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# Catalytic Properties and Stability of the Heteropolytungstate $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ in $H_2O_2$-Based Oxidations

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Catalytic properties of the sandwich-type heteropolytungstate $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ (**1**) in the selective oxidation of three representative organic substrates, methyl phenyl sulfide, cyclohexene, and cyclohexanol, with aqueous $H_2O_2$ have been studied in acetonitrile. With one equivalent of hydrogen peroxide, methyl phenyl sulfide readily produced the corresponding sulfoxide with 92–94 % selectivity at 95–97 % conversion. The substituent effect on the oxidation rates of the set of aryl methyl sulfides followed the Hammett free-energy relationship ($\rho = -0.85$). The catalytic activity of heteropolyacid H-**1** in thioether oxidation was several times higher than the activity of its tetrabutylammonium salt, TBA-**1**. In contrast, H-**1** was completely inactive in the oxidation of cyclohexanol, while TBA-**1** catalyzed this reaction effectively to give cyclohexanone with 94 % yield. Neither H-**1** nor TBA-**1** was active in the oxidation of cyclohexene. The catalytic performance of **1** in $H_2O_2$-based oxidations in MeCN is similar to that of the Keggin heteropolyanion $[PW_{12}O_{40}]^{3-}$ ($PW_{12}$) and differs significantly from the performance of the Venturello complex $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$. The stability of **1** and $PW_{12}$ towards solvolytic destruction under turnover conditions (50–100 equiv. $H_2O_2$, 25–70 °C, 2–72 h) was confirmed by using $^{31}P$ NMR, IR, and Raman spectroscopic techniques.

## Introduction

Tungsten-based catalytic systems are widely used for the selective oxidation of a wide range of organic compounds with aqueous hydrogen peroxide as oxidant.[1] The activation of $H_2O_2$ occurs through the formation of peroxidotungsten complexes, the reactivity of which strongly depends on their composition and structure.[1,2] In the mid-1980s, highly effective catalytic systems based on the use of polyoxometalates (POMs) $\{PO_4[WO(O_2)_2]_4\}^{3-}$ ($PW_4$) and $[PW_{12}O_{40}]^{3-}$ ($PW_{12}$) were discovered independently by Venturello[3] and Ishii.[4] Later on, several research groups demonstrated that the catalytic activity of the $PW_{12}/H_2O_2$ system in alkene epoxidation is caused by the in situ formation of lower-nuclearity peroxidotungstates including $PW_4$.[5] The use of an organic medium (acetophenone, DMF, MeCN, etc.) enables increasing POM stability towards $H_2O_2$.[5a,6] Yet, Neumann suggested that POM resistance towards solvolytic destruction with $H_2O_2$ should increase with increasing negative charge of the polyanion.[7]

Several sandwich-type POMs containing $W^{VI}$ and other transition metals (Zn, Mn, Fe, Rh, Ru, etc.) in the belt have been identified as highly efficient catalysts for a range of selective oxidations with $H_2O_2$.[7,8] Meanwhile, the role of the "belt" and "cap" (Keggin) tungsten atoms in the activation of hydrogen peroxide is not clear enough. To the best of our knowledge, no direct studies on the catalytic activity of sandwich-type heteropolytungstates containing solely W atoms at the equatorial (belt) position have been reported.

Heteropolytungstate $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ (**1**) comprises two $[\alpha\text{-}A\text{-}PW_9O_{34}]^{9-}$ fragments linked by three $WO_5(H_2O)$ octahedra (the structure is shown in Figure S1 in the Supporting Information).[9] Recently, this POM has been prepared in the form of a heteropolyacid (H-**1**).[10] In this work, we performed a comparative study on the catalytic properties of **1**, $PW_{12}$, and $PW_4$ in the selective oxidation of three representative organic compounds, methyl phenyl sulfide, cyclohexene, and cyclohexanol, with aqueous hydrogen peroxide in MeCN. The effect of counterions ($H^+$ and $TBA^+$) on the catalytic performance has been investigated. The stability of **1** and $PW_{12}$ under turnover conditions has been explored by using $^{31}P$ NMR, IR, and Raman spectroscopic techniques.

