalates.²⁰⁻²¹ Reactivity of H_2O_2 as a nucleophilic oxidant has been much-less studied. One important example is the use of a Sn-substituted beta zeolite for the Baeyer-Villiger reaction where the Lewis acidic Sn centers activate the ketone rendering it susceptible to nucleophilic attack by H_2O_2 .²² Also with electron-donating com-

plexes, typically based on Pd^{II} and Pt^{II} , nucleophilic peroxo intermediates have been suggested.²³ Under basic conditions (pK_a of $H_2O_2 = 11.75$) HO_2^- species can be easily formed. In the presence of a polyamino acid, enantioselective epoxidation of electron poor chalcones was observed.²⁴⁻²⁵ More typically, however, HO_2^- decomposes to singlet oxygen (1O_2), the O_2 ($^1\Delta_g$) state. Thus, addition of NaOCl to H_2O_2 or Cl_2 to basic H_2O_2 is a possible, method for the “dark” formation of 1O_2 .²⁶⁻²⁷ The reactivity of singlet oxygen with alkenes, dienes and other compounds is well documented and very different than what is observed with peroxo species.²⁸⁻³³ More recently use of transition metal compounds such as molybdenum and lanthanum based compounds and materials have been shown to be efficient for 1O_2 type oxygenations.³⁴⁻⁴¹ In the “sandwich” type polyoxometalate framework, it has been suggested that there is an interaction of H_2O_2 between a reactive tungsten center and an adjacent Lewis acidic site, such as Zn^{II} , at the terminal position that increases the electrophilicity of the oxygen atom of H_2O_2 and thus increases reactivity towards nucleophiles. However, we know of no reports describing the use of tungsten-based catalysts for the formation of a nucleophilic oxidant from H_2O_2 or for the formation of 1O_2 .

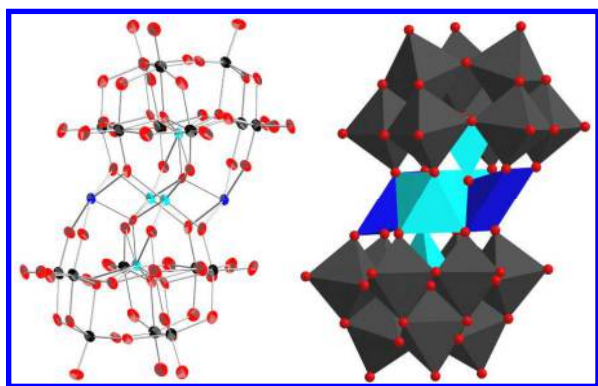


Figure 1. ORTEP presentation showing the 50% probability of the thermal ellipsoids (left) and polyhedral representation (right) of the $[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ anion. W-black, O-red, Zn-cyan, Bi-blue. The cations and water molecules are omitted for clarity.

We were therefore interested in investigating the effect of the substitution of a Lewis base site at the terminal position within a “sandwich” polyoxometalate framework, Figure 1, with the hypothesis that this could lead to umpolung of H_2O_2 to a nucleophilic intermediate species through deprotonation. This would then significantly influence the reactivity of H_2O_2 and the chemoselectivity of the reactions.

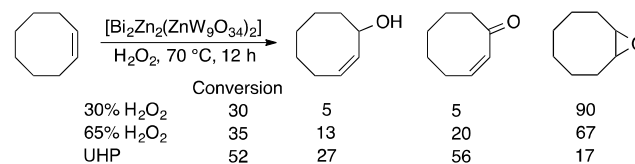
Results and Discussion

Towards realization of the above stated hypothesis we prepared a “sandwich” type polyoxometalate with Bi^{III} atoms at the terminal positions with accessible lone pairs that can act as a Lewis base, Figure 1. The synthesis of this compound appears to be novel although a very similar compound the $[\beta\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ isomer has been reported.⁴² On the whole $[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ can be considered nearly isostructural with the similar “sandwich” compound with $\text{Zn}^{\text{II}}\text{-H}_2\text{O}$ replacing Bi at the terminal positions, $[\text{WZn}(\text{ZnH}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$.⁴³ It should be noted, however, that the bond lengths Bi – O in the equatorial plane are significantly longer (average ~ 2.30 Å) than those found for the Zn compound (average ~ 2.05 Å).

