

## 34% 과산화 수소와 함께 알코올의 산화에서 수분-관용적인 촉매로서의 간단한 헤테로 다중산

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## Simple Heteropoly Acids as Water-Tolerant Catalysts in the Oxidation of Alcohols with 34% Hydrogen Peroxide, A Mechanistic Approach

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**요 약.** 간단한 Keggin형의 텅스텐과 몰리브덴의 헤테로 다중산인,  $H_3PW_{12}O_{40}$ 과  $H_3PMo_{12}O_{40}$ 는 표준식수에서 34% 과산화 수소와 함께 알코올의 산화를 위한 수분-관용적인 촉매로 사용되어졌다. 우리의 실험결과에 따르면  $H_3PW_{12}O_{40}$ 는 좋은 수율로 표준식수에서 치환을 위한 간단하고, 효과적이고, 값싼 촉매로 사용되어질 수 있다. 반응 과정 중 25-80 °C에서 다른 용매 효과와 촉매의 농도변화와 기질 또한 연구하였다.

**주제어:** 산화, 헤테로 다중산, 촉매작용, 과산화 수소

**ABSTRACT.** Simple Keggin type tungsten and molybdenum heteropoly acids,  $H_3PW_{12}O_{40}$  and  $H_3PMo_{12}O_{40}$ , were used as water-tolerant catalysts for the oxidation of alcohols with 34% hydrogen peroxide in normal drinking water. According to our findings,  $H_3PW_{12}O_{40}$  may be used as a simple, effective, and cheap catalyst for this type of transformation in normal drinking water with excellent yields. Effects of different solvents at 25-80 °C and changing concentration of catalyst and substrate on the reaction progress were also studied.

**Keywords:** Oxidation, Heteropoly acid, Catalysis, Hydrogen Peroxide

### INTRODUCTION

Development of effective, safe, and environmentally benign protocols to carry out selective oxidation of alcohols mediated by Lewis acids in water, as the most fundamentally functional transformation in practical and academic organic synthesis, has been a challenge for many years.<sup>1-7</sup> A variety of stoichiometric and catalytic routes have been explored to accomplish such a conversion.<sup>8-16</sup>

However, much of these methods involve the use of expensive reagents, harsh reaction conditions, and leading to the generation of a large amount of

toxic waste.<sup>17,18</sup> Because of these facts, there is still a need to develop new environmentally benign routes that meet industrial demands for this transformation.

Because of the unique properties of polyoxometalates, they are promising acid, redox and bifunctional catalysts. The catalytic reactions can be performed in homogeneous as well as in heterogenous systems. Polyoxometalates are environment-friendly and economically feasible solid acids due to several advantages such as high catalytic activities, ease of handling, cleaner reaction conditions, non-toxicity and experimental simplicity.<sup>19</sup> These compounds

effectively catalyze oxidation of a variety of organic compounds such as olefins, thioethers, and alcohols with several terminal oxidants such as alkyl hydroperoxide, molecular oxygen, iodanyl benzene, as well as hydrogen peroxide.<sup>20-23</sup>

Now, in continuation to our previous findings,<sup>24</sup> we summarized here our recent developments on different reaction parameters affect oxidation of alcohols with aqueous hydrogen peroxide catalyzed by water-tolerant catalysts,  $H_3PW_{12}O_{40}$  and  $H_3PMo_{12}O_{40}$ , in normal drinking water. Role of solvent system, effect of catalyst/substrate mole ratio, and temperature on the reaction progress are presented.

## RESULTS AND DISCUSSION

### General

Polyoxometalates are coordination compounds containing  $d^n$ metal-oxygen clusters whose chemical properties can be controlled by transition metal substitution and the counter cation used. One important class of polyoxometalates is heteropoly anions, which are more studied and are useful as catalysts. The two main structures of heteropolyoxometalates are *Keggin* and *Wells-Dawson* types (Fig. 1).<sup>29</sup>

The *Keggin* structure is roughly spherical and gives a general formula of  $XM_{12}O_{40}$ , where X is the heteroatom and M is the addenda  $d^n$ metal atom. Each corner of the heteroatom tetrahedron is associated with an  $M_3O_{13}$  unit. Three  $MO_6$  of octahedron unit form a triplet  $M_3O_{13}$  by sharing octahedral

edges, and four such triplets share the octahedral vertexes and arrange tetrahedrally around the heteroatom, that is, the three-fold shared oxygen atoms in the triplet  $M_3O_{13}$  are coordinated to a heteroatom, resulting in a  $T_d$  symmetric polyoxometalate. Another structure is the Wells-Dawson type structure that is ellipsoidal, of formula  $X_2M_{18}$ . This structure consists of two heteroatoms stacked one atop the other, and each end is composed of an  $M_3O_{13}$  cap, with two six-metal belts circling the molecule.