## Results and Discussion

### Catalytic Study

In Figure 1 are presented the results for the selective oxidation of methyl phenyl sulfide (MPS) with $H_2O_2$ in the presence of **1**. The results observed under the same condi-

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tions by using $PW_{12}$ and $PW_4$ are given for comparison. Note that both the TBA salts and the corresponding heteropolyacids of **1** and $PW_{12}$ are completely soluble in MeCN in the concentrations used in this work ($2–5 \times 10^{-3}$ м). With both H-**1** and TBA-**1**, MPS produced sulfoxide with approximately 90 % yield (92–94 % selectivity at 95–97 % MPS conversion) with one equivalent of $H_2O_2$. A similar selectivity was found in the presence of $PW_{12}$, but a lower MPS conversion (83 %) was achieved (see Figure 1).

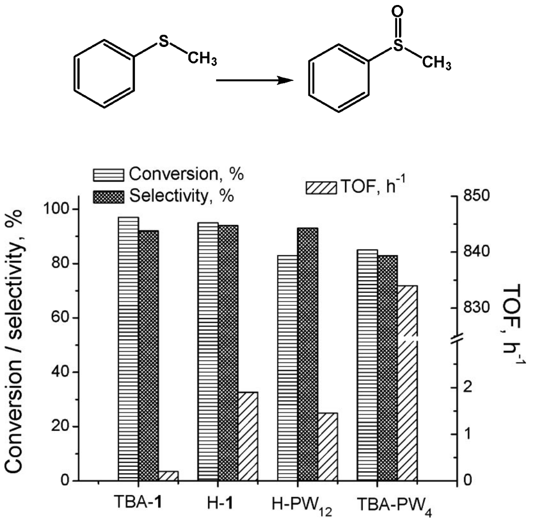

Figure 1. Methyl phenyl sulfide oxidation to sulfoxide with $H_2O_2$ in the presence of different POMs. Reaction conditions: MPS 0.1 м, $H_2O_2$ 0.1 м, POM $2 \times 10^{-3}$ м, MeCN, 25 °C (reaction time: H-**1** and H-$PW_{12}$: 3 h, TBA-**1**: 24 h, and TBA-$PW_4$: 5 min).

The high selectivity of sulfoxidation implies that the sulfide oxidation proceeds significantly faster than the consecutive oxidation of the corresponding sulfoxide (the reaction which leads to the formation of the by-product, sulfone). This indicates that the main mechanism operating in the system studied is electrophilic oxygen transfer, because sulfide is a more nucleophilic substrate than sulfoxide.[11] If some contribution of a nucleophilic-type oxidation or electron transfer mechanism took place, a significant amount of sulfone would be expected among the oxidation products:[11,12] MPS oxidation in the presence of Ti-monosubstituted Keggin heteropolytungstate $PW_{11}Ti$, for which an electron transfer mechanism has been suggested, produced about 20 % sulfone under the same reaction conditions as those used in the present work.[12b]

To probe the reaction mechanism, we studied the oxidation of a series of methyl aryl sulfides, in which the *para* substituents were placed on the phenyl ring, and found that an electron-donating group ($CH_3$) accelerated the reaction, while electron-withdrawing groups (Br, $NO_2$) produced the opposite effect. These results could be correlated by a Hammett-type linear free-energy relationship. Indeed, the plot of log $W_0$ against the substituent constant $\sigma$ (Figure 2) gives a straight line with a negative slope, $\rho = -0.85$ ($R = 0.981$). The negative value of $\rho$ indicates an accumulation of positive charge at the sulfur center in the transition state, which is consistent with nucleophilic attack of the thioether on the electrophilic peroxo oxygen.[11] The $\rho$ value is close to the corresponding parameters established for a few peroxidomolybdenum and peroxidotungsten complexes.[11] Interestingly, some anionic peroxido complexes are supposed to be poor electrophiles on the basis of the low $\rho$ values found for the oxidation of aryl methyl sulfide.[11c,11e,11f] Meanwhile, some of them, for example peroxo species formed from $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ ($\rho = -0.54$), are highly active in alkene epoxidation,[11f] while others, for example $[MoO(O_2)_2C_5H_4N(O)CO_2]^-$ ($\rho = -0.49$),[11b] are not capable of oxidizing alkenes.[11c] Note that no Hammett correlation was found for thioether oxidation by the monoprotonated peroxidotitanium complex $TBA_4[HPW_{11}Ti(O_2)O_{39}]$, which is known to react with organic substrates by homolytic oxidation mechanisms.[12]