In order to use the $[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ as a catalyst in organic solvent the cations were partially exchanged with tetrabutyl ammonium (Q) cations. A thermogravimetric measurement, Figure S1, showed that six Q cations are associated with the $[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ anion leading to a formulation of $\text{Q}_6\text{Zn}_2\text{Na}_y\text{H}_z[\text{Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]$, (QBiPOM). MALDI-TOF MS measurements in the negative anion, reflector mode showed that various combinations of Zn, Na, and H cations are possible with all peaks showing an intact $[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]$ polyoxometalate moiety, Figure S2-S3 and Table S1. The catalytic activity of QBiPOM was first tested using cyclooctene as a model substrate, chosen because it is typically highly reactive and selective towards epoxidation with peroxide oxidants. Surprisingly, the reactions yielded a significant amount of allylic oxidation that was especially high using urea-hydrogen peroxide (UHP) as an anhydrous form of H_2O_2 , Scheme 1. All other polyoxotungstate catalysts including $\text{Q}_{12}[\text{WZn}(\text{Zn-}$

$\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ that have been examined for this oxidation with H_2O_2 exclusively yielded cyclooctene oxide.^{5-21,44}

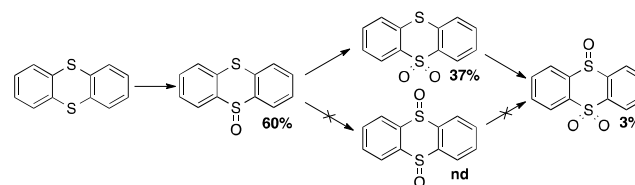
Scheme 1. Oxidation of cyclooctene with H_2O_2 catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol cyclooctene, 0.5 mmol H_2O_2 , 2 μmol QBiPOM, 0.5 mL acetonitrile, 70 °C, 12 h.

Three most probable reasons for the preponderance of oxidation at the allylic position are: (i) C-H bond activation at the allylic position by the polyoxometalate followed by oxygen transfer, (ii) oxidation by a hydroxide radical formed by a redox reaction between the polyoxometalate and H_2O_2 , and (iii) formation of $^1\text{O}_2$ via a HO_2^- species and formation of an allylic hydroperoxide through an ene reaction followed by decomposition of the hydroperoxide. We chose the latter possibility as the working hypothesis. In order to first provide evidence for the formation of a nucleophilic oxidant, the reactivity of a sulfide and a relatively more electrophilic sulfoxide can be compared.⁴⁵⁻⁴⁶ Thus, a catalytic reaction of thianthrene with UHP catalyzed by QBiPOM, Scheme 2, showed the formation of the monosulfoxide and then *only* the monosulfone but *not* the disulfoxide, indicating the initial presence of a nucleophilic oxidant.

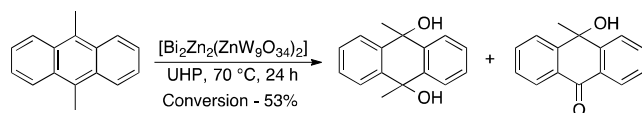
Scheme 2. Oxidation of thianthrene with UHP catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol thianthrene, 0.5 mmol UHP, 2 μmol QBiPOM, 2 mL acetonitrile, 70 °C, 2 h. nd-not detected.