For catalysis, *Keggin*-type heteropoly acids with the general formula of  $H_{x-y}X^yM^{VI}_{12}O_{40}$  (where  $X=Si^{IV}$ ,  $Ge^{IV}$ ,  $P^V$ ,  $As^V$  and  $M=Mo^{VI}$ ,  $W^V$ ) are of great importance. The considerable number of studies performed during the past years allowed to formulate the selection principles of effective catalysts in the series of *Keggin*-structure. Their significantly higher *Bronsted* acidity, compared with the acidity of traditional mineral acid catalysts, is of great importance for catalysis. Using heteropoly acid-based catalysts, it is frequently possible to obtain higher selectivity and successfully solve ecological problems.

### Oxidation of cyclohexanol with $H_2O_2$ - $H_3PW_{12}O_{40}$ catalytic system in different solvents at 25-80 °C

It is well known that the nature of solvent plays a very important role in the catalytic reactions carried out in liquid phase.<sup>30,31</sup> To study the influence of the nature of solvent, the oxidation of cyclohexanol with  $H_2O_2$ - $H_3PW_{12}O_{40}$  catalytic system was carried out in different solvents. Cyclohexanol as model substrate and  $H_3PW_{12}O_{40}$  as catalyst were conducted in normal water, <sup>1</sup>butanol, and chloroform, as solvents, at 25-80 °C (Table 1). The results showed that the catalytic performance was strongly affected by the type of solvent. The highest reaction activity was achieved in the system of using water as a solvent. The results showed that efficiency and yield of the reactions in <sup>1</sup>butanol and chloroform, as organic solvents, were much less than those observed in water. Normal water (electrical conductivity, 550; total dissolved solids, 350; and pH, 8.3) led to complete conversion of cyclohexanol to cyclohexanone with 100% selectivity at 65 °C after 2.5 h; whereas, chloroform and <sup>1</sup>butanol produced <5% of

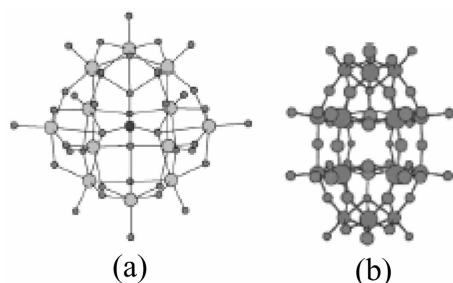


Fig. 1. The structure of *Keggin* (a) and *Wells Dawson* (b) heteropoly anion  $[XM_{12}O_{40}]^n$ . Red corners, black, and pink (blue) balls represent oxygen atoms, metal ions, and heteroatoms in the structures, respectively.

**Table 1.** Oxidation of cyclohexanol to cyclohexanone with  $H_2O_2$ - $H_3PW_{12}O_{40}$  catalytic oxidation system in different solvents at 25-80 °C.<sup>a</sup>

Temperature (°C)	Yield (%) after 1 h		
	Normal water	Butanol	Chloroform
25	15	2	3
65	45	<3	<5
80	65	11	16

<sup>a</sup>To a solution of  $H_3PW_{12}O_{40}$  (0.018 mmol) and 34%  $H_2O_2$  (5 mmol) in the appropriate solvent (5 ml) was added cyclohexanol (0.94 mmol). The reaction mixture was stirred by a magnetic stirrer for the required time. Progress of the reactions was followed by the aliquots withdrawn directly and periodically from the reaction mixture, analyzed by gas chromatography.

cyclohexanone at the same reaction conditions.

*Table 1* also describes effect of temperature elevation on the oxidation of cyclohexanol. The conversion found to increase substantially with increasing temperature, which suggested that the reaction was intrinsically kinetically controlled. At ambient temperature (25 °C), the reaction hardly happened; while, the conversion increased with increasing temperature. A sharp increase in the yield occurred by elevation of temperature and 65% of cyclohexanone obtained with  $H_2O_2$ - $H_3PW_{12}O_{40}$  catalytic system in water at 80 °C after 1h. Whereas, only 15% of the product observed at ambient temperature at the same time (*Fig. 2*).

#### Oxidation of cyclohexanol with $H_2O_2$ over some Keggin-type heteropoly acids

Based on the effect of solvent, we selected nor-

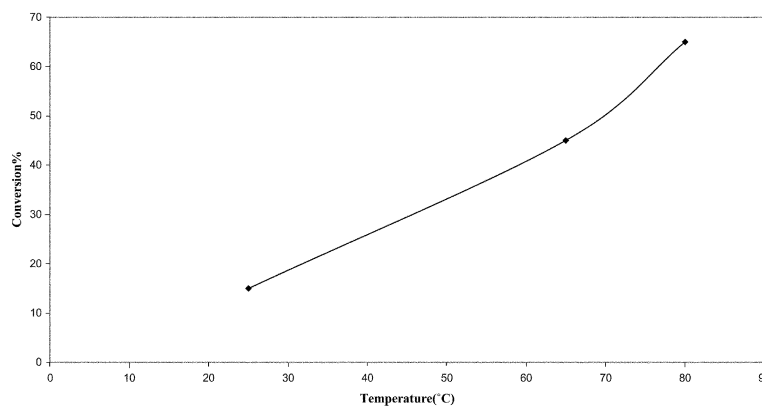
**Table 2.** Effect of the type and concentration of heteropoly acid on the yield% of cyclohexanol oxidation in water.<sup>a</sup>

