

Communication

H₁₄[NaP₅W₃₀O₁₁₀] as a Heterogeneous Recyclable Catalyst for the Air Oxidation of Thiols Under Solvent Free Conditions

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Abstract: The catalytic oxidation of thiols to the corresponding disulfides using Preyssler's catalyst H₁₄[NaP₅W₃₀O₁₁₀] has been studied. These highly selective oxidations gave good yields of the target disulfides.

Keywords: Disulfides; green catalyst; heteropolyacid; *Preyssler*; reusable catalyst.

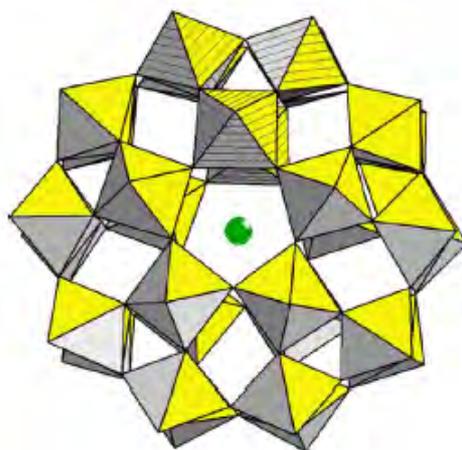
Introduction

The conversion of thiols to disulfides is important from both the biological and synthetic chemistry points of view. In biological systems, thiols are oxidized by flavins, cytochromes and dehydroascorbic acid to control the cellular redox potential and prevent oxidative damage. On the other hand, disulfides are important reagents in organic synthesis and can be used to prepare sulfinyl and sulfenyl compounds [1]. Several methods based on oxidative S-S coupling have already been reported. These include, among others, cerium (IV) salts, transition metal oxides [2], air in combination with transition metal catalysts [3], ferric chloride, sodium chlorite, nitric oxide, hydrogen peroxide, halogens [4] and heterogeneous permanganate [5].

Some of these methods suffer from obvious disadvantages such as long reaction times, limited availability of the oxidant, toxicity of reagents and difficult isolation of products. For example, halogens are inexpensive, but they are nonselective, the hydrogen halide by-products complicate the oxidation reaction and they aren't particularly safe [4]. Consequently, the introduction of readily available, safe and stable reagents for the oxidation of thiols to disulfides is still a necessity.

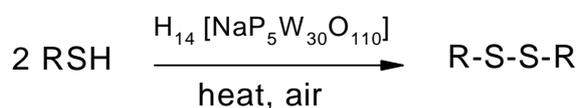
The catalytic function of heteropolyacids (*HPAs*) and related polyoxometalate compounds have attracted much attention, particularly over the last two decades [6]. Polyoxometalates (*POMs*) are a class of molecularly define organic metal-oxide clusters, possessing intriguing structures and diverse properties [7]. These compounds exhibit high activity in acid-base type catalytic reactions, hence they are used in many catalytic areas as homogeneous and heterogeneous catalysts. The application of the *Preyssler* catalyst is mostly limited and only a few demonstrations of its catalytic activity have been reported. This heteropolyacid nevertheless has important advantages such as: strong Bronsted acidity with 14 acidic protons, high thermal stability, high hydrolytic stability (pH 0–12), reusability, safety, low quantity of waste, separability, low corrosiveness, high oxidation potential and general “greenness”, along with an exclusive structure, which have attracted much attention on this catalyst. In the so called *Preyssler's* anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, Na^+ is encrypted inside a central cavity formed by five PW_6O_{22} units arranged in a crown [8], as shown schematically in Figure 1.

Figure 1. *Preyssler* structure.



Recently we have explored the application of *Preyssler* catalyst in various organic reactions [8-14]. This paper reports the results of the oxidation of thiols to disulfides utilizing $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ as catalyst. The greatest advantages of this procedure (Scheme 1) arise from its “greenness”, reusable catalyst, high yields, the fact that in most cases the reaction was solvent free and side reaction products resulting from acid catalysis were not found.

Scheme 1.



Results and Discussion

Previously it was shown that in the oxidations of anilines with H₂O₂ catalyzed by *Preyssler* and *Keggin HPA* catalysts, in order to compare the stability of the *Preyssler* catalyst structure in the presence of H₂O₂, with respect to that of *Keggin HPAs*, separation of the *Preyssler* catalyst was performed after the catalytic reaction. Interestingly, in contrast to *Keggin HPAs*, *Preyssler's* anion catalyzes oxidations of primary aromatic amines by H₂O₂ without any degradation of its structure, a very important feature in catalytic processes, specially, in industry. It is well known that *Keggin HPAs* at 60–70 °C in the presence of H₂O₂ are degraded to peroxopolyoxometalates and the reaction actually takes place via the oxygen atom transfer from the peroxopolyoxometalate to the substrate. Consequently we were interested in developing of applications of the *Preyssler* catalyst in other oxidation reactions because of its exclusive structure and properties.

In our studies it has been found that *Preyssler's* anion catalyzes the air oxidation of thiols to disulfides in excellent yields in a solvent free system. The results of attempted oxidations of these thiols are presented in Table 1. Separation of the *Preyssler* catalyst was made after the catalytic reaction. Both alkyl and aryl thiols gave similar results. Sterically hindered thiols took slightly longer to react. We also found that the presence of an electron-donating or an electron-withdrawing group on the aromatic ring did not affect upon the reaction times and yields.

