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Solvent free oxidation of sulfides to sulfones by H_2O_2 in the presence of chromium substituted polyoxometalate as catalyst



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ABSTRACT

Solvent-free oxidation of sulfides into sulfones by 30% hydrogen peroxide has been achieved using chromium substituted Keggin type polyoxometalate under mild reaction conditions in 94–100% yield. This catalytic system showed excellent activity in the oxidation of sulfide groups. The other active functional groups such as hydroxyl and C—C bond have been tolerated.

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Because of environmental rules limiting the sulfur content in fuel oils to the few ppm levels, ultra-deep desulfurization has become an important topic of research. The oxidation of sulfide compounds is of much current interest in the context of the preparation of synthetically useful sulfones [1–3] as well as of the desulfurization of fuels [4–6]. Sulfone compounds are important synthetic intermediates in various chemicals and are also very useful building blocks for the preparation of elaborated organic structures [7]. As well, oxidation of organo-sulfur compounds finds also application in the removal of sulfur-containing pollutants during air and wastewater treatment [8]. For the oxidation of sulfides to sulfones, a range of oxidants have been investigated. For example, stoichiometric oxidation of sulfides by sodium percarbonate, sodium perborate, H₅IO₆, and the other unclean oxidant with different catalysts was studied [1-3]. Unfortunately, most of these reagents are not satisfactory for medium- to large-scale synthesis because of the low content of effective oxygen, toxic oxidants and solvents, the formation of environmentally unfavorable co-products, and high cost [9].

Obviously, current demand for environmentally friendly processes requires the development of green oxidation methods that employ clean oxidants, such as hydrogen peroxide. During recent years, aqueous hydrogen peroxide has been one of the most attractive "green

* Corresponding author. *E-mail addresses:* yadollahi@chem.ui.ac.ir, yadollahi.b@gmail.com (B. Yadollahi). oxidants" for its environmentally benign characteristics, only producing harmless water as by-product, safety in storage and operation, cheapness, readily available and the high effective oxygen content [10]. Also solid-phase-assisted reaction systems without organic solvents have been increasingly attracted as environmentally benign organic reaction systems [11].

In the past years, many catalytic systems such as ionic liquids [12], H_2WO_4 [13], Na_2WO_4 [14], $K_{12}WZnMn_2(ZnW_9O_{34})_2$ [15], $H_3PW_{12}O_{40}$ [16], [($C_{18}H_{37})_2(CH_3)_2N$]₇PW₁₁O₃₉ [17], polymer-immobilized peroxotungsten [18], and metal catalysts including Se, Mn, and Re [19–21], have been implied on sulfide oxidation with H_2O_2 .

Polyoxometalates (POMs) and transition metal substituted POMs are large classes of highly modifiable discrete metal–oxygen anionic clusters [22] with substantial structural diversity and widely ranging properties facilitating applications in catalysis [23]. POMs have been extensively applied as catalysts for the oxidation of a variety of organic compounds such as alkenes, alcohols, and sulfides [24–26]. For example, it was reported that $[\gamma$ -PW₁₀O₃₈V₂(μ -OH)₂]^{3–} and [TBA]₄[γ -SiW₁₀O₃₄(H₂O)₂] [27,28] homogeneously catalyze oxidation of various sulfides. POM-based ionic liquids [29] and H₃PW₁₂O₄₀ supported nanoparticle catalysts were also reported on dibenzothiophene oxidation [30].

Environmentally highly important catalytic oxidation of sulfides to sulfones is still a key challenge [31–33]. Herein, we want to report a practical and green method for selective oxidation of various



Fig. 1. FTIR spectrum of TBAPWCr.

sulfides to corresponding sulfones by aqueous H_2O_2 in the presence of chromium substituted Keggin type POM, $(TBA)_4[PW_{11}CrO_{39}]\cdot 3H_2O$ (TBAPWCr), as a catalyst at solvent free conditions [34,35].

As shown in Fig. 1, in the FTIR spectrum of TBAPWCr the peaks in the IR spectral range of 600–1100 cm⁻¹ correspond to Keggin structural vibrations that could be easily distinguished at 1090, 975, 893, and 808 cm⁻¹. The peaks were attributed to the asymmetry vibrations $P-O_a$ (internal oxygen connecting P and W), $W-O_d$ (terminal oxygen bonding to W atom), $W-O_b$ (edge-sharing oxygen connecting W), and $W-O_c$ (corner-sharing oxygen connecting W_3O_{13} units), respectively. Comparison between FT-IR spectrum, in the range of 600–1100 cm⁻¹, for KPWCr [36] and TBAPWCr indicated that the characteristic peaks did not shift. These results confirmed that Keggin structure in PWCr is preserved (see Supplementary data, Fig. S1).

