

Multiphase oxidation of alcohols and sulfides with hydrogen peroxide catalyzed by heteropolyacids

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ABSTRACT

This work describes the application of a multiphase system for the oxidation of alcohols to ketones or aldehydes, and the selective conversion of sulfides to sulfoxides or sulfones using Keggin-type heteropolyacids and hydrogen peroxide. Benzylic and secondary alcohols were oxidized to ketones or aldehydes at 70 °C in good yield and selectivity. Similarly, sulfides were converted to sulfoxides or sulfones at room temperature with high yields and selectivity.

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1. Introduction

The selective oxidation of organic substrates is an important transformation in organic synthesis, as the corresponding products are essential intermediates for many drugs, vitamins and fragrances [1,2]. In particular, the oxidation of alcohols to aldehydes or ketones is a fundamental preparative reaction, which has been widely investigated [1,2]. Several common oxidation procedures use heavy metal complexes that are often toxic, corrosive and expensive. Furthermore, they are employed in large amounts ranging from stoichiometric to excess. Additionally these methods include harsh conditions such as high pressure or temperature and they generally require the presence of a strong acid [3].

Similarly, the selective catalytic oxidation of sulfides to sulfoxides has been thoroughly examined for many years due to the importance of sulfoxides as intermediates in organic synthesis [4]. For the synthesis of such compounds in industrial processes and laboratory experimentations, the use of aqueous hydrogen peroxide as an oxidant is very attractive, since it is environmentally friendly and easy to handle [5].

A variety of different catalytic systems for hydrogen peroxide promoted oxidation of alcohols have been developed e.g. tungsten-based polyoxometalate catalysts [6–8], Lewis acid iron aluminium chloride [9] and dinuclear Mn (IV) complexes [10]. However, some

organic substrates are insoluble in aqueous hydrogen peroxide, which can subsequently lower the selectivity and efficiency of the oxidation reaction. This problem can be avoided with the use of a phase transfer catalyst (PTC). For example, the use of a co-catalyst [11], such as sodium tungstate [12] with a PTC has shown to increase the rate of oxidation in the presence of hydrogen peroxide. Besides, selective catalytic oxidation of sulfides to sulfoxides with hydrogen peroxide has been studied with catalysts such as Jacobsen (salen) Mn(III) complexes [13], vanadium bromoperoxidase and cetyl trimethyl ammonium tribromide [14].

Herein for the first time, an alternative approach for the oxidation of such organic substrates involving the use of a triphasic system is reported. In the triphasic system the homogeneous catalyst is solubilized in one phase (e.g., Aliquat 336) where the reaction takes place; the substrate and products are taken up in the organic phase; the third phase is the aqueous phase. Thus, the reduction product can be obtained by a simple separation.

Multiphase systems have been used for a variety of important reduction processes which include: hydrodehalogenation of polychlorinated benzenes [15,16], hydrodechlorination of chlorophenoxypesticides such as dieldrin and DDT [17,18], selective removal of halogens from functionalized aryl ketones [19,20], and enantioselective hydrogenation of acetophenone [21].

Heteropolyacids are attractive as catalysts for oxidation processes due to their low toxicity and high acidity. Heteropolyacids have been used in a variety of acid-catalyzed reactions such as esterification, etherification, hydration of olefins and dehydration of alcohols [22]. Additionally, Keggin-type polyoxoanions have been widely employed

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as homogeneous and heterogeneous catalysts for the oxidation of organic compounds [23–29]. They have been used in the presence of hydrogen peroxide for the epoxidation of olefins and allylic alcohols, oxidation of alcohols and diols to ketones, cleavage of 1,2-diols [9] and selective oxidation of benzyl alcohol [16].

Recently, we have applied the use of Keggin heteropolyacids in a range of processes i.e. preparation of heterocycles [29,30], protection/deprotection of organic functional groups [30,31], and oxidation processes, as well as, conversion of 2,6-dimethylphenol to 2,6-dimethyl-1,4-benzoquinone [32], and selective oxidation of sulfides to sulfoxides with hydrogen peroxide [33].

