Tetra-(tetraalkylammonium)octamolybdate catalysts for selective oxidation of sulfides to sulfoxides with hydrogen peroxide†

Chuanbo Yang,[a,c] Qingping Jin,[b] Hua Zhang,[a] Jian Liao,[a] Jin Zhu,[a] Bin Yu[b] and Jingen Deng*[a]

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Tetra-(tetraalkylammonium)octamolybdate catalysts are successfully applied in the selective oxidation of various sulfides to sulfoxides with 30% aqueous hydrogen peroxide as oxidant under mild reaction conditions in 94–100% yield and 95–100% selectivity. The octamolybdate catalysts show high catalytic activity in a high ratio of substrate to catalyst (up to 10000:1) and are recyclable, with actively functional groups, including hydroxyl group and C=C bonds, tolerated in the oxidation.

Introduction

Organic sulfoxides are important synthetic intermediates for the construction of various chemically and biologically active molecules including drugs,[1] flavors,[2] germicides[3] as well as catabolism regulators.[4] When considering the methods of sulfoxide synthesis, oxidation of sulfides is the most straightforward one. There are lots of reagents and oxidation procedures available for the conformation.[5] However, most of them are not satisfactory because of the formation of environmentally unfavourable by-product, the over-oxidation to sulfones and low oxygen atom efficiency. Seeking catalytic processes with environmentally benign oxidants, catalysts and solvents (such as halogen-free solvent) has become one of the goals that modern green chemistry is pursuing.

During recent years, aqueous hydrogen peroxide has been one of the most attractive "green oxidants" for its environmentally benign characteristics, only producing harmless water as by-product, safety in storage and operation, cheap, readily available and the high effective oxygen content.[6] These advantages have sped up the development of valuable procedures for oxidation of sulfides to sulfoxides with aqueous hydrogen peroxide and various molybdenum or tungsten catalyst systems such as MoO_2Cl_2,[7] $PPh_4[MO(O_2)_2L]$ (M = Mo or W),[8] $LiNbMoO_6$,[9] $[Cp^*_2M_2O_5]$ (M = Mo or W),[10] $Cp'Mo(CO)_3Cl$,[11] $[L]_3PM_{12}O_{40}$, $[L]_3\{PO_4[M(O)(O_2)_2]_4\}$ [M = Mo or W, L = H, Bu_4N^+ or π-$C_5H_5N^+(CH_2)_{15}CH_3$],[12] WO_3/MCM-48,[13] $Na_2WO_4/C_6H_5PO_3H_2/[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$,[14] WO_4^{2-}/Silica-NH_3^+,[15] $[PW_{11}TiO_{40}]^{5-}$,[16] $[\gamma\text{-}SiW_{10}O_m(L)_2]^{4-}$ (L = H_2O, m = 34; L = PhPO, m = 36),[17] $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}/SiO_2$[18] and $[(n\text{-}C_4H_9)_4N]_8[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]$.[19]

Polyoxometalates have many excellent catalytic features such as good catalytic activity and selectivity, the feasible design of catalytically active sites and controllable redox and acidic properties at atomic or molecular levels.[20] These characteristics make them economical and environmentally attractive in both academic and industrial applications. Especially, polyoxomolybdate and polyoxotungstate compounds show excellent catalytic performance and a potential application foreground.[21] During our continuous study into the selective and green synthesis of sulfoxides,[22,1d] we recently found that tetra-(tetraalkylammonium)octamolybdates are efficient catalysts for selective oxidation of sulfides to sulfoxides. To the best of our knowledge, the use of octamolybdates as catalysts in the oxidation of sulfides to sulfoxides has not been previously reported. Herein, we report a high-efficient, recyclable and green method for selective oxidation of a series of sulfides by using 30% aqueous hydrogen peroxide as oxidant and tetra-(tetraalkylammonium)octamolybdates as catalysts to corresponding sulfoxides in excellent yield and selectivity under mild reaction conditions.

Results and discussion

Influence of different solvents and oxidants

We first investigated the oxidation reaction with thioanisole as model substrate by using 30% aqueous hydrogen peroxide as oxidant. To a solution of 4 ml PhSMe (2.5 mmol) and 0.005 mmol $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$ were added different solvents and oxidants at 25 °C. The results are given in Table 1 and show that the reaction is sensitive to solvent. Polar solvents are suitable for the oxidation reaction, especially alcoholic solvents (entries 3–5). Low yield and selectivity were obtained in the non-polar solvent, such as hexane (entry 9) due to the solubility of the catalyst in that solvent. Methanol is the best solvent to provide the highest yield (97%) and selectivity (98%). While no solvent was added, it led to a decrease in both yield and selectivity

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[a] *National Engineering Research Center of Chiral Drugs and Key Laboratory of Asymmetric Synthesis & Chirotechnology of Sichuan Province, Chengdu Institute of Organic Chemistry, The Chinese Academy of Sciences, Chengdu, 610041, China*
[b] *Zhejiang Jinhua CONBA Bio-pharm. Co., Ltd., Jinhua, 321016, Zhejiang, China*
[c] *Graduate University of the Chinese Academy of Sciences, Beijing, 100049, China. E-mail: jgdeng@cioc.ac.cn*