Table 2. Oxidation of thiols to disulfides.

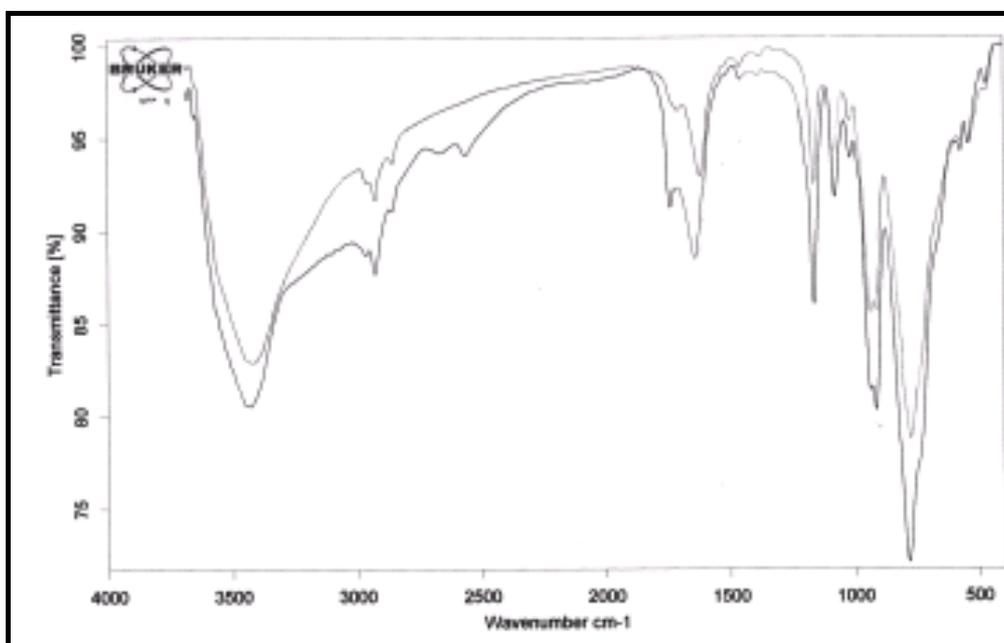
Entry	Thiol	Disulfide	Yield/%
1	<i>p</i> -Tolylthiol	Di- <i>p</i> -ditolyl disulfide	98
2	Thiophenol	Diphenyl disulfide	97
3	Naphtylthiol	Di-naphtyl disulfide	91
4	Cyclohexylthiol	Dicyclohexyl disulfide	95
5	<i>p</i> -Chlorophenylthiol	Bis[<i>p</i> -chlorophenyl] disulfide	97
6	Ethanethiol	Diethyl disulfide	92
7	Propylthiol	Dipropyl disulfide	95
8	Octylthiol	Di-octyl disulfide	98
9	Phenyl-methanethiol	Dibenzyl disulfide	94
10	<i>sec</i> -Butylthiol	Di- <i>sec</i> -butyl disulfide	97

Reusability of the Catalyst

In order to know whether the catalyst would succumb to poisoning and lose its catalytic activity during the reaction, we investigated the reusability of the catalyst. For this purpose we first carried out the reaction in the presence of the catalyst. After completion of the reaction, the catalyst was removed and washed with diethyl ether and subjected to a second run of the reaction process with the same substrate. The first experiment and subsequent experiments gave almost identical yields. We have thus found that *Preyssler* catalyst can be reused several times, without any appreciable loss of activity and after recovery the catalytic activity was decreased only 2–4%, pointing to the stability and retention of

catalytic capability of this useful polyanion. IR spectra of the resulting solids indicate that the catalyst can be recovered without structural degradation (Figure 2).

Figure 2. IR spectrum of *Preyssler's* anion before (a) and after (b) use.



Conclusions

In conclusion, a new and efficient method for oxidation of thiols developed. The significant features of the system are as follows: less toxic and hazardous chemicals can be used; high yields are obtained without side products; using of *Preyssler's* anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, a heteropolyanion with interesting catalytic properties as a green, reusable and eco- friendly catalyst.

Experimental

General

Melting points were measured by using the capillary tube method with an Electrothermal 9200 apparatus. $^1\text{H-NMR}$ spectra were recorded on a Bruker AC-80 MHz spectrometer using TMS as an internal standard (CDCl_3 solution). IR spectra were recorded from KBr disk on the FT-IR Bruker Tensor 27. GC spectra were carried out on a Network GC System-Agilent 5973 spectrometer. All products gave satisfactory spectral data in accord with the assigned structures [4].

Catalyst Preparation

$\text{H}_{14}\text{-P}_5$ was prepared by passage of a solution of the potassium salt in water through a column (50 cm \times 1 cm) of Dowex50W \times 8 in the H^+ form and evaporation of the eluate to dryness under vacuum [15].

Oxidation of Thiols: General Procedure

In a sample run, a dry 25 mL round bottomed flask was charged with thiol (1 mmole) and 0.01 mmole of heteropolyacid. The reaction mixture was heated to 90 °C in an oil bath. For solid thiols chloroform was used as solvent. Time of reaction was between 1-2 hours, the progress of reaction was monitored by TLC (chloroform was used as solvent for TLC). After completion of the reaction, the mixture was diluted with chloroform and catalyst was removed by simple filtration. After evaporation of solvent, products were obtained in good yields.

Acknowledgements

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Sample Availability: Available from authors.