As shown in Fig. 2, the UV–vis spectrum of TBAPWCr illustrated two broad peaks at 265 nm and 637 nm. The first peak at 265 nm was assigned to the oxygen to tungsten charge transfer band of POM. The broad envelope centered at 637 nm is typically for octahedral chromium(III) complexes [36] and could be assigned to spinallowed transitions to the excited quarter state. Comparing between the UV–vis spectra of KPWCr and TBAPWCr was also confirmed that in the latter Keggin structure was maintained (see Supplementary data, Fig. S2).



Fig. 2. UV-vis spectrum of TBAPWCr.

Table 1

Optimum amounts of H_2O_2 and POM catalyst for selective oxidation of diphenyl sulfide to diphenyl sulfone.^a

Entry	H ₂ O ₂ (equiv)	TBAPWCr (µmol)	Yield (%) ^b
1	3.5	16.3	70
2	4.5	16.3	90
3	5.5	16.3	96
4	6.5	16.3	100
5	6.5	19.5	85
6	6.5	24.5	80
7	6.5	32.7	77
8	6.5	49.2	74

^a The reactions was performed by 1 mmol diphenyl sulfide at room temperature in 15 min

^b Yields refer to GC yields.

The oxidation reaction of diphenyl sulfide, as a model compound. was carried out by various amounts of catalyst from 16.3 to 49.2 µmol at 25 °C for 15 min, and other reaction conditions remained constant. Results showed that the reaction yield and selectivity were affected crucially by the catalyst amount (Table 1). By raising the catalyst amounts, a general trend of increasing conversion for diphenyl sulfide was obtained. These results demonstrated clearly that TBAPWCr catalyst is very active in this reaction system, and that even small amount (16.3 µmol) of the catalyst could lead to significant conversion. For optimization of hydrogen peroxide amounts, the reactions were carried out at room temperature by using 16.3 and 49.2 µmol catalyst and different amounts of hydrogen peroxide for a fixed amount of diphenyl sulfide (1 mmol) (Table 2). In this oxidation system the selectivity pattern was changed by variety amounts of H₂O₂ (Fig. 3). Results have been shown that 6.5 equivalent of H_2O_2 is an optimum amount for desired yields and selectivity of sulfone in oxidation of diphenyl sulfide.

Using the optimized reaction conditions [37], oxidation of various aromatic and aliphatic sulfides by 6.5 mmol H_2O_2 was performed. Reactions proceeded smoothly with a substrate/catalyst ratio of 61.5 at 298 K. Various sulfides were selectively oxidized to the corresponding sulfones with high H_2O_2 efficiency (Scheme 1).

In this catalytic system not only aryl sulfides (Table 2, entries 1–7) but also alkyl ones could be oxidized to the corresponding sulfone in excellent yields (Table 2, entry 8). It is also interesting to mention that even the presence of strong electron withdrawing NO₂ group on the phenyl ring of aryl sulfides did not noticeably affect the synthesis of sulfone (Table 2, entry 5). The oxidation of diallylsulfide, 2-(hydroxyethyl) phenylsulfide, and phenyl allylsulfide proceeded chemoselectively to the corresponding sulfones without oxidation of C=C double bonds and dehydrogenation of the hydroxyl groups (Table 2, entries 11, 7 and 10).

As mention above, the oxidation of diphenyl sulfide by H_2O_2 in the presence of TBAPWCr catalyst has been performed in 393:60:1 M ratios respectively. The stability of POM catalyst in this system was monitored using multiple sequential oxidation of diphenyl sulfide with H_2O_2 . By addition of new samples of the sulfide to the reaction mixture, it has been observed that the catalyst is reusable for at least three times. Also, the FTIR spectrum of the recovered TBAPWCr after each run still shows the typical bands of the embedded POMs (Fig. 4).

The applicability and efficiency of our catalytic system in the oxidation of sulfides by hydrogen peroxide have been compared with some of the other reported methods. Result showed that compared to the most of these methods our catalytic system is superior [1–3,9, 12–30].

