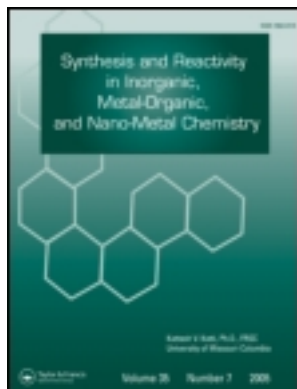


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Aerobic Oxidation of Thioles to Disulfides Catalyzed by Mixed-Addenda Vanadium (V) Substituted Heteropolyacids

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The oxidation of thiols to related disulfides using mixed-addenda heteropolyacids as catalyst under mild condition has been studied. This system provides an efficient, convenient, and practical method for the syntheses of symmetrical disulfides. In this work, the comparisons among the Keggin- and Dawson-type polyoxometalates are addressed in term of relative stability hardness and acidity.

Keywords Dawson, disulfides, heteropolyacids, Keggin-type polyoxometalate, thiols

INTRODUCTION

The catalytic function of heteropoly acids (HPAs) and related polyoxometalate compounds have attracted much attention, particularly over the last two decades.^[1] In this context, HPAs are promising catalysts. A common and important class of these acids, and those used in the majority of catalytic applications, is the Keggin compounds, with the general formula $H_nXM_{12}O_{40}$ ($X = P, Si, As, Ge, B; M = Mo, W$).^[2] These solid acids are usually insoluble in nonpolar solvents but highly soluble in polar ones. They can be used in bulk or supported forms in homogeneous and heterogeneous systems. Furthermore, these HPAs have several advantages, including high flexibility in modification of the acid strength, ease of handling, environmental compatibility, nontoxicity, and experimental simplicity.^[3] Keggin-type polyoxoanions (Figure 1) have widely been studied as homogeneous and heterogeneous catalyst for the oxidation of organic compounds.^[4] Generally, Keggin structures show more acidity and catalytic activity among HPAs.^[5]

The application of Wells-Dawson type polyoxoanions (Figure 1) is mostly limited to homogeneous^[6] or gas phase application,^[7] and only few of them demonstrate catalytic activity in heterogeneous form.^[8] Further catalytically important subclasses of the Keggin compounds are the mixed-addenda

vanadium (V) substituted HPAs with the general formula of $H_{3+n}PM_{12-n}V_nO_{40}$ ($M = Mo$ and $W; n = 1-6$). 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 most well known of these HPAs is the 10-molybdo-2-vanadophosphoric acid $H_5PV_2Mo_{10}O_{40}$ (Figure 2). This figure shows polyhedral representation of this compound which contains a central PO_4 tetrahedron surrounded by 12 MO_6 ($10MoO_6 + 2VO_6$) octahedral arranged in four M_3O_{13} groups edge-sharing octahedral. The edge-sharing M_3O_{13} groups are linked to each other and to the central tetrahedron by shared corners. This structure allows the molecule to hydrate and dehydrate without significant structural changes and the molecule is thermally stable in the solid state for use in vapor phase reactions at high temperatures (400–500°C). $H_5[PMo_{10}V_2O_{40}]$ has been extensively used as the effective redox catalyst in homogeneous oxidation processes.^[9] There is less report regarding the application of $H_5PV_2Mo_{10}O_{40}$ as the acid catalyst for organic transformations for the simple reason that V^{5+} ion is the most strongly oxidizing element and can be readily reduced to V^{4+} with concomitant oxidation of organic substrate. In fact, the introduction of V^{5+} into the Keggin framework shifts its catalytic activity from acid-dominated to redox-dominated.

The oxidation of thiols to disulfides remains a valuable reaction in biochemistry and synthetic organic chemistry.^[10–13] Disulfides play important roles in biological and chemical processes.^[14] Oxidation of thiols is the most exploited method for disulfide synthesis mainly because a large number of thiols are commercially available and/or are easily synthesized. Several methods for oxidation of thiols have already been reported. These include, among others, cerium (IV) salts, *trans* cerium (IV) salts, permanganates, transition metal oxides, air in combination with transition metal catalysts, sodium perborate, ferric chloride, sodium chlorite, nitric oxide, hydrogen peroxide, and halogens, among others, have been utilized for oxidation of thiols to disulfides.^[15–25] 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. Consequently, the introduction of readily available, safe, and stable reagents for the oxidation of thiols to disulfide

