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Highly selective and efficient oxidation of sulfides with hydrogen peroxide catalyzed by a chromium substituted Keggin type polyoxometalate

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ABSTRACT

The catalytic oxidation of sulfides into the corresponding sulfones by a chromium substituted Keggin type polyoxometalate, $(TBA)_4[PW_{11}CrO_{39}]\cdot 3H_2O$, was achieved using mild reaction conditions. Excellent yields were obtained using four equivalents of 30% H_2O_2. Under these reaction conditions, the sulfide group was highly reactive and other functional groups such as hydroxyl or a double bond were unaffected. Using a commercially available, eco-friendly, and cheap oxidant, mild reaction conditions, operational simplicity, practicality, short reaction times, high to excellent yields, and excellent chemoselectivity are some of the advantages of this catalytic system.

Organosulfur compounds such as sulfoxides and sulfones are important synthetic intermediates, for example, in the synthesis of natural products and biologically significant molecules,[1] and are also utilized for the extraction and separation of some metals.[2,3] The selective oxidation of sulfides into sulfoxides and sulfones is conventionally performed by using stoichiometric oxidants such as peracids, dioxiranes, $NaIO_4$, MnO_2, CrO_3, SeO_2, and PhIO, but these stoichiometric systems are not atom-efficient.[4,5] In contrast, 'green oxidants' such as oxygen and hydrogen peroxide are very attractive, because these oxidants are readily available, inexpensive, and environmentally benign.[6–8] There are many reports on the H_2O_2-based oxidation of sulfides into sulfoxides and sulfones by homogeneous and heterogeneous organocatalysts, acid catalysts, enzymes, metal catalysts, and polyoxometalates (POMs).[9]

In POMs, the ability to alter extensively the molecular properties (potentials, charges, sizes, etc.), coupled with their chemically robust nature, has led to a wide range of applications. A number of processes, for example, oxidation and acid-dependent reactions are catalyzed by Keggin and Wells-Dawson type POMs.[10]

Transition metal substituted POMs are thermodynamically stable to oxidation and, furthermore, possess hydrolytic stability under appropriate pH conditions.[11] This unique combination of properties has made this class of compounds very attractive catalysts for the oxidation of a variety of compounds such as alkenes, alcohols, and sulfides.[12–16] In particular, the environmentally important oxidation of sulfides into sulfones, and the development of efficient oxidations of various sulfides by H_2O_2 are still in demand.[17]

Herein, a highly efficient and simple route for the oxidation of sulfides with H_2O_2 catalyzed by a monosubstituted Keggin-type POM, $[(n\text{-}C_4H_9)_4N]_4[PW_{11}CrO_{39}]\cdot 3H_2O$ (PWCr)[24] is reported. Notably, in the presence of small amounts of catalyst excellent conversions of sulfides into the corresponding sulfones using the appropriate amount of H_2O_2 was achieved.

The catalytic activity of the PWCr was examined in the oxidation of diphenylsulfide by 30% H_2O_2 as a model reaction. To a solution of Ph_2S (1 mmol) and PWCr (0.0245 mmol) in different solvents was added 4 mmol of an oxidant at 25 °C (Scheme 1).[25] The results (Table 1) show that acetonitrile was the best solvent providing the highest yields and selectivity (100%). The use of other solvents such as methanol, dichloromethane, and chloroform led to lower catalytic activities being observed.

The amount of catalyst was varied from 0.0163 to 0.0493 mmol and the other reaction conditions remained constant. The results for the oxidation reaction at 25 °C over 15 min are shown in Table 2. A general trend of increase in the conversion of diphenylsulfide by raising the amount of catalyst was observed. These results demonstrate that PWCr is a very active catalyst in this

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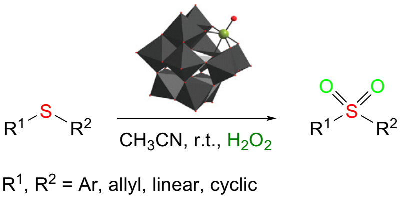


Scheme 1. Selective oxidation of sulfides by H_2O_2 in the presence of PWCr as the catalyst.