The formation of $^1\text{O}_2$ can be probed indirectly in several ways, for example by the formation of an endoperoxide from α -terpinene or 9,10-dimethylantracene and the observation of a migration of a double bond during an ene reaction. The oxidation of 9,10-dimethylantracene Scheme 3, showed the formation of 9,10-dimethyl-9,10-dihydroanthracene-9,10-diol and 10-hydroxy-10-methylantracene-9(10H)-one, instead of the expected endoperoxide. It was demonstrated, however, that these products are obtained from the initially formed endoperoxide. Thus, preparation of the endoperoxide by photooxygenation using tetraphenylporphyrin as sensitizer followed by addition of QBiPOM and further reaction in fact yielded the aforementioned products.

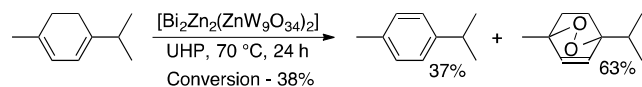
Scheme 3. Oxidation of 9,10-dimethylantracene with UHP catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol 9,10-dimethylantracene, 0.5 mmol UHP, QBiPOM, 0.5 mL acetonitrile, 70 °C, 24 h.

The oxidation of α -terpinene, Scheme 4, was unambiguous vis a vis formation of the endoperoxide, ascaridole. *p*-Cymene was formed as by-product via aromatization.

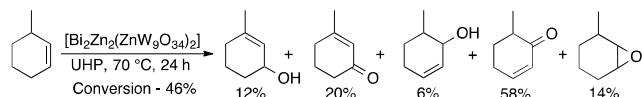
Scheme 4. Oxidation of α -terpinene with UHP catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol α -terpinene, 0.5 mmol UHP, 2 μ mol QBiPOM, 0.5 mL acetonitrile, 70 °C, 24 h.

Similarly, the oxidation of 3-methylcyclohexene, showed the formation of four allylic alcohols and ketones that can be attributed to the formation of hydroperoxides by the ene reaction followed by oxidation to the corresponding allylic alcohols and ketones by UHP in the presence of QBiPOM, Scheme 5; 3-methylcyclohexane oxide was formed only in small amounts.

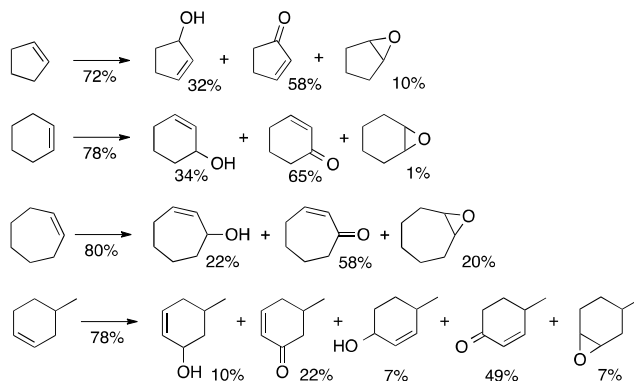
Scheme 5. Oxidation of 3-methylcyclohexene with UHP catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol 3-methylcyclohexene, 0.5 mmol UHP, 2 μ mol QBiPOM, 0.5 mL acetonitrile, 70 °C, 24 h

Additional oxidations of cyclic alkenes are presented in Chart 1. As may be observed, generally high yields of α , β -unsaturated alcohols and ketones were obtained. There is a clear preference for ene type reactions with decomposition of the initially formed hydroperoxides. It should be noted that the formation of epoxides as minor co-products could be from reaction with an electrophilic peroxy species, but epoxide formation can be explained also by intramolecular rearrangement.⁴⁷ Noticeably, the reaction yields can be quite high although the reactions are rather slow. Seemingly the formation of singlet oxygen is sluggish, but the efficiency of oxidation (yield in H_2O_2) is high once the active oxidant, $^1\text{O}_2$, is formed. Therefore, these initial studies of oxidation reactions, preferably with anhydrous H_2O_2 , catalyzed by QBiPOM indicated that a nucleophilic peroxide was formed and can account for the reactivity observed.