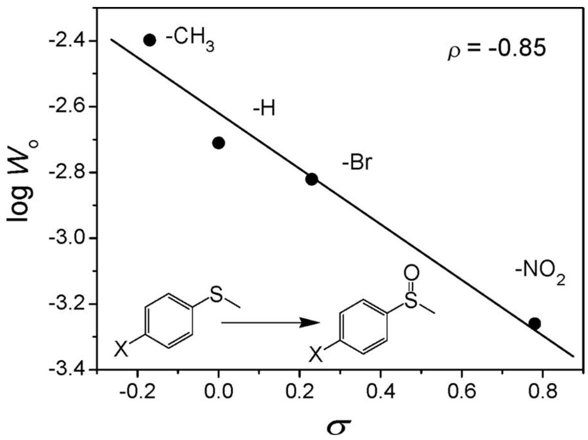

Figure 2. Hammett plot for the oxidation of substituted methyl phenyl sulfides by hydrogen peroxide with H-**1** as catalyst ($W_0$ is initial rate of sulfide consumption).

The kinetic curves for MPS consumption in the presence of **1** and $PW_{12}$ revealed no induction period (see Figure S2 in the Supporting Information), suggesting that both polyanions retain their structure under the turnover conditions. As one can see, the rate of MPS oxidation in the presence of H-**1** was several times higher than that in the presence of TBA-**1**. The same trend was found for $PW_{12}$. As a result, the maximal thioether conversions (shown in Figure 1) were attained in approximately 3 h with the heteropoly acids, while 24 h was needed for the corresponding TBA salts. This finding is consistent with an electrophilic oxygen transfer mechanism, because protonation of the polyanion would decrease the negative charge and, therefore, facilitate the approach of a nucleophilic substrate. In turn, protonation of the peroxo group may increase its electrophilic character. On the other hand, protonation could increase the oxidation potential of the peroxo group.[12b] At the present stage of the investigation, we can not rule out an electron transfer mechanism completely for the thioether oxidation in the presence of **1**. Further kinetic and mechanistic studies are needed to establish the rate-limiting step of the reaction.

It is worth noting that the catalytic activity of TBA-$PW_4$ was more than two orders of magnitude higher than those of both H-**1** and H-$PW_{12}$, but only 85% of MPS conversion was attained, and the selectivity of sulfoxidation was lower (see Figure 1) because of sulfoxide overoxidation to the corresponding sulfone. The different catalytic performance of **1** and $PW_{12}$ relative to $PW_4$ implies that different active species operate in these systems.

Importantly, neither **1** nor $PW_{12}$ (regardless of whether the H or TBA form was used) were active in the oxidation of cyclohexene with $H_2O_2$ in MeCN. After 5 h at 50 °C, alkene conversion was close to zero. This corroborates the stability of both **1** and $PW_{12}$ toward $H_2O_2$ in MeCN and contrasts with the catalytic performance of $PW_{12}$ in water and two-phase systems where, as we mentioned above, this POM degrades easily, producing lower-nuclearity species that readily accomplish alkene epoxidation.[4,5] Indeed, under the same conditions, TBA-$PW_4$ produced cyclohexene epoxide with 98% selectivity at 84% conversion (TOF = 9 $h^{-1}$).