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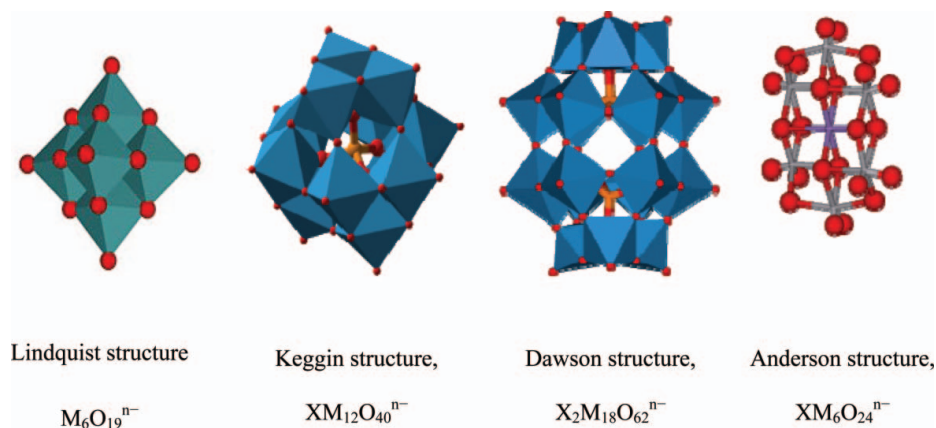
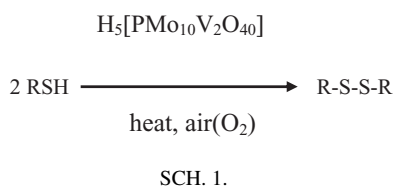


FIG. 1. Examples of some fundamental polyoxometalate structures (color figure available online).

is still a necessity. In continuation of our group research on the syntheses and application of HPAs in organic syntheses^[26–40] and due to the importance of derivatives of disulfides in biological and chemical processes, we hereby report the applicability of HPA for efficient oxidation of thiols to the corresponding disulfides. We wish to report a very efficient and simple method for oxidative coupling of thiols into the corresponding disulfides using mixed-addenda vanadium (V) substituted HPA as catalyst under aerated and mild conditions. The greatest advantages of this procedure (Scheme 1) arise from its “greenness,” reusable catalyst, high yields, and the fact that in most cases the reaction was solvent free and side reaction products resulting from acid catalysis were not found.



EXPERIMENTAL

All reagents and solvents used in this work are available commercially and used as received, unless otherwise indicated. Previously reported methods were used to purify the thi-

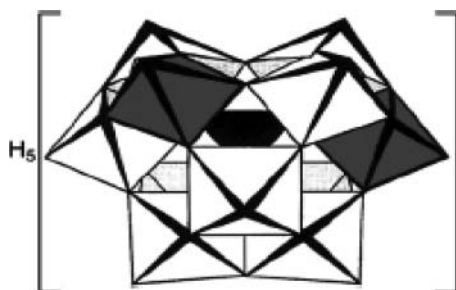


FIG. 2. Polyhedral representation of $H_5PV_2Mo_{10}O_{40}$. The central PO_4 tetrahedron and VO_6 octahedral are dark gray.

ols.^[41] Preparation of $H_5[PMo_{10}V_2O_{40}]$ catalyst and other mixed-addenda HPAs and salts were based on a literature procedure with the following modifications.^[42] The acids of $[NaP_5W_{30}O_{110}]^{14-}$, $[P_2W_{18}O_{62}]^{6-}$, and $[P_2Mo_{18}O_{62}]^{6-}$ were prepared according to published methods and were identified by infrared spectroscopy.^[43–45] All chemicals were purchased from Merck and used without purification (Darmstadt, Germany). ¹HNMR spectra were recorded on an FT-NMR Bruker 100 MHz Aspect 3000 (Daltonik GmbH, Bremen, Germany). IR spectra were recorded on a Bruker 500 Scientific Spectrometer (KBr Pellets) (Daltonik GmbH, Bremen, Germany). Mass spectra were obtained with a POEKTRO METER CH – 7A VARIN MAT BREMEN spectrometer.

Preparation of Catalyst^[42]

$H_5[PMo_{10}V_2O_{40}]$ (10-Molybdo-2-vanadophosphoric acid)

Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 mL of water and then mixed with (3.55 g 25 mmol) of Na_2HPO_4 in 50 mL of water. After the solution was cooled, (5 mL, 17 M, 85 mmol) of concentrated sulfuric acid was added, and the solution developed a red color. An addition of (60.5 g, 250 mmol) of $Na_2MoO_4 \cdot 2H_2O$ dissolved in 100 mL of water and then was added to the red solution with vigorous stirring, followed by slow addition of concentrated sulfuric acid (42 mL, 17 m, 714 mmol). The hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with 500 mL of ethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it of ether. The solid remaining behind was dissolved in water, concentrated to first crystal formation, as already described, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water, and air dried.