In conclusion, the chromium substituted POM, TBAPWCr, showed an excellent catalytic activity for the oxidation of sulfides with H₂O₂. The remarkable feature could be the selective oxidation of sulfides to

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Table 2

TBAPWCr catalyzed selective oxidation of sulfides to sulfones using 30% H₂O₂.^a

Entry	Sulfide	Sulfone	Time (min) ^b
1			20
2			15
3	5		30
4	s S		30
5			25
6	NG ₂		10
7	С С С С С С С С С С С С С С С С С С С	С С С С С С С С С С С С С С С С С С С	30
8	Bu ^{∕S} ∖Bu	O Bu Bu	25
9	Š		10
10	○ - S - - - - - - - - - -		20
11	۶۶		40

^a Reactions conditions: 1 mmol sulfide and 6.5 mmol H₂O₂ in the presence of TBAPWCr (16.3 µmol) at 25 °C.

^b Yields are quantitative on the basis of sulfide and refer to GC yields with biphenyl as an internal standard.

the sulfones by using an inexpensive reagent under safe and mild conditions without any additional reagents. Additionally, the sulfone products could be easily separated from the reaction mixture.



Fig. 3. Screening of hydrogen peroxide amount in the oxidation of diphenyl sulfide, the reactions were run for 15 min at 25 $^{\circ}$ C using 16.3 µmol of TBAPWCr and yields are determined by GC.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2014.10.034. This data include MOL file and InChiKey of the most important compounds described in this article.





Scheme 1. Selective oxidation of sulfides by hydrogen peroxide in the presence of TBAPWCr as catalyst.



Fig. 4. FT-IR spectrum of the TBAPWCr recovered at runs 1 to 3.

References

- B.M. Choudary, C.R.V. Reddy, B.V. Prakash, M.L. Kantam, B. Sreedhar, Chem. Commun. (2003) 754–755.
- [2] L. Xu, J. Cheng, M.L. Trudell, J. Org. Chem. 68 (2003) 5388–5391.
- [3] D.H.R. Barton, W. Li, J.A. Smith, Tetrahedron Lett. 39 (1998) 7055–7058.
- [4] F. Figueras, J. Palomeque, S. Loridant, C. Feche, N. Essayem, G. Gelbard, J. Catal. 226 (2004) 25–31.
- [5] D. Wang, E.W. Qian, H. Amano, K. Okata, A. Ishihara, T. Kabe, Appl. Catal. A 253 (2003) 91–99.
- [6] A. Chica, G. Gatti, B. Moden, L. Marchese, E. Iglesia, Chem. Eur. J. 12 (2006) 1960–1967.
- [7] T. Noguchi, Y. Hirai, M. Kirihara, Chem. Commun. (2008) 3040-3042.
- [8] S.K. Karmee, L. Greiner, A. Kraynov, T.E. Müller, B. Niemeijer, W. Leitner, Chem. Commun. (2010) 6705–6707.
- [9] K. Sato, M. Hyodo, M. Aoki, X.Q. Zheng, R. Noyori, Tetrahedron 57 (2001) 2469–2476.
- [10] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199-217.
- [11] Y. Hou, L. Xu, M.J. Cichon, S. Lense, K.I. Hardcastle, C.L. Hill, Inorg. Chem. 49 (2010) 4125–4132.
- [12] B.Y. Zhang, Z.X. Jiang, J. Li, Y.N. Zhang, F. Lin, Y. Liu, C. Li, J. Catal. 287 (2012) 5–12.
- [13] S.H. Schultz, H.B. Freyermuth, S.R. Buc, J. Org. Chem. 28 (1963) 1140–1142.
- [14] Z. Stec, J. Zawadiak, A. Skibinski, G. Pastuch, Pol. J. Chem 70 (1996) 1121–1123.
- [15] R. Neumann, D. Juwiler, Tetrahedron 52 (1996) 8781–8788.
- [16] F.M. Collins, A.R. Lucy, C.J. Sharp, J. Mol. Catal. A 117 (1997) 397-403.
- [17] X. Xue, W. Zhao, B. Ma, Y. Ding, Catal. Commun. 29 (2012) 73-76.