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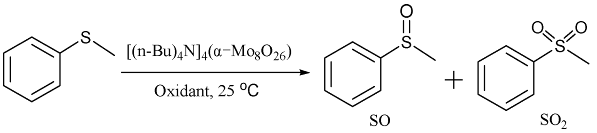
Table 1 Oxidation of thioanisole in different solvents and with different oxidants[a]



Entry	Oxidant	Solvent	Conversion (%)[b]	Yield (%)[b,c]	Selectivity (%)[b,c]
1	H_2O_2	—	94	85	90
2	H_2O_2	H_2O	66	62	94
3	H_2O_2	MeOH	99	97	98
4	H_2O_2	EtOH	99	94	95
5	H_2O_2	*i*-PrOH	98	93	95
6	H_2O_2	MeCN	96	87	91
7	H_2O_2	2-Butanone	91	80	88
8	H_2O_2	1,4-Dioxane	91	73	80
9	H_2O_2	Hexane	56	35	63
10	H_2O_2	C_6H_6	74	63	85
11	H_2O_2	CCl_4	74	69	94
12	MCPBA	MeOH	98	94	96
13	TBHP	MeOH	52	51	99

[a] Reaction conditions: 4 ml of solvent; 2.5 mmol of thioanisole; 2.5 mmol H_2O_2; 0.005 mmol $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$; reaction temperature: 25 °C; reaction time: 10 min. [b] Determined by GC on the crude reaction mixture. [c] Yield = moles of SO/moles of substrate; selectivity = SO/(SO + SO_2).

Table 2 Catalytic oxidation of thioanisole at different temperatures[a]

Entry	Temperature (°C)	Time (min)	Conversion (%)[b]	Yield (%)[b,c]	Selectivity (%)[b,c]
1	−20	180	98	96	98
2	0	60	>99	98	99
3	25	10	99	97	98
4	45	7	99	96	97
5	65	5	>99	96	96

[a] Reaction conditions: 2.5 mmol of thioanisole; 2.5 mmol H_2O_2; 0.005 mmol $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$; solvent: 4 ml of methanol. [b] Determined by GC on the crude reaction mixture. [c] Yield = moles of SO/moles of substrate; selectivity = SO/(SO + SO_2).

(entry 1). An obvious decrease of oxidative activity was observed by added water due to direct reduction of the concentration of aqueous hydrogen peroxide (entry 2). As compared, organic oxidants (MCPBA and TBHP) were used and we are delighted to find that H_2O_2 provided even better results than MCPBA and TBHP (entry 3 vs. entries 12 and 13). The activity of catalytic reaction decreased greatly with TBHP as an oxidant. In addition to its catalytic oxidation performances, H_2O_2 is superior to MCPBA and TBHP in terms of its environmentally benign property.

Influence of reaction temperature

Oxidation of thioanisole under different temperatures was investigated as well. As clearly indicated in Table 2, a higher reaction temperature led to an acceleration of thioanisole oxidation, but rendered a slight decrease in selectivity accordingly.

We also noticed that a lower temperature was disadvantageous to the oxidation reaction, which greatly prolonged the reaction time (entry 1). Although the best selectivity (99%) of the oxidation reaction was given at 0 °C, the reaction took a longer reaction time compared to room temperature (entry 2 vs. entry 3). Based on the reaction at room temperature for saving energy, high reaction effect, and maintaining both high yield (97%) and selectivity (98%), room temperature was finally chosen for further work in view of the environmentally benign aspect.

Table 3 Oxidation of thioanisole with different catalysts[a]

Entry	Catalyst	Conversion (%)[b]	Yield (%)[b,c]	Selectivity (%)[b,c]
1	—	63	59	94
2	MoO_3[d]	90	87	97
3	$Na_2MoO_4\cdot 2H_2O$[d]	93	89	96
4	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$[d]	94	89	95
5	$(NH_4)_3H_4[P(Mo_2O_7)_6]\cdot xH_2O$[d]	77	73	95
6	$(NH_4)_3PO_4\cdot 12MoO_3\cdot 3H_2O$[d]	81	79	97
7	WO_3[d]	76	72	95
8	Na_2WO_4[d]	93	86	93
9	$(NH_4)_5H_5[H_2(WO_4)_6]$[d]	90	84	93
10	$(NH_4)_3PO_4\cdot 12WO_3\cdot 3H_2O$[d]	85	82	96
11	$[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$	99	97	98
12	$[(n\text{-}C_4H_9)(\pi\text{-}C_5H_5N)]_4(\beta\text{-}Mo_8O_{26})$	97	96	99

[a] Reaction conditions: 2.5 mmol of thioanisole; 2.5 mmol H_2O_2; 0.005 mmol of catalyst; solvent: 4 ml of methanol; reaction temperature: 25 °C; reaction time: 10 min. [b] Determined by GC on the crude reaction mixture. [c] Yield = moles of SO/moles of substrate; selectivity = SO/(SO + SO_2). [d] The catalysts were available from commercial sources.

Influence of different catalysts

In this work, various molybdenum and tungsten compounds were used as catalysts in the oxidation of thioanisole with 30% aqueous hydrogen peroxide and the results are given in Table 3. Amongst all catalysts, tetra-(tetraalkylammonium)octamolybdates were outstanding in both reactivity and selectivity for the oxidation of thioanisole. While the oxidation of thioanisole was conducted without catalyst, the reaction obviously became slower and gave lower selectivity (entry