$H_4[PMO_{11}VO_{40}]$ (11-Molybdo-1-vanadophosphoric acid)

Na_2HPO_4 (3.55 g, 25 mmol) was dissolved in 50 mL of water and mixed with (3.05 g, 25 mmol) of sodium metavanadate that had been dissolved by boiling in 50 mL of water. The mixture was cooled and acidified to a red color with (2.5 mL, 17 M,

TABLE 1
Reuse of the catalyst for oxidation of 4-chlorothiophenol
(Table 3, entry 4)

Entry	Isolated yield (%)
1	94
2	90
3	91
4	91
5	93

42.5 mmol) of concentrated sulfuric acid. To this mixture was added a solution of (66.5 g, 274.8 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 100 mL of water. Finally, 42.5 mL of concentrated sulfuric acid was added slowly with vigorous stirring of the solution. With this addition the dark red color changed to a lighter red. The HPA was then extracted with 200 mL of ethyl ether after the water solution was cooled. In this extraction, the heteropoly etherate was present as a middle layer; the bottom layer (water) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that remained was dissolved in 50 mL of water, concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallize further. The orange crystals that formed were filtered, washed with water, and air dried.

General Procedure for the Oxidation of Thiols to Disulfides

The substrate thiol (5 mmol) and $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ (0.5 g, 0.2 mmol) was added in a dry 25 mL round bottomed flask.

TABLE 2
Results of the oxidation of thiols was examined in the presence
of a variety of heteropolyacids

Entry	Catalyst	Time (h)	Temperature (°C)	Yield (%) ^a
1	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	5	90	97
2	$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$	5	90	97
3	$\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$	5	90	97
4	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	5	100	93
5	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	6	100	91
6	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	6	100	84
7	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	7	110	71
8	$\text{Na}_3\text{PMo}_{12}\text{O}_{40}$	7	110	62
9	$\text{Na}_3\text{PW}_{12}\text{O}_{40}$	7	110	61
10	$(\text{NH}_4)_3\text{H}[\text{PMo}_{11}\text{VO}_{40}]$	8	120	52
11	$\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$	6	100	85
12	$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	6	100	81
13	None	10	120	28

^aIsolated product.

TABLE 3
Results of the oxidation of thiols by $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ in
different solvents

Entry	$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (g)	Solvent	Time (h)	Temperature (°C)	Yield (%) ^a
1	0.5	EtOH + H_2O	5	90	97
2	None	EtOH + H_2O	8	100	28
3 ^b	0.5	EtOH + H_2O	5	90	97
4 ^c	0.5	EtOH + H_2O	5	90	97
5	1	EtOH + H_2O	5	90	97
6	0.2	EtOH + H_2O	7	100	87
7	0.5	MeOH + H_2O	5	90	92
8	0.5	EtOH	4	90	72
9	0.5	MeOH	3	90	71
10	0.5	CH_3Ph	6	100	63
11	0.5	CH_3NO_2	6	90	21
12	0.5	CH_3CN	5	90	17
13	0.5	CH_2Cl_2	3	90	73
14	0.5	DMF	3	90	71


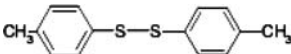
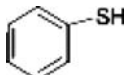
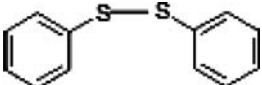

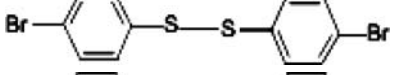
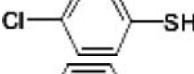
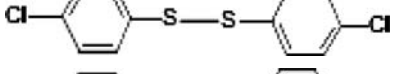
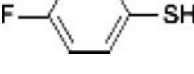
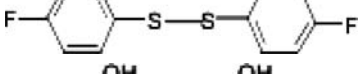
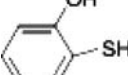
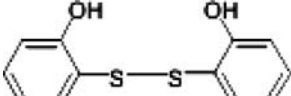
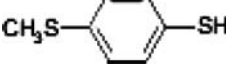
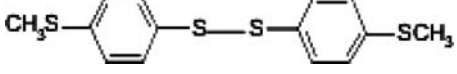
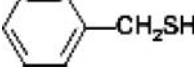
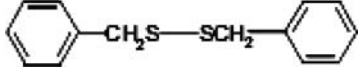
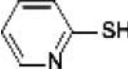
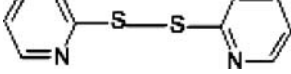
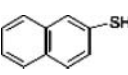
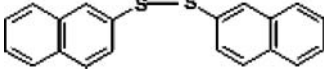
^aIsolated yield on the basis of the weight of the pure product obtained. ^bThe reaction was carried out with the first recycled catalyst. ^cThe reaction was carried out with the second recycled catalyst.