Table 1
Oxidation of diphenylsulfide into diphenylsulfone by 30% hydrogen peroxide in different solvents[a]

Entry	Solvent	Yield[b] (%)
1	MeOH	10
2	CH_2Cl_2	17
3	$CHCl_3$	21
4	CH_3CN	94
5	DMF	6
6	Me_2CO–AcOH	34
7	MeOH–H_2O	11

[a] Reaction conditions: diphenylsulfide (1 mmol), catalyst (0.0245 mmol), H_2O_2 (4 mmol), solvent (3 mL), room temperature, 15 min.
[b] Yields refer to GC yields.

reaction system, and even a small amount of the POM catalyst (0.0245 mmol) leads to significant conversion.

The amount of oxidant (H_2O_2) in the reaction was optimized by using 0.0245 mmol of the POM catalyst, acetonitrile (3 mL), and different amounts of hydrogen peroxide with diphenylsulfide (1 mmol) at room temperature. Samples were drawn at regular intervals and analyzed by GC (Table 2). The results indicated that 4 mmol H_2O_2 is the optimum amount for the oxidation of diphenylsulfide in this catalytic system.

Table 2
Optimization of the amounts of H_2O_2 and the catalyst for the selective oxidation of diphenylsulfide into diphenylsulfone[a]

Entry	H_2O_2 (mmol)	Catalyst (mmol)	Yield[b] (%)
1	0.5	0.0245	4
2	1	0.0245	18
3	1.5	0.0245	35
4	2	0.0245	47
5	3	0.0245	61
6	4	0.0245	94
7	5.4	0.0245	96
8	4	0.0163	88
9	4	0.0195	62
10	4	0.0327	77
11	4	0.0493	72

[a] Reaction conditions: diphenylsulfide (1 mmol), catalyst, H_2O_2, CH_3CN (3 mL), room temperature, 15 min.
[b] Yields refer to GC yields.

Using the optimized catalytic conditions, the scope of the method was extended to the oxidation of different sulfides including cyclic, benzylalkyl, substituted arylalkyl, and dialkyl sulfides bearing different functional groups with 30% aqueous hydrogen peroxide as the oxidant (Scheme 1). From the results in Table 3, aromatic and aliphatic sulfones were mostly obtained with more than 99% selectivity. It was observed that a small amount of the catalyst (0.0245 mmol) was sufficient for the oxidation of aliphatic sulfides. In the oxidation of aryl methyl sulfides into the corresponding sulfones, methyl substitution at the *para*-position of the phenyl ring had an affect on the reaction time but not on the product selectivity (Table 3, entries 3 and 4). This indicated that the reaction proceeds by an oxygen transfer mechanism. If the reaction involves electron transfer instead of oxygen transfer, substantial amounts of benzaldehyde would be formed.[22,23] The chemoselectivity was noteworthy under our oxidation conditions: the sulfide

Table 3
Selective oxidation of various sulfides by 30% H_2O_2 at room temperature in the presence of PWCr as the catalyst[a,b]

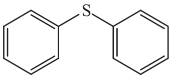
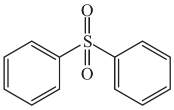
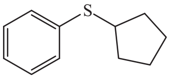
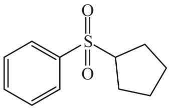
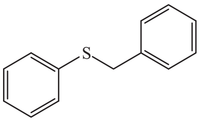
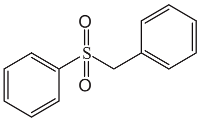
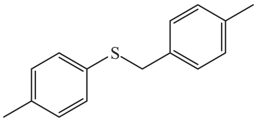
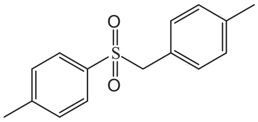
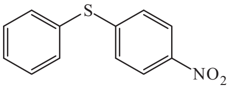
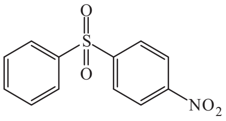
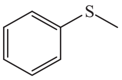
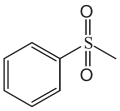
Entry	Sulfide	Sulfone	Time (min)
1			45
2			25
3			10
4			60
5			25
6			8