Catalyst (mmol)	Yield (%) after 1h		
	$H_3PW_{12}O_{40}$	$H_3PMo_{12}O_{40}$	$H_4SiW_{12}O_{40}$
0	0	0	0
0.0036	29	12	3
0.018	45	18	<5
0.09	80	26	12

<sup>a</sup>To a solution of catalyst (0-0.09 mmol) and 34%  $H_2O_2$  (5 mmol) in normal water (5 ml) was added cyclohexanol (0.94 mmol). The reactions were carried out as described below *Table 1*.

mal water as the solvent for the oxidation of cyclohexanol. Effect of the type and concentration of heteropoly acid on the oxidation of cyclohexanol in normal water is studied. *Table 2* shows that  $H_3PW_{12}O_{40}$  acted distinctly more efficient than  $H_3PMo_{12}O_{40}$  and  $H_4SiW_{12}O_{40}$  in the oxidation of cyclohexanol with  $H_2O_2$  in normal water. It's considerable, no conversion of cyclohexanol was observed in the absence of catalyst.

An increase in the catalyst concentration (with respect to cyclohexanol) resulted in an increase in the conversion. 5-fold increase in concentration of  $H_3PW_{12}O_{40}$ , from 0.0036 to 0.018 mmol, enhanced the conversion from 29 to 45% in water, as solvent, after 1 h. Moreover, increase in concentration of  $H_3PMo_{12}O_{40}$  from 0.018 to 0.09 mmol, caused an increase in the conversion from 18 to 26% at the same time. *Fig. 3* shows the effect of catalyst concentration on the oxidation of cyclohexanol with  $H_2O_2$  in water.



**Fig. 2.** Effect of temperature on the conv.% of cyclohexanol with  $H_2O_2$ - $H_3PW_{12}O_{40}$  catalytic system after 1 h.

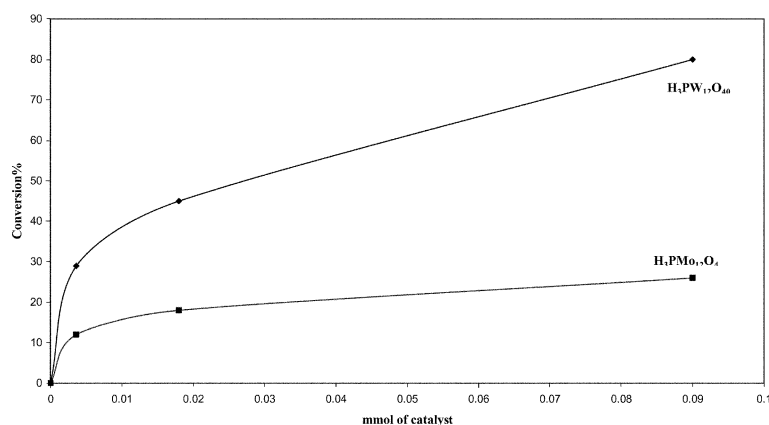


Fig. 3. Effect of catalyst concentration on the conv.% of cyclohexanol with H<sub>2</sub>O<sub>2</sub> in water after 1 h.

#### Oxidation of some alcohols into their corresponding oxygenated products with H<sub>2</sub>O<sub>2</sub> - H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-H<sub>2</sub>O catalytic oxidation system

Treatment of an appropriate alcohol with hydrogen peroxide by the mediation of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> in water afforded the corresponding carbonyl compound after the indicated time in Table 3. Cyclohexanol, as a secondary alcohol, showed the best results under different mole ratios of sub./cat. It led to complete conversion with sub./cat. mole ratio of 52 after 2.5 h. While, benzyl alcohol showed less reactivity toward oxidation and produced 78% benzaldehyde under the same reaction conditions. n-Butanol, as a linear primary aliphatic alcohol, resulted in the least reactivity and obtained 30% of conversion toward the corresponding aldehyde after 2.5h.