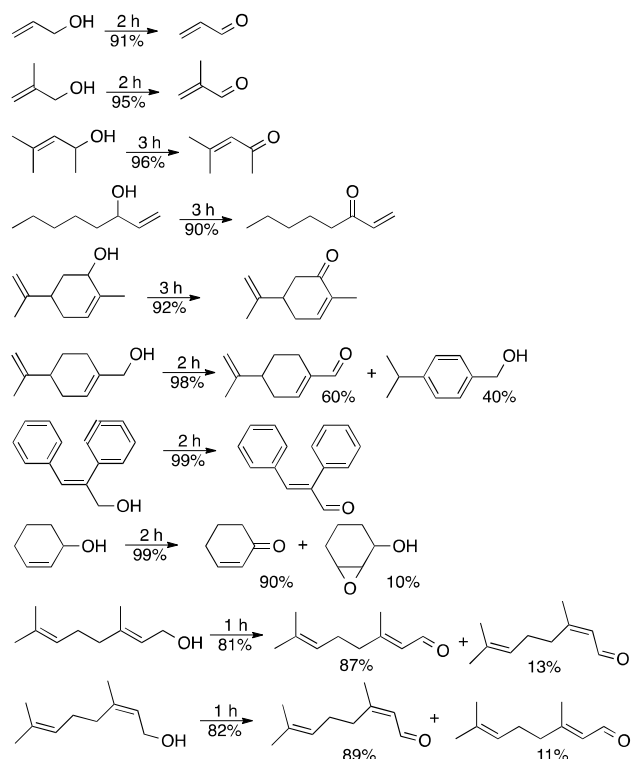
Chart 1. Oxidation of alkenes with UHP catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol cyclic alkene, 0.5 mmol UHP, 2 μ mol QBiPOM, 0.5 mL acetonitrile, 70 °C, 24 h. The percentages shown below the products represent relative amounts, i.e. selectivity.

Typically, oxidation reactions of α , β -unsaturated alcohols with H_2O_2 catalyzed by polyoxometalates including "sandwich" type polyoxometalates such as $[\text{WZn}(\text{ZnH}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, proceed efficiently with a chemoselectivity that favors the formation of the epoxide versus the ketone or aldehyde in an approximately 95:5 ratio.⁴⁸⁻⁴⁹ On the other hand, α , β -unsaturated alcohols react with photochemically prepared singlet oxygen, via an ene reaction to yield diols as the major products.²⁹ Here, α , β -unsaturated alcohols reacted with UHP quite differently in transformations catalyzed by QBiPOM to yield α , β -unsaturated aldehydes or ketones chemoselectively, Chart 2. As can be observed from the reaction conditions these reactions are much faster than the oxidation of unfunctionalized alkenes. In fact, the reaction profiles, Table S2, (see Supporting Information) for a number of α , β -unsaturated alcohols showed that the reaction was bimodal with around 65-75% conversion within 15 minutes, followed by a slower rate regime until the reported yields were obtained, Chart 2.⁵⁰ Primary aliphatic alcohols such as allyl alcohol and methallyl alcohol, as well a secondary aliphatic alcohols such as 1-octene-3-ol and 2-methyl-2-pentene-4-ol yielded only the respective aldehyde and ketone products. Geraniol also reacted to give geranial and the isomeric neral that suggests that there may be an accessible planar intermediate species. A cyclic substrate such as carveol yielded carveone as the only product although the analogous but less sterically hindered cyclohexen-3-ol did yield some epoxide as by product. Interestingly, 4-isopropyl-cyclohexene-1-methanol yielded the expected aldehyde but also the aromatized 4-isopropylbenzyl alcohol in significant amounts.

Chart 2. Oxidation of α , β -unsaturated alcohols with UHP catalyzed by QBiPOM.



Reaction conditions: 0.5 mmol substrate, 0.5 mmol UHP, 2 μmol **QBiPOM**, 0.5 mL acetonitrile, 70 $^{\circ}\text{C}$. The percentages shown below the products represent relative amounts, i.e. selectivity.