The results of cyclohexanol oxidation with four equivalents of $H_2O_2$ in the presence of **1**, $PW_{12}$, and $PW_4$ are presented in Figure 3. In contrast to the thioether oxidation, both H-**1** and H-$PW_{12}$ were completely inactive in the oxidation of cyclohexanol, while TBA-**1** and TBA-$PW_{12}$ catalyzed this reaction effectively and gave cyclohexanone with 98% selectivity at 96 and 80% substrate conversion, respectively, after 24 h at 70 °C. A similar effect of countercations was reported by Ishii for alcohol oxidation by the $PW_{12}/H_2O_2$ system under two-phase conditions.[4c]

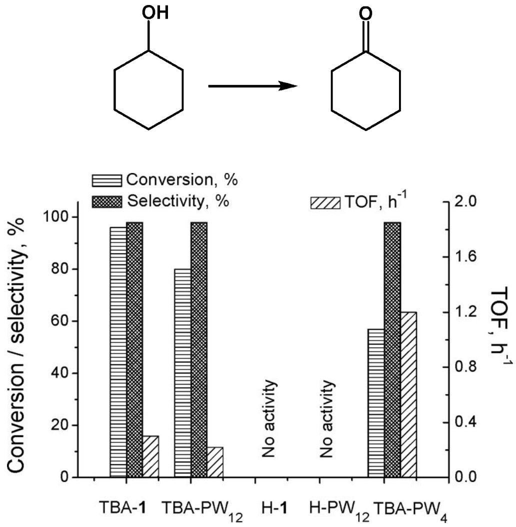

Figure 3. Cyclohexanol oxidation to cyclohexanone with $H_2O_2$ in the presence of different POMs. Reaction conditions: substrate 0.1 M, $H_2O_2$ 0.4 M, POM $4\times10^{-3}$ M, MeCN, 70 °C, 24 h.

Again, both the product yield and TOF were higher for **1** than for $PW_{12}$, indicating that the belt tungsten atoms are more efficient than the cap (Keggin) tungsten atoms in $H_2O_2$ activation.

As in the case of the thioether oxidation, the oxidation of cyclohexanol proceeded more rapidly in the presence of $PW_4$, but the difference in the TOF values was not so dramatic (compare the TOF values in Figure 1 and Figure 3). In spite of the higher reaction rate, significantly lower alcohol conversion and ketone yield were achieved for $PW_4$ relative to **1** after 24 h, most likely because of rapid deactivation of the Venturello complex under the turnover conditions.

Recently, we have found that $\alpha$-*B*-$[As_2W_{21}O_{67}(H_2O)]^{6-}$ (**2**) is also capable of catalyzing cyclohexanol oxidation (TOF = 0.1 $h^{-1}$), but is not active in cyclohexene epoxidation with $H_2O_2$.[13] Hence, the nature of the central atom and the specific sandwich POM structure (*A* vs. *B*) do not affect dramatically the catalytic properties of the belt tungsten atoms. Meanwhile, the higher reaction rate found for **1** (TOF = 0.3 $h^{-1}$) is consistent with a better accessibility of the equatorial W in structure *A* relative to structure *B* and/or three W-($OH_2$) fragments in **1** as opposed to one W-($OH_2$) in **2**. Importantly, the catalytic performance of **1** differs drastically from that of the divacant Keggin-type polyoxometalate $\gamma$-$[(SiO_4)W_{10}O_{30}(H_2O)_2]^{4-}$ ($SiW_{10}$) recently reported by Mizuno et al., which is a highly active and selective catalyst for $H_2O_2$-based alkene epoxidation.[1g] The unique catalytic activity and selectivity of $SiW_{10}$ was ascribed to the presence of two terminal aqua ligands at the lacunary W sites;[1g,1h] however, later Hill and co-workers suggested the presence of four terminal hydroxido ligands in this POM $\{\gamma$-$[(SiO_4)W_{10}O_{28}(OH)_4]^{4-}\}$.[14] Regardless of the number of aqua ligands, the catalytic properties of the "vacant" and "belt" tungsten atoms are completely different.