2. Experimental

The commercially available heteropolyacids $H_3PMo_{12}O_{40}$ and $H_3SiMo_{12}O_{40}$ were purchased from Aldrich and $H_4PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ from Fluka. The heteropolyacids containing vanadium, aluminium and Al–V in the Keggin primary structure ($H_6PMo_{11}AlO_{40}$, $H_4PMo_{11}VO_{40}$ and $H_5PMo_{11}Al_{0.5}V_{0.5}O_{40}$) were prepared and fully characterized according to the procedure already published in the literature [22]. Thus, starting from these heteropolyacids, different salts with pyridinium as cation were obtained ($Py_3PMo_{12}O_{40}$, $H_3PyPMo_{11}VO_{40}$, $HPy_3PMo_{11}VO_{40}$ and $Py_4PMo_{11}VO_{40}$). For comparative purposes, the $Py_5PMo_{10}V_2O_{40}$ catalyst was tested in homogeneous and multiphase conditions. GC analyses on the reaction mixture were performed using a Varian GC 3400 using a fused silica capillary column “Chromapack CP Sil 8 CB” (film thickness 0.25 μ m). GC–MS analyses were performed using a HP 5971 mass detector coupled to a HP gas chromatograph fitted with a 30 m \times 0.25 nm DB5 capillary column.

2.1. General procedure for homogeneous oxidation

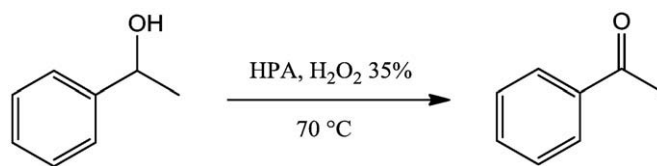
In all the reactions, a 25 mL three-necked round-bottomed flask was used, heated at the reaction temperature and connected with a water-jacketed condenser. The reactor was loaded with a mixture of 0.7 mmol of substrate, 5 mL of CH_3CN , 1 mL of hydrogen peroxide 35% (w/v), *n*-decane as internal standard (0.056 g, 0.39 mmol) and 3% of the heteropolyacid (mmol) with respect to the amount of substrate. The mixture was stirred at 700 rpm.

2.2. General procedure for multiphase oxidation

In all the reactions, a 25 mL three-necked round-bottomed flask was employed, heated at the reaction temperature and connected with a water-jacketed condenser. The reactor was loaded with a mixture of aqueous phase (1 mL of aq. hydrogen peroxide 35% (w/v) and 4 mL of water), Aliquat 336 (tricaprylmethylammonium chloride, 0.232 g, 0.59 mmol), 0.7 mmol of substrate, *n*-decane as the internal standard (0.056 g, 0.39 mmol) and 3% of heteropolyacid with respect to the employed substrate. The organic phase was adjusted to 10 mL by adding isooctane. The reaction mixture was magnetically stirred at 700 rpm.

2.3. Sampling procedure and GC analyses

The samples were periodically collected from the organic phase. Approximately 20 μ L of the reaction mixture was removed and then diluted with 1 mL isooctane or acetonitrile to a volume of 1–2 mL. The sample was then mixed with silica and filtered with cotton wool to eliminate any impurities of Aliquat 336. Determination of the concentration for the reaction components was performed using the internal standard technique.



Scheme 1. Oxidation of 1-phenylethanol in a multiphase system.

3. Results and discussion

This work describes the first application of a multiphase system for the oxidation of alcohols to ketones or aldehydes, and the selective conversion of sulfides to sulfoxides or sulfones with hydrogen peroxide in the presence of Keggin-type heteropolyacids. The oxidation reactions were carried out using a system comprising of a hydrocarbon solvent (isooctane), an aqueous phase and a phase-transfer (PT) agent (Aliquat 336 (C_8H_{17})₃(CH_3)NCl) in the presence of hydrogen peroxide and a Keggin heteropolyacid (HPA) catalyst. Employing this system, benzylic and secondary alcohols were oxidized to ketones or aldehydes at 70 °C with high yield and excellent selectivity.

Similarly, sulfides were converted to sulfoxides or sulfones (depending on the concentration of hydrogen peroxide) at room temperature with high yields and selectivity. Some preliminary investigations were conducted on the oxidation of 1-phenylethanol in the multiphase system using various catalysts (Scheme 1). The results obtained are summarized in Table 1. When Aliquat was used without catalyst (entry 2), the conversion of 1-phenylethanol into acetophenone was lower in homogeneous conditions (1%) compared with the multiphase conditions (22%). However, in the absence of a catalyst and Aliquat (entry 1), the yields were low in both cases (3 and 12%, respectively). These lower yields are due to the absence of an interphase between the substrate and the catalyst.

Besides, it is interesting to note that commercially available heteropolyacids containing phosphorous as the heteroatom i.e. $H_3PMo_{12}O_{40}$ (entry 3) and $H_3PW_{12}O_{40}$ (entry 4), were more active than those containing silicon $H_4SiMo_{12}O_{40}$ (entry 5) and $H_4SiW_{12}O_{40}$ (entry 6) within the Keggin primary structure. In

Table 1

Comparison of oxidation of 1-phenylethanol to acetophenone in homogeneous and multiphase system.