Effect of changing concentration of alcohols was also introduced in Table 3. As is expected, conversion decreased by enhancing alcohol concentration. For example, cyclohexanol produced 62, 45, and 13% of conversions with sub./cat. mole ratios of 26, 52, and 260, respectively. However, as is shown in Table 3 and Fig. 4, turnover frequency,<sup>12</sup> TOF, increases with enhancing concentration of alcohol. This may partly be due to lower deactivation of catalyst during the reaction and higher number of effective collisions between substrate and the catalytically active oxidizing species. Finally, in all cases no over oxidation products, carboxylic acids, were observed even after extended reaction times.

Table 3. Effect of the type and concentration of some alcohols on the efficiency of H<sub>2</sub>O<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-H<sub>2</sub>O catalytic oxidation system.<sup>a</sup>

Alcohol (mmol)	Yield% (TOF) <sup>b</sup> after 1h		
	n-Butanol	Cyclohexanol	Benzyl alcohol
0.47	25(6.5)	62(16)	53(13.8)
0.94	18(9.3)	45(23.4)	40(20.8)
4.7	4(10.4)	13(34)	10(26.1)

<sup>a</sup>To a solution of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (0.018 mmol) and 34% H<sub>2</sub>O<sub>2</sub> (5 mmol) in normal water (5 ml) was added the corresponding alcohol (0.47-4.7 mmol). The reactions were carried out as described below Table 1. <sup>b</sup>Turnover frequency, TOF, was calculated by the expression ([product]/[catalyst])×time (h<sup>-1</sup>).<sup>12</sup>

#### Catalytically active oxidizing species in H<sub>2</sub>O<sub>2</sub> - H<sub>3</sub>PM<sub>12</sub>O<sub>40</sub>-H<sub>2</sub>O oxidation system

The groups of Venturello<sup>32, 33</sup> and Ishii<sup>34-36</sup> independently developed highly effective and mechanistically closely related polyoxometalates-based catalyst systems for oxygenation of some organic compounds by hydrogen peroxide. Heteropoly acids with the Keggin structure are degraded in the presence of excess H<sub>2</sub>O<sub>2</sub> to form peroxo species {PO<sub>4</sub>[MO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>}<sup>2-</sup> and [M<sub>2</sub>O<sub>2</sub>(O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> (M=W, Mo), which are the true catalytically active intermediate in the oxygenation of organic compounds by hydrogen peroxide catalyzed by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>. It is recommended that these two peroxo species are responsible for the oxidation of alcohols with H<sub>2</sub>O<sub>2</sub>-H<sub>3</sub>PM<sub>12</sub>O<sub>40</sub>-H<sub>2</sub>O (M=W and Mo) catalytic oxida-



GLC analyses were performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector using CPB 5-20 (25 m  $\times$  0.25 mm, 0.1 to 5.0  $\mu$ m film thickness) and fused silica WCOT 25 m  $\times$  0.32 mm capillary columns with 5.0  $\mu$ m film thickness. The heteropoly acids  $H_3PW_{12}O_{40}$ ,  $H_3PMo_{12}O_{40}$ , and  $H_4SiW_{12}O_{40}$  were prepared and characterized according to literature procedures or were purchased commercially.<sup>25-28</sup>

#### General procedure for oxidation of alcohols to carbonyl compounds in normal drinking water

To a solution of catalyst (0.018 mmol) and 34%  $H_2O_2$  (5 mmol) in normal water (5 ml) as solvent, was added alcohol (0.94 mmol) and the reaction mixture was allowed to stir at 65 °C for the required time. Progress of the reaction was followed by the aliquots withdrawn directly from the reaction mixture, analyzed by gas chromatography using n-decane as internal standard. After completion of the reaction, products were extracted with 20 ml  $CHCl_3$ . The extract was dried over anhydrous sodium sulfate and then was filtered. The filtrate was concentrated under reduced pressure. Finally, the concentrated filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound.

#### Reusability of $H_3PW_{12}O_{40}$

At the end of the reaction,  $H_3PW_{12}O_{40}$  recovered by slow drying the aqueous phase of the reaction mixture at 50 °C under intense light for 2 h and then at 130 °C for 3 h. The regenerated solid acid catalyst was washed with dichloromethane, dried at 130 °C for 1 h, and re-used in another reaction. The reusability of the catalyst was studied by using the separated catalyst in another reaction. Therefore, two experiments were done, one with the fresh catalyst and another with the recycled  $H_3PW_{12}O_{40}$ . It is concluded that there is no considerable deactivation of the catalyst and it is recyclable. The recycled catalyst could be reused for several times without considerable loss of activity. IR spectroscopy of the catalyst confirmed that the *Keggin* structure was almost retained at least after four repeated runs.

## CONCLUSION

To conform to green chemistry, it is important to realize reaction systems in water instead of organic solvents, to use safe reagents, to decrease hazardous inorganic and organic wastes, and to use a minimal amounts of reusable catalysts.<sup>43</sup> Present report established a unique green protocol to achieve some of these goals by using the simplest heteropoly acid catalysts, which offer substantial economic and environmental benefits.

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