Since, α , β -unsaturated alcohols underwent oxidation at the alcohol moiety, it was not surprising to observe that **QBiPOM** also catalyzed the very selective oxidation of alcohols with UHP efficiently, Table 1.

Table 1. Oxidation of alcohols with UHP catalyzed by QBiPOM.

Substrate	Product	Time, h	Conversion, mol%
cyclooctanol	cyclooctanone	12	>99
cyclohexanol	cyclohexanone	12	95
cycloheptanol	cycloheptanone	12	96
cyclopentanol	cyclopentanone	12	96
mesityl alcohol	mesitylaldehyde	5	96
1-octanol	1-octanal ^a	24	85
benzyl alcohol	benzaldehyde	4.5	95
3,3'-diphenylpropanol	3,3'-diphenylpropanal	24	90
diphenylmethanol	benzophenone	3	91

Reaction conditions: 0.5 mmol substrate, 0.5 mmol UHP, 2 μmol **QBiPOM**, 0.5 mL acetonitrile, 70 $^{\circ}\text{C}$. (a) the selectivity was 92% 1-octanal, 8% octanoic acid.

The different reactivity and chemoselectivity observed in **QBiPOM** catalyzed transformations with UHP warranted further kinetic elucidation and a mechanistic hypothesis. In the past it has been reported that the analo-

gous antimony(III) compound $[\text{Sb}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ reacted with H_2O_2 to yield the antimony(V)-hydroxide compound $[(\text{Sb}^{\text{V}}\text{OH})_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ as the catalytically active precursor species.⁵¹ As opposed to Sb(V) species that are rather accessible and common, Bi(V) oxide compounds are rather rare,⁵² and their use in oxidation reactions is uncommon.⁵³ An almost singular example is the oxidation of alkenes to monoacetylated diols in acetic acid.⁵⁴ It was therefore not surprising that we were not able to isolate any Bi(V) species upon treatment with 65% H_2O_2 , UHP, Cl_2 or $\text{S}_2\text{O}_8^{2-}$. Only the reaction of $[\text{Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ with ozone yielded $[\text{Bi}^{\text{V}}\text{O}-\text{Bi}^{\text{III}}\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ as identified by X-ray crystallography, Figure 2. This compound was unreactive towards alkenes and alcohols and therefore can be excluded as a possible reactive intermediate.

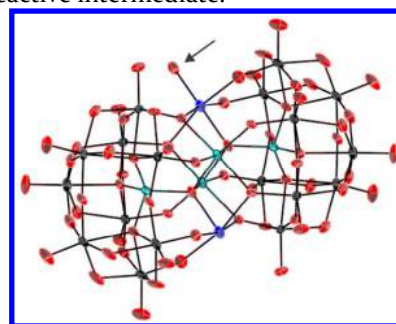


Figure 2. ORTEP presentation showing the 50% probability of the thermal ellipsoids of the $[\text{Bi}^{\text{V}}\text{O}\text{Bi}^{\text{III}}\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ anion. W-black, O-red, Zn-cyan, Bi-blue. The cations and water molecules are omitted for clarity.⁵⁶ The oxygen terminal to Bi(V) is shown with the arrow.

The slow reaction of alkenes compared to the much faster reactions of α , β -unsaturated alcohols suggests they react by a different mechanism. First, analysis of alkene and diene oxidation as well as the product distribution in the oxidation of thianthrene catalyzed by **QBiPOM** indicates a nucleophilic peroxy intermediate while alkene epoxidation catalyzed by structurally similar $[\text{WZn}(\text{M}-\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ (M = Mn, Zn, etc.) indicates an electrophilic peroxy intermediate. It should be noted that the unique activity of $\text{Q}_{12}[\text{WZn}(\text{M}-\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ has in the past been attributed to the tungsten atoms in proximity to the terminal metal position since reactivity was highly influenced by steric effects (cyclohexene > 1-methylcyclohexene ~ 2-carene >> α -pinene).⁵⁵ This difference in reactivity strongly suggests that the metal at the accessible terminal position, Lewis acidic Zn^{II} or Mn^{II} versus Lewis basic Bi^{III} , is the determining factor in the umpolung of the peroxy species. This umpolung then leads to the observed different reactivity pattern. Therefore, conceivable or exemplary reactive intermediates illustrating the umpolung of H_2O_2 are presented in Figure 3. The observation that aqueous H_2O_2 , Scheme 1, is far less selective towards the ene reaction of cyclooctene and also other examples can also be understood from Figure 3. Water can compete for the Bi^{III} site, therefore, preventing the formation of a nucleophilic peroxy species and thereby shifting the chemoselectivity towards epoxidation.