Entry	Catalyst	Time (h)	Hom. cond. ^a (%)	Mult. cond. ^b (%)
1	None ^c	20	3	12
2	None ^d	20	1	22
3	$H_3PMo_{12}O_{40}$	7	5	93
4	$H_3PW_{12}O_{40}$	7	4	76
5	$H_4SiMo_{12}O_{40}$	7	3	78
6	$H_4SiW_{12}O_{40}$	7	2	76
7	$H_6PMo_{11}AlO_{40}$	7	4	99
8	$H_4PMo_{11}VO_{40}$	7	–	70
9	$H_5PMo_{11}Al_{0.5}V_{0.5}O_{40}$	7	57(95) ^e	81
10	$Py_3PMo_{12}O_{40}$	5	7	100
11	$H_3PyPMo_{11}VO_{40}$	7	–	73
12	$HPy_3PMo_{11}VO_{40}$	7	–	78
13	$Py_4PMo_{11}VO_{40}$	7	–	79
14	$Py_5PMo_{10}V_2O_{40}$	7	–	68

^a Homogeneous conditions: catalyst (3% in mmol), solvent acetonitrile, H_2O_2 35% p/v (1 mL), 1-phenylethanol (0.7 mmol).

^b Multiphase conditions: catalyst (3% in mmol), solvent isooctane–water, H_2O_2 35% p/v (1 mL), 1-phenylethanol (0.7 mmol), Aliquat 336 (0.59 mmol).

^c Without Aliquat.

^d With Aliquat.

^e Further addition of two aliquots of 35% p/v H_2O_2 at 1 and 2 h.

Table 2
Oxidation of alcohols with hydrogen peroxide catalyzed by different heteropolyacids at 70 °C in multiphase conditions.

#	Substrate	Product	Catalyst	Time (h)	PhCOCH ₃ (%)	Other products (%)
1	1-Phenylethanol	Acetophenone	H ₃ PMo ₁₂ O ₄₀	9	95 (5) ^a	None
2	1-Phenylethanol	Acetophenone	Py ₃ PMo ₁₂ O ₄₀	5	100 (6) ^a	None
3	1-Phenylethanol	Acetophenone	H ₆ PMo ₁₁ AlO ₄₀	7	99	None
4	Benzhydrol	Benzophenone	H ₃ PMo ₁₂ O ₄₀	5	99 (8) ^a	None
5	Benzhydrol	Benzophenone	Py ₃ PMo ₁₂ O ₄₀	4	99	None
6	Benzyl alcohol	Benzaldehyde	H ₃ PMo ₁₂ O ₄₀	5	84 (12) ^a	(Benzoic acid) (4)
7	Benzyl alcohol	Benzaldehyde	Py ₃ PMo ₁₂ O ₄₀	3	89 (5) ^a	(Benzoic acid) (2)
8	Benzyl alcohol	Benzaldehyde	H ₆ PMo ₁₁ AlO ₄₀	4	85	(Benzoic acid) (2)
9	4-Chloro-benzyl alcohol	4-Chloro benzaldehyde	H ₃ PMo ₁₂ O ₄₀	5	93 (10) ^a	(4-Chlorobenzoic acid) (1)
10	4-Chloro-benzyl alcohol	4-Chloro benzaldehyde	H ₆ PMo ₁₁ AlO ₄₀	3	95	(4-Chlorobenzoic acid) (2)
11	4-Methyl-benzyl alcohol	4-Methyl benzaldehyde	H ₃ PMo ₁₂ O ₄₀	4	96 (7) ^a	(4-Methylbenzoic acid) (3)
12	4-Methyl-benzyl alcohol	4-Methyl benzaldehyde	Py ₃ PMo ₁₂ O ₄₀	3	96	(4-Methylbenzoic acid) (3)
13	4-Methoxy-benzyl alcohol	4-Methoxy benzaldehyde	H ₃ PMo ₁₂ O ₄₀	3	90	(4-Methoxybenzoic acid) (6)
14	4-Methoxy-benzyl alcohol	4-Methoxy benzaldehyde	Py ₃ PMo ₁₂ O ₄₀	2	91	(4-Methoxybenzoic acid) (5)
15	2-Octanol	2-Octanone	H ₃ PMo ₁₂ O ₄₀	7	68	None
16	2-Octanol	2-Octanone	Py ₃ PMo ₁₂ O ₄₀	6	71 (3) ^a	None
17	2-Octanol	2-Octanone	H ₆ PMo ₁₁ AlO ₄₀	6	68	None
18	2-Decanol	2-Decanone	H ₃ PMo ₁₂ O ₄₀	7	64 (3) ^a	None
19	2-Decanol	2-Decanone	H ₆ PMo ₁₁ AlO ₄₀	6	69	None
20	1-Decanol	2-Decanal	H ₃ PMo ₁₂ O ₄₀	7	20	None
21	1-Decanol	2-Decanal	Py ₃ PMo ₁₂ O ₄₀	7	22 (1) ^a	(Decanoic acid) (1)
22	1-Decanol	2-Decanal	H ₆ PMo ₁₁ AlO ₄₀	7	19	None

^a In homogeneous system corresponding to the numbers in the parentheses.