## Stability Study

Stability of the structural unit of **1** toward 50–100 equiv. of $H_2O_2$ in MeCN at 25–70 °C has been explored by using IR, Raman, and $^{31}P$ NMR spectroscopic techniques. Keeping in mind that the most severe reaction conditions were used for the oxidation of cyclohexanol, we separated TBA-**1** after the catalytic reaction and checked the catalyst structure by IR spectroscopy. As one can judge from the comparison of the IR spectra in Figure 4, polyanion **1** preserves its structure under the turnover conditions. The Raman spectra of **1** in MeCN before and after the addition of $H_2O_2$ are shown in Figure 5. The only new band, which appeared after the addition of $H_2O_2$, was that located at 869 $cm^{-1}$. This band most likely belongs to O–O stretching vibrations of free hydrogen peroxide.[5a,15] No bands at 855 and 553 $cm^{-1}$, which are characteristic for $PW_4$ and some other low-nuclearity peroxidotungsten species,[5a] have been detected even after 72 h. Furthermore, we did not observe any new bands that could be ascribed to a peroxo species formed by the belt or cap W atoms in **1**. This may indicate that either the peroxido complexes are rather weak or they are in fast exchange on the spectroscopic time scale.

Figure 6 presents the $^{31}P$ NMR spectrum of **1** after the addition of $H_2O_2$ ($[H_2O_2]/[\mathbf{1}] = 50$) and storage of the solution at room temperature for 48 h. A low-intensity signal at 3.8 ppm evidently belongs to $PW_4$.[5] The amount of $PW_4$

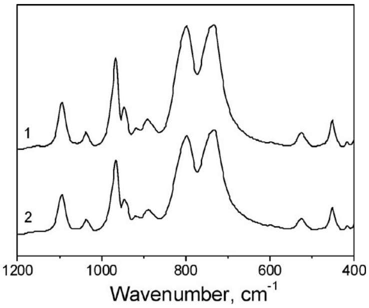

Figure 4. IR spectra (in KBr) of TBA-**1** after (1) and before (2) the reaction of cyclohexanol oxidation with $H_2O_2$ (reaction conditions as in Figure 3).

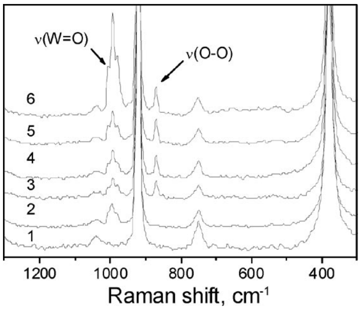

Figure 5. Raman spectra of: (1) MeCN; (2) H-**1** in MeCN; (3, 4, 5, and 6) H-**1** in MeCN + $H_2O_2$ (50 equiv.) after 1, 11, 24, and 72 h, respectively.

species in the MeCN/$H_2O_2$ solution of **1** is, however, very low (less than 1%) compared to **1** ($\delta$ = –13.17). A broad, low-intensity signal at approximately –11 ppm was always present in the spectrum of TBA-**1** in MeCN without $H_2O_2$. Since this peak was absent in the spectrum of H-**1** dissolved in water, we may suppose that it originates from a partial substitution of water molecules in the coordination sphere of the equatorial W atoms by MeCN molecules. The signal broadening may be due to some exchange processes (e.g. between polyanions with different numbers of $CH_3CN$ molecules).

Under the same conditions (50 equiv. $H_2O_2$, MeCN, 25 °C), $PW_{12}$ was also found to be stable towards solvolytic degradation [only traces of a lower-nuclearity peroxidotungstate ($\delta$ = 0.24 ppm) were detected by $^{31}P$ NMR spectroscopy in several days]. Note that in water, $PW_{12}$ completely transforms to $PW_4$ and other peroxidotungstates after treatment with 50 equiv. of $H_2O_2$ for 1 h at room temperature.[5c] Taking into account that the catalytic oxidation reactions were rather fast, it seems very unlikely that the lower-nuclearity peroxidotungstates could be responsible for the observed catalytic activity of **1** and $PW_{12}$ in MeCN. In effect, we did not observe any signals that could be attributed to the low-nuclearity species in the $^{31}P$ NMR spectra of the reaction mixtures after the catalytic runs. Therefore, we can conclude that the use of acetonitrile does allow increasing the stability of POMs significantly towards solvolytic destruction in the presence of $H_2O_2$, and the observed catalytic activity of **1** and $PW_{12}$ is not related to their destruction. This conclusion is strongly supported by the lack of the catalytic activity of **1** and $PW_{12}$ in cyclohexene epoxidation under the conditions studied. Hence, the results of the stability study are in good agreement with the results of the catalytic study.