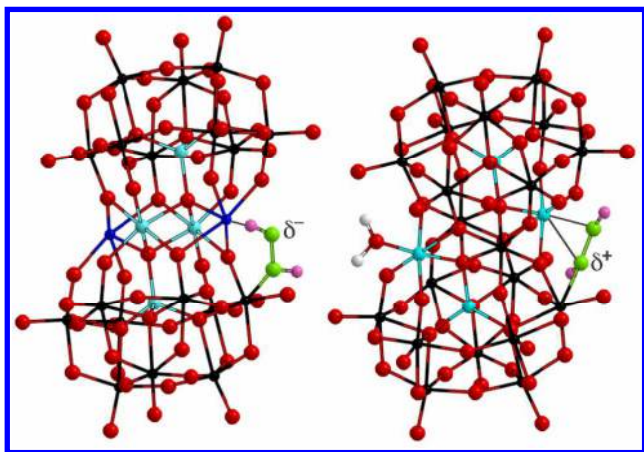


Figure 3. Conceivable or exemplary peroxyoxygen species (not crystal structures) formed upon reaction with the $[\text{Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]^{14-}$ (left) and $[\text{WZn}(\text{ZnH}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ (right) anions. Black - W; red - O; turquoise - Zn; Blue - Bi; green - O from H_2O_2 ; pink - H from O from H_2O_2 .

A consensus mechanism for the oxidation of alcohols by peroxyoxygen oxidants is that the reactions occur by coordination of both reacting species, H_2O_2 and $\text{RR}'\text{CHOH}$ to the same metal center to yield a $\text{HOO-M-OCHRR}'$ intermediate species that lead to formation of $\text{RR}'\text{C}=\text{O}$ and H_2O .⁵⁶ Such a peroxy-metal pathway with W^{VI} , Mo^{VI} , V^{V} , and Ti^{IV} based catalysts are thought to be typical.⁵⁶ However, when the substrates are allylic alcohols, typically epoxidation products are obtained with high chemoselectivity as is the case also with $[\text{WZn}(\text{ZnH}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$.⁴⁸⁻⁴⁹ Contrarily, **QBiPOM** catalyzes the oxidation of α , β -unsaturated alcohols with a chemoselectivity strongly favoring C-H bond activation and formation of carbonyl products. In addition, there are some anomalies such as the formation of 4-isopropylbenzyl alcohol (cuminol) by aromatization from ((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methanol (perillyl alcohol), and the cis \leftrightarrow trans isomerization observed in the oxidation of geraniol and nerol. One may reasonably suggest that the reactivity observed in the oxidation of allylic alcohols can be best explained as a base assisted or promoted oxidation reaction where the Bi^{III} center leads to formation of an alkoxide intermediate that is then oxidized by a tungsten-peroxo species by oxidative β -elimination to yield the carbonyl product, as commonly observed in Pd^{II} catalyzed oxidations of alcohols. In the case of perillyl alcohol in addition to the formation of perillaldehyde, the formation of an alkoxide can yield to a series of double bond isomerizations.⁵⁷ Upon formation of an endo-diene, oxidation will lead to formation of the aromatic cuminol. Similarly, the isomerization observed in the geraniol and nerol oxidations can also be attributed to catalysis involving a base.⁵⁸