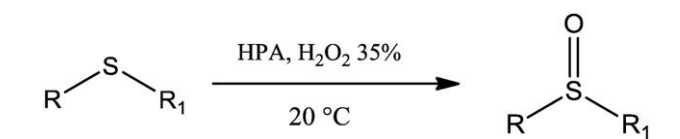
addition, among the HPA examined, those containing molybdenum were more reactive than those containing tungsten (entries 3 and 4). This is attributed to the differing redox properties of tungsten and molybdenum heteropolycompounds and is consistent with the fact that molybdenum is a better oxidant [31–35].

The substitution of a molybdenum atom by an aluminium atom within the Keggin primary structure (entry 7) leads to achieve a quantitative yield of acetophenone in multiphase conditions. Similar results were obtained with H₃PMo₁₂O₄₀ (93%, entry 3). On the other hand, substituting one vanadium atom in place of the aluminium atom led to a lower yield (70%) (entry 8).

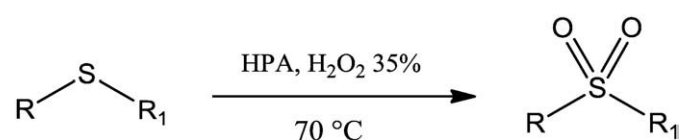
Further experiments conducted using a Keggin structure where a molybdenum atom was substituted by Al–V atoms (H₅PMo₁₁Al_{0.5}V_{0.5}O₄₀) (entry 9), led to 57 and 81% yield of acetophenone for homogeneous and multiphase conditions, respectively. In the homogeneous conditions, it was possible to further increase the yield of acetophenone to 95% (entry 9, note e) by a supplementary addition of hydrogen peroxide that, in these reaction conditions, tends to decompose very quickly. Overall, the results showed that H₆PMo₁₁AlO₄₀ was the most active catalyst among those incorporating 11 Mo atoms in the Keggin structure. Besides, when Al and V atoms are both present in the Keggin primary structure the yield of acetophenone increased in comparison to the result obtained

with a Keggin structure that incorporates only a V atom. In this case, the V atom stabilizes the Keggin structure [29–32] and this avoids the formation of catalytic compounds in the interphase. In addition, when Py₃PMo₁₂O₄₀ was used as catalyst it was possible to obtain acetophenone in quantitative yield after 5 h of reaction (Table 1, entry 10). For comparative purposes, the pyridinium salts H₃PyPMo₁₁VO₄₀, HPy₃PMo₁₁VO₄₀ and Py₄PMo₁₁VO₄₀, obtained from H₄PMo₁₁VO₄₀, were also employed as catalyst (Table 1, entries 11–14). These salts gave higher yields compared to those obtained when no pyridinium cations were present (entry 9). It is evident that an increasing number of pyridinium cations leads to higher yield (entries 12–14). The presence of two V atoms in the primary structure decreased the oxidative properties of the Keggin heteropolyacid. In fact when Py₅PMo₁₀V₂O₄₀ was used (entry 14) the yield decreased (68%).

The oxidation of additional alcohols was then investigated using the HPA catalysts that were found to be the most active in the preliminary oxidation of 1-phenylethanol (Py₃PMo₁₂O₄₀, H₆PAImo₁₁O₄₀, and H₃PMo₁₂O₄₀ (Table 1)); results shown in Table 2. In most cases, no appreciable amount of by-product was detected. However, in the case of benzyl alcohols and 4-chloro benzyl alcohol, additional hydrogen peroxide was twice added as it decomposes very quickly under homogeneous conditions. This



Scheme 2. Oxidation of sulfides to sulfoxides in a multiphase system.



Scheme 3. Oxidation of sulfides to sulfones in a multiphase system.

Table 3

Oxidation of sulfides with hydrogen peroxide (1.1 mmol unless otherwise stated) catalyzed by different heteropolyacids in multiphase condition, at room temperature.