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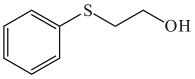
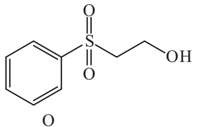
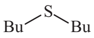
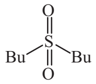
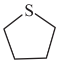
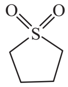
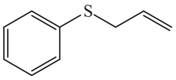
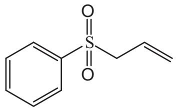
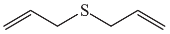
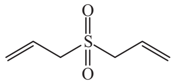
Table 3 (*continued*)

Entry	Sulfide	Sulfone	Time (min)
7			10
8			25
9			10
10			10
11			25

[a] Reaction conditions: sulfide (1 mmol), H_2O_2 (4 mmol), PWCr (0.0245 mmol), 25 °C.

[b] Yields are quantitative on the basis of sulfide conversion and refer to GC yields.

functional group was highly reactive and various other functional groups were tolerated. Sulfides containing allyl and hydroxyl groups (Table 3, entries 7, 10, and 11) were selectively oxidized into their corresponding sulfones, and these reactive functional groups remained intact. Diallyl sulfide was cleanly converted into diallylsulfone without epoxidation. It is also interesting to note that the presence of a strong electron-withdrawing NO_2 group on the phenyl ring of the diaryl sulfide, did not affect considerably the formation of the corresponding sulfone (Table 3, entry 5).

In summary, we have demonstrated that PWCr can act as a highly efficient catalyst for the selective oxidation of various sulfides into sulfones using H_2O_2 under mild reaction conditions. The advantages of this catalytic system are that the reactions occur at room temperature, are operationally simple, practice, require short reaction times, give high to excellent yields and chemoselectivity, and use commercially available, eco-friendly, and cheap H_2O_2 as the oxidant. These advantages make this POM a promising catalyst as material for practical and large scale applications.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014. 05.026.

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24. Preparation of the $(TBA)_4[PW_{11}CrO_{39}]\cdot 3H_2O$ catalyst: $K_4[PW_{11}CrO_{39}]\cdot nH_2O$ was synthesized according to the published procedure. The structure was confirmed by elemental analysis, UV–vis, and infrared spectroscopy.[18] A sample of $K_4[PW_{11}CrO_{39}]\cdot nH_2O$ (0.062 g) was dissolved in 0.5 M $NaHSO_4$ (5 mL, pH = 1) and dropwise added to an aqueous solution of tetra-*n*-butylammonium bromide (TBABr) (0.026 g) in 5 mL H_2O. The resulting solid was filtered and recrystallized from acetonitrile.[19–21] IR, UV–vis, and elemental analyses established that the product had not changed during counter ion exchange (see Supplementary Data, Figures S1–S4).
25. Typical procedure for the catalytic oxidation of sulfides to sulfones: PWCr catalyst (0.0245 mmol), CH_3CN (3 mL), sulfide (1 mmol), and hydrogen peroxide (4 mmol, 30% aq solution) were added to a glass tube as the reaction vessel. The reaction was carried out at 298 K. The mixture was sampled periodically and analyzed by GC. After completion of the reaction, the product was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the corresponding pure sulfone. The products were identified by comparison of their ^1H NMR and ^{13}C NMR signals with the literature data (see Supplementary Data, Figures S5–S18).

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