Conclusion

Incorporation of the Lewis basic Bi^{III} at the accessible terminal position of a "sandwich" type polyoxometalate led to a change in the chemoselectivity of catalytic oxidation reactions of alkenes and α , β -unsaturated alcohols. As opposed to the previously reported and structurally

similar Zn^{II} or Mn^{II} substituted polyoxometalates that showed chemoselectivity strongly favoring epoxidation, the Bi^{III} substituted polyoxometalate catalyzed reactions with minimal epoxide formation. In reactions with alkenes and dienes, ene type reactivity was observed, a hallmark of singlet oxygen formation, that is explained by an umpolung of a reactive peroxo intermediate; electrophilic for substitution with Mn^{II} or Zn^{II} to nucleophilic for substitution with Bi^{III} . The chemoselectivity observed in the oxidation of α , β -unsaturated alcohols strongly favors C-H bond activation rather than epoxidation and is explained by alkoxide formation at the Lewis basic Bi^{III} followed by an oxidative β -elimination.

Experimental Part

$\text{Na}_4(\text{Zn}(\text{H}_2\text{O})_2)_2\text{H}_6[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 26\text{H}_2\text{O}$
 $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (3 g, 9 mmol) was dissolved in solution of 25 mL water and 0.5 mL 6 M HNO_3 and heated for 15 min at 90 °C. After cooling to room temperature, a solution of 0.60 g of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (2 mmol) in 2 mL of water was added followed by the drop wise addition of a solution of 0.48 g of $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (1 mmol) dissolved in 1 mL of 6 M HNO_3 with vigorous stirring. The pH of the solution adjusted to 8 by adding aqueous ammonia and then heated at 90 °C for 1 h. The mixture was filtered and the filtrate was allowed to cool to room temperature. Within 24 h colorless crystals of $\text{Na}_4(\text{Zn}(\text{H}_2\text{O})_2)_2\text{H}_6[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 26\text{H}_2\text{O}$ were formed. These crystals were used for analysis by X-ray diffraction. The yield was 1.65 g (50 %, based on W). IR - 918, 868, 765 cm^{-1} . Elemental Analysis: Calc (exp) Na 1.57 (1.63); Zn 6.75 (6.55); Bi 7.16 (7.33); W 56.61 (55.98); H_2O 9.24 (9.5).

$\text{Q}_6\text{Zn}_2\text{Na}_4[\text{Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]$. $\text{Na}_4(\text{Zn}(\text{H}_2\text{O})_2)_2\text{H}_6[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 26\text{H}_2\text{O}$ (0.200 g) were dissolved in 6 mL of distilled water (pH-8.5); 20 equivalents of tetrabutylammonium bromide were added and the product was precipitated by the addition of 2 μL 6M H_2SO_4 (pH-7.4). The crude precipitate, $\text{Q}_6\text{Zn}_x\text{Na}_y\text{H}_z[\text{Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]$, was collected by filtration, washed several times with water to remove unreacted tetrabutylammonium salt and dried under vacuum. The number of tetrabutyl ammonium cations was determined by thermogravimetric analysis, Figure S1 (see supporting information) and the presence of the intact $[\text{Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]$ anion only along with various combinations of cations was verified by negative anion MALDI-TOF MS in the reflector mode.

$\text{Na}_{10}\text{H}_{-4}[\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}[\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 37\text{H}_2\text{O}$
 $\text{Na}_4(\text{Zn}(\text{H}_2\text{O})_2)_2\text{H}_6[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 26\text{H}_2\text{O}$ (0.2 g, 33 μmol) was dissolved in 2 mL distilled water by heating at 70 °C for 10 min. Ozone (concentration - 25 mg/L, rate - 6.25 mg/min), prepared by an ozonator, was then bubbled through this solution for 1 h at room temperature during which time the solution became mildly yellowish. The solution was let to stand under ambient conditions; light yellowish crystals of $\text{Na}_{10}\text{H}_{-4}[\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}[\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 37\text{H}_2\text{O}$ were obtained after ten days and analyzed by X-ray crystallography. Elemental Analysis: Calc (exp) Na 3.84 (4.02); Zn 4.36 (4.51); Bi 6.97 (7.10); W 55.22 (55.00); H_2O 11.13 (11.5). Yield - 0.08