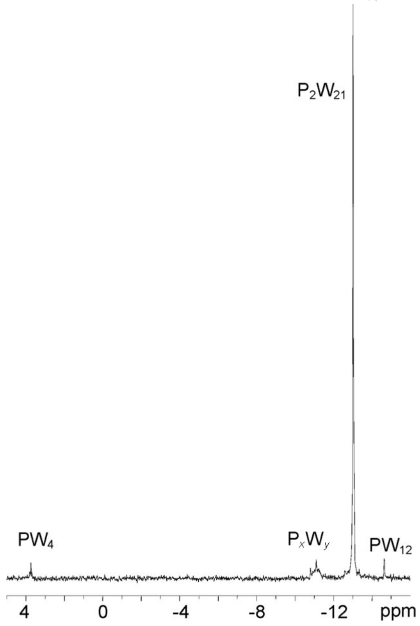

Figure 6. $^{31}P$ NMR spectrum of TBA-**1** ($5 \times 10^{-3}$ M in MeCN) after interaction with $H_2O_2$ (50 equiv.) at room temperature for 48 h.

## Conclusions

The stability of the sandwich and Keggin heteropolyanions, **1** and $PW_{12}$, toward 50–100 equiv. of $H_2O_2$ in acetonitrile at 25–70 °C has been established by using $^{31}P$ NMR, IR, and Raman spectroscopic techniques. The ability of **1** and $PW_{12}$ to activate hydrogen peroxide with respect to the selective sulfoxidation of thioethers and ketonization of cyclic alcohols in MeCN solution has been demonstrated. Polyanion **1** has revealed some advantages in terms of both substrate conversion and product yield. The high selectivity of sulfoxidation and the Hammett-type correlation found for the oxidation of *p*-substituted methyl phenyl sulfides in the presence of **1** indicate the mechanism of electrophilic oxygen transfer from an active peroxidotungsten species to organic sulfide. However, the electrophilicity of this peroxo oxygen seems to be too low to accomplish alkene epoxidation, which easily proceeds in the presence of $PW_4$ but does not occur with **1** or $PW_{12}$ in MeCN. The nature of the countercations strongly affects the oxidation rate: while heteropolyacids H-**1** and H-$PW_{12}$ are more active than the corresponding TBA salts in the thioether oxidation, they are not active at all in the oxidation of alcohols. On the contrary, the TBA salts are highly efficient in the latter reaction. Under comparable conditions, $PW_4$ is a more active catalyst but undergoes rapid deactivation. In general, the catalytic behavior of **1** and $PW_{12}$ in MeCN contrasts significantly with the behavior of $PW_4$, which allowed us to conclude that different active species operate in these catalytic systems. This conclusion is corroborated by the results of the spectroscopic study on the stability of **1**. In fact, our work first demonstrated that the "belt" and "cap" tungsten atoms in sandwich and Keggin POMs are capable of catalyzing the selective oxidation of thioethers and alcohols with $H_2O_2$; however, in sharp contrast to the tungsten centers in $PW_4$ or $SiW_{10}$, they are not able to accomplish alkene epoxidation.

## Experimental Section

**Materials:** Acetonitrile, cyclohexene, cyclohexanol, and methyl phenyl sulfide were purchased from Aldrich. Hydrogen peroxide was used as a 30 wt.-% solution in water; its concentration was determined iodometrically prior to use. Heteropolyacid $H_3PW_{12}O_{40}\cdot 6H_2O$ was a commercial product and was purified by extraction with diethyl ether. The compound purity was confirmed by $^{31}P$ NMR spectroscopy (a single peak at –15.05 ppm in $H_2O$). All the other reactants were the best available reagent grade and were used without purification.