- [18] S.P. Das, J.J. Boruah, N. Sharma, N.S. Islam, J. Mol. Catal. A 356 (2012) 36–45.
- [19] K. Kamata, T. Hirano, R. Ishimoto, N. Mizuno, Dalton Trans. 39 (2010) 5509–5518.
- [20] G.B. Shulpin, G. Süss-Fink, L.S. Shulpina, J. Mol. Catal. A 170 (2001) 17–34.
 [21] Y. Wang, J.H. Espenson, J. Org. Chem. 65 (2000) 104–107.
- [22] C.L. Hill, J. Mol. Catal. A 262 (2007) 1–2.
- [23] N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944–1956.
- [24] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
- [25] M.V. Vasylyev, R. Neumann, J. Am. Chem. Soc. 126 (2004) 884–890.
- [26] W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He, J. Xia, Green Chem. 10 (2008) 641–646.
 [27] S. Gronowitz, G. Nikitidis, A. Hallberg, R. Servin, J. Org. Chem. 58 (1988) 3351–3353.
- [27] S. Gronowitz, G. Nikitidis, A. Hallberg, R. Servin, J. Org. Chem. 58 (1988) 3351–3353.
 [28] K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno, Chem. Eur. J. 13 (2007) 639–648
- [29] J.H. Xu, S. Zhao, W. Chen, M. Wang, Y.F. Song, Chem. Eur. J. 18 (2012) 4775–4781.
 [30] Z.X. Zhang, F.W. Zhang, Q.Q. Zhu, W. Zhao, B.C. Ma, Y. Ding, J. Colloid Interface Sci.
- 360 (2011) 189–194.
- [31] I. Fernández, N. Khiar, Chem. Rev. 103 (2003) 3651-3706.
- [32] P. De Filippis, M. Scarsella, Energy Fuel 17 (2003) 1452–1455.
- [33] A. Nisar, Y. Lu, J. Zhuang, X. Wang, Angew. Chem. 123 (2011) 3245–3250.
- [34] Materials and methods: All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated. Infrared spectra (KBr pellets) were recorded on a FTIR Bruker Vector 22 instrument. UV-vis spectra were recorded on a Cary 100 UV-vis spectrophotometer (190–2700 nm). The elemental analysis was performed on a Leco, CHNS-932 and a Perkin-Elmer 7300 DV elemental analyzer. The oxidation products were quantitatively analyzed by gas chromatography (GC) on a Varian CP-3800 instrument using a Varian CP-3800 gas chromatograph using capillary column CP-Wax 52 CB and/or CP-Sil 8 CB and FID detector. ¹HNMR and ¹³CNMR spectra were obtained in chloroform on Bruker 250 (296 K) and referenced to TMS (0.0 ppm) as external standard.
- [35] Preparation of the TBAPWCr catalyst: KPWCr was synthesized according to published procedure, and their synthesis was confirmed by element analysis, UVvis and infrared spectroscopy [36]. A 0.062 g sample of KPWCr dissolved in 5 mL of 0.5 M NaHSO₄ (pH = 1) was added to an aqueous solution of tetra-nbutylammonium (TBA) bromide (0.026 g in 5 mL). The resulting precipitate was filtered, washed with water, and dried at 50 °C under vacuum. Elemental analysis calcd for (TBA)₄[PW₁₁CrO₃₉] [20-22]: C, 20.78; H, 3.92; Cr, 1.41; N, 1.51; P, 0.84; W, 54.67; Found: C, 20.73; H, 3.88; Cr, 1.44; N, 1.54; P, 0.81; W, 53.27. IR, UV-vis and elemental analysis established that product had not changed during the counter-ions exchange (see Supplementary data, Figs. S1, S2).
- [36] C. Rong, F.C. Anson, Inorg. Chem. 33 (1994) 1064–1070.
- [37] General procedure for the oxidation of sulfides to sulfones: The sulfide (1 mmol) was added to a solution of 30% H_2O_2 (6.5 equiv) and TBAPWCr (16.5 µmol), and the mixture was stirred at room temperature for the time specified in Table 2. The progress of reactions was monitored by TLC and GC. After completion of the reaction, the product was extracted with ethyl acetate. Further purification was achieved by short-column chromatography on silica gel with EtOAc/n-hexane (1/10) as eluent. All of the products were known and characterized by ¹HNMR and ¹³CNMR (see Supplementary data, Figs. S3–S15) [38–41].
- [38] H. Danafar, B. Yadollahi, Catal. Commun. 10 (2009) 842-847.
- [39] B.M. Choudary, B. Bharathi, C.V. Reddy, M.L. Kantam, J. Chem. Soc. Perkin Trans. 1 (2002) 2069–2074.
- [40] E.D. Savin, V.I. Nedelkin, D.V. Zverev, Chem. Heterocycl. Compd. 33 (1997) 333–337.
 [41] C.J. Pouchert, J. Behnke, 1st ed., The Aldrich Library of ¹³C and ¹H FT NMR Spectra,
- vol. 1, Aldrich Chemical Company, Inc., Milwaukee, WI, 1993.