g (40%). IR – 1090, 883, 848, 735 cm^{-1} . Note that the crystal structure shows that only one of the Bi^{III} centers was oxidized to $\text{Bi}^{\text{V}}\text{-O}$. Attempts to further oxidize this compound by ozonation for longer time periods did not appear to yield the di- $\text{Bi}^{\text{V}}\text{O}$ species, but rather yielded a compound that was not identifiable.

X-ray Crystallography. Crystals were coated in Paratone-N oil (Hampton Research) and mounted by liquid nitrogen flash freezing within a MiTeGen cryo-loop. Single crystal X-ray data was collected on either a Bruker APEX-II or a Nonius Kappa CCD diffractometer with $\text{MoK}\alpha$ ($\lambda=0.71073$ nm) radiation. The data were processed using SAINT and DENZO respectively. Structures were solved by direct methods with SHELXS. Full-matrix least-squares refinement was based on F^2 with SHELX-97.

Crystallographic data:

$\text{Na}_4(\text{Zn}(\text{H}_2\text{O})_2)_2\text{H}_6[\alpha\text{-Bi}^{\text{III}}_2\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 26\text{H}_2\text{O}$ Empirical formula - $\text{Bi}_2\text{O}_{98.55}\text{W}_{18}\text{Zn}_6\text{Na}_4$; formula weight - 5788.24; crystal system - orthorhombic; space group - $Pnmm$; $T - 120$ K; $a = 16.187$ (3) Å; $b = 19.430$ (4) Å; $c = 14.641$ (3); $\alpha = \beta = \gamma = 90^\circ$; $V = 4604.8$ (16) Å³; $Z = 2$; $D_{\text{calc}} = 4.175$ g/cm³; $\mu = 27.850$ mm⁻¹; total reflections - 4891; independent reflections 4891 ($R_{\text{int}} = 0.0258$); $R(I > 2\sigma(I)) = 0.0423$; $wR_1(I > 2\sigma(I)) = 0.1119$; R (all data) = 0.0499; R (all data) = 0.1153; GOF = 1.063.

$\text{Na}_{10}\text{H}_{-4}[\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}[\text{Zn}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 37\text{H}_2\text{O}$ Empirical formula - $\text{Bi}_4\text{Na}_{20.72}\text{O}_{213.36}\text{W}_{36}\text{Zn}_8$ formula weight - 11867.39; crystal system - monoclinic; space group - $P2_1/n$; $T - 100$ K; $a = 13.234$ (3) Å; $b = 17.661$ (4) Å; $c = 20.966$ (4); $\alpha = \gamma = 90^\circ$, $\beta = 93.12$ (3); $V = 4893.0$ (17) Å³; $Z = 1$; $D_{\text{calc}} = 4.028$ g/cm³; $\mu = 25.771$ mm⁻¹; total reflections - 85156; independent reflections 12704 ($R_{\text{int}} = 0.0610$); $R(I > 2\sigma(I)) = 0.0401$; $wR_1(I > 2\sigma(I)) = 0.0985$; R (all data) = 0.0602; wR (all data) = 0.1096; GOF = 1.081.

Catalytic Reactions. Typically the oxidation reactions were carried out in 10 mL vials in air using the conditions given in the tables and schemes. The products were analysed by gas chromatography. Quantitative GC-FID (HP 6890) and qualitative for product identification GC-MSD (HP 5973) instruments were used equipped with a 5% phenyl methylsilicone 0.32 mm ID, 0.25 mm coating, 30 m column (Restek 5MS) using helium as carrier gas.

ASSOCIATED CONTENT

Supporting Information. Additional X-ray diffraction data (cif files) and other data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors who have given approval to the final version of the manuscript.

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