Entry	Substrate	Catalyst	Time (min)	RR ₁ SO (%)	RR ₁ SO ₂ (%)
1	PhSMe	H ₃ PMo ₁₂ O ₄₀	60	95	2
2	PhSMe ^a	H ₃ PMo ₁₂ O ₄₀	45	1	99
3	PhSMe	H ₃ PMo ₁₂ O ₄₀ ^b	60	64	1
4	PhSMe ^a	H ₃ PMo ₁₂ O ₄₀ ^b	60	88	11
5	PhSMe	Py ₃ PMo ₁₂ O ₄₀	120	97	2
6	PhSPh	H ₃ PMo ₁₂ O ₄₀	120	98	1
7	PhSPh	Py ₃ PMo ₁₂ O ₄₀	120	100	–
8	(C ₄ H ₉) ₂ S	H ₃ PMo ₁₂ O ₄₀	60	99	1
9	(C ₄ H ₉) ₂ S	Py ₃ PMo ₁₂ O ₄₀	60	100	–
10	(PhCH ₂) ₂ S	H ₃ PMo ₁₂ O ₄₀	60	99	1

^a Molar ratio substrate/H₂O₂ 1/20 mmol.

^b In homogeneous system the use of an excess of hydrogen peroxide (1:20 equivalents) afforded the corresponding sulfone.

Table 4

Oxidation of sulfides with hydrogen peroxide (20 mmol) catalyzed by different heteropolyacids in multiphase condition, at 70 °C.

Entry	Substrate	Catalyst	Time (min)	RR ₁ SO (%)	RR ₁ SO ₂ (%)
1	PhSMe	H ₃ PMo ₁₂ O ₄₀	15	1	99
2	PhSMe	H ₆ PMo ₁₁ AlO ₄	10	–	100
3	PhSMe	Py ₃ PMo ₁₂ O ₄₀	10	–	100
4	PhSPh	H ₃ PMo ₁₂ O ₄₀	20	–	98
5	PhSPh	Py ₃ PMo ₁₂ O ₄₀	20	–	99
6	(C ₄ H ₉) ₂ S	H ₃ PMo ₁₂ O ₄₀	15	2	97
7	(C ₄ H ₉) ₂ S	Py ₃ PMo ₁₂ O ₄₀	15	–	100
8	(PhCH ₂) ₂ S	H ₃ PMo ₁₂ O ₄₀	15	1	97

addition led to the formation of small amounts of benzoic and 4-chlorobenzoic acid, respectively (Table 2, entries 6 to 10). Using the same conditions it was possible to oxidize secondary alcohols to ketones in good yield (Table 2, entries 14 to 19). Only in the case of oxidation of 1-decanol the yields were moderately low (Table 2, entries 20 to 22).

The selective oxidation of sulfide to sulfoxide or sulfone in multiphase conditions was also investigated (Schemes 2 and 3). The reactions were carried out at room temperature (Table 3) and at 70 °C (Table 4), respectively.

The reaction conditions were optimized using thioanisole as substrate. The study of the oxidation reaction of thioanisole with H₂O₂ using different HPAs is summarized in Table 3. When the commercially available HPA H₃PMo₁₂O₄₀ was used (entry 1, Table 3), the yield was of 95% after 1 h of reaction, with 98% selectivity to sulfoxide. Although Py₃PMo₁₂O₄₀ is noticeably less active than commercial HPAs, it is more selective (yields 100% and selectivity 100% in 2 h, entry 7, Table 3).

In order to explore the applicability of the method for a selective oxidation of sulfides to either sulfoxides or sulfones, various functionalized sulfides were investigated according to the general procedure, using H₃PMo₁₂O₄₀ and PyH₃PMo₁₁VO₄₀ as catalysts (Tables 3 and 4). The reactions precede to completion very quickly (10 to 120 min), and the sulfoxides or sulfones were obtained in excellent yields. As reported in Table 4 employing an excess of H₂O₂ at 70 °C, the sulfides were oxidized selectively to the relative sulfone.

4. Conclusion

In conclusion, the multiphase system studied was found to be an excellent medium for the selective oxidation, in high yields, of sulfides to either sulfoxides or sulfones, and benzylic and secondary alcohols to their corresponding carbonyl derivatives. In comparison with oxidation in homogeneous conditions, the multiphase system has a reduced reaction time and requires less hydrogen peroxide. The oxidation of alcohols to aldehydes in a multiphase system is an extremely appealing process since it is very selective (with only traces of product in a higher oxidation state). This is due to the fact that the heteropolyacid and H₂O₂ are in contact only in the third phase

(Aliquat 336) while the majority of H₂O₂ remains in the aqueous phase. Besides, oxidation in homogeneous systems leads to the formation of benzoic acid due to the excess of H₂O₂ in the reaction mixture.

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