The reaction mixture was heated to 90°C in an oil bath until TLC indicated the reaction was complete. For solid thiols, the mixture of 30 mL of ethanol and 10 mL of H_2O was used as solvent. The solvent was then removed and the resulting residue was then washed with CH_2Cl_2 . A simple filtration followed by removal of the solvent from the filtrate gave the product of acceptable purity. The products were isolated and identified by comparison of their physical and spectral data with authentic samples prepared according to a previous method.^[46]

Recycling of the Catalyst

At the end of the oxidation of thiols to disulfides, the catalyst was filtered and then washed with dichloromethane. 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 model reaction (Scheme 1), dichloromethane was added to the solid reaction mixture. All products are soluble in dichloromethane but the catalyst is not. So it could be separated by a simple filtration and washed with dichloromethane and dried at 90°C for 1 h, and reused in another reaction with the same substrate. Even after five runs for the reaction, the catalytic activity of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ was almost the same as that freshly used catalyst. The results are summarized in Table 1. IR spectra of the resulting solids indicate that the catalyst can be recovered without structural degradation.

TABLE 4
Result of the oxidation of thiols with different substituents by $H_5[PMo_{10}V_2O_{40}]$ as a catalyst^a

Entry	Thiol	Disulfide	Time (h)	Yield ^{b,c} (%)	M.P.(°C) found	M.P.(°C) literature
L			5	95	43–44	44–45
2			5.5	96	60–61	61
3			5.5	93	90–92	91–93
4			5	97	72–73	70–71
5			4	80	liquid	—
6			4.5	86	liquid	—
7			7	82	40–43	40–43
8			6	78	69–71	69–70
9			5	74	55–56	55–57
10			6.5	62	144–146	142–145

^aThe reactions were carried out with 5 mmol substrate and 0.2 mmol HPA catalyst and air (O_2) into the solution. ^bIsolated yield on the basis of the weight of the pure product obtained. ^cThe products were identified by comparison of physical and spectroscopic properties with authentic compounds.

RESULTS AND DISCUSSION

We were interested in developing of applications of mixed structure and properties.^[26–41] In our studies it has been found that mixed-addenda HPAs catalyzes the air oxidation of thiols to disulfides in excellent yields in a solvent free system. 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 have an affect on the reaction times and yields.

Effect of the Catalyst Structure

Table 1 shows catalyst structure effect on aerobic oxidation of thiols. 4-Chlorothiophenol was taken as a model compound. Also, the amount of each catalyst is used

the same. In the Keggin-type polyoxometalates series including $H_3[PW_{12}O_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_4[PMo_{11}VO_{40}]$, $H_4[SiW_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$, the mixed-addenda HPA $H_5[PMo_{10}V_2O_{40}]$ shows the highest catalytic activity. In general, the heteropoly salt type catalysts were less efficient than HPAs. The Keggin-type polyoxometalates lead to effective reaction in comparison with wells-Dawson type polyoxometalates. But $H_6[P_2Mo_{18}O_{62}]$ is more effective than $H_6[P_2W_{18}O_{62}]$ in oxidation of thiols. It may be difference in tungsten and molybdenum reduction potentials. However, the results indicate that the highest yield of disulfides is obtained when the oxidation of substrates is carried out with $H_5[PMo_{10}V_2O_{40}]$ as catalyst. This behavior is found to be quite general. The high activity of $H_5[PMo_{10}V_2O_{40}]$ in comparison with other HPAs (Table 2) confirms that in addition to H^+ , the V^{5+} ions probably play a catalytic role in the reaction.

Effect of the Solvent

Table 3 shows solvent effect on oxidation of solid thiols. 4-Chlorothiophenol was taken as a model compound and the reaction conditions were optimized by varying the solvent. We examined various solvents to facilitate this transformation and determined that (EtOH + H₂O) was the most effective (Table 3 entries 1–13).

Effect of the Substituent

The effects of various substituents on the yields of produced disulfides have been examined in the presence of H₅[PMo₁₀V₂O₄₀] catalyst. As shown in Table 4, not only the nature of the substituent is important, but so is its position. As examples of electron-withdrawing groups, bromo-, chloro-, and nitro-substituted thiophen were chosen and were converted to their corresponding disulfides. Methyl and hydroxy groups were chosen as electron-donating groups. Thiols with electron-donation substituents were oxidized easily respect to thiols with electron-drawing substituents.

CONCLUSION

The H₅[PMo₁₀V₂O₄₀] HPA was the most successful HPA in this reaction. Although it is difficult to offer an explanation for the different activity between these HPAs, certainly there is a complex relationship between the activity and structure of polyanion. By changing the constituent elements of polyanion (both hetero and addenda atoms), the acid strength of HPAs as well as its catalytic activity is able to vary in a wide range.^[8] For the first time, by an inexpensive solid acid catalyst and an easily prepared H₅[PMo₁₀V₂O₄₀] oxidation of thiols with electron-withdrawing and electron-donating groups to the corresponding disulfides have been studied. The results show that the catalyst type, the nature and positions of substituents, and temperature are important factors. The Keggin-type polyoxometalates lead to effective reaction in comparison with Well-Dawson type polyoxometalates.

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