**Synthesis:** Heteropolyacid $H_6P_2W_{21}O_{71}(H_2O)_3\cdot 14H_2O$ (**1**) was synthesized by the electrodialysis method according to the published procedure.[10] $^{31}P$ NMR spectroscopy in $H_2O$: –13.70 ppm. About 2% of admixture of $H_3PW_{12}O_{40}$ was present according to the $^{31}P$ NMR spectrum. The tetra-*n*-butylammonium (TBA) salt of **1** (TBA-**1**) was prepared according to the following procedure: A solution of **1** (7.6 g, 1.42 mmol) in water (50 mL) was added to the solution of TBABr (3.2 g, 10 mmol) in water (50 mL). After 5 min of intensive stirring, a white precipitate was separated by centrifugation, washed with water (100 mL), and dried in an oven at 100 °C. The resulting solid was dissolved in a minimal volume of MeCN, re-precipitated with water, and dried again. The solid contained about 10% TBA-$PW_{12}$ ($^{31}P$ NMR spectroscopy in dry MeCN: –14.7 ppm). To purify TBA-**1**, it was dissolved in a minimal volume of hot MeCN and kept in a closed vessel overnight at room temp. Laid-down crystals of TBA-$PW_{12}$ were removed by filtration. The filtrate was steamed to dryness in a warm place, and then the solid was dried at 100 °C. $^{31}P$ NMR spectroscopy in dry MeCN: –13.17 ppm. IR (KBr, 1200–550 $cm^{-1}$): $\tilde{\nu}$ = 1094, 1037, 966, 946, 889, 798, 733 $cm^{-1}$. The amount of TBA cations was determined by ignition. The TBA salt of the Venturello complex $TBA_3\{PO_4[W(O)(O_2)_2]_4\}$ (TBA-$PW_4$) was prepared by the peroxide-mediated decomposition of $H_3PW_{12}O_{40}$ following the slightly modified published procedure.[4c]

**Catalytic Oxidations:** The catalytic oxidations were carried out in temperature-controlled glass vessels at 25–70 °C in MeCN solution. Typical reaction conditions were as follows: MPS 0.1 M, $H_2O_2$ 0.1 M, POM $2\times10^{-3}$ M, 25 °C; cyclohexene 0.2 M, $H_2O_2$ 0.2 M, POM $2\times10^{-3}$ M, 50 °C; cyclohexanol 0.1 M, $H_2O_2$ 0.4 M, POM $4\times10^{-3}$ M, 70 °C. The reactions were initiated by the addition of hydrogen peroxide. Samples were taken during the course of the reaction by a syringe, and the reaction products were identified by GC–MS and GC by using reference compounds. The substrate conversions and product yields were quantified by GC by using biphenyl as internal standard. The TOF (turnover frequency) values were determined from the initial rates of substrate consumption and normalized to the number of W atoms. After the reaction, water was added to the reaction mixture, the catalyst was separated by centrifugation, washed with water, dried in air, and checked by IR spectroscopy.

**Instrumentation:** GC analyses were performed by using a gas chromatograph "Tsvet-500" equipped with a flame ionization detector and a quartz capillary column (30 m × 0.25 mm, Agilent DB-5MS). FTIR spectra were recorded in KBr pellets containing 2 mg of a sample and 500 mg of KBr with a BOMEM-MB-102 spectrometer or a Nicolet Avatar spectrometer. The $^{31}P$ NMR spectra were measured in 10 mm o.d. ampoules with a Bruker Avance-400 spectrometer at an operating frequency of 161.98 MHz, with a 5 kHz sweep width, 10 µs pulse width, and 30 s interpulse delay. Chemical shifts were referenced to 85% $H_3PO_4$ as an external standard.

**Supporting Information** (see footnote on the first page of this article): Structure of **1** and kinetic profiles for MPS oxidation with $H_2O_2$ in the presence of **1** and $PW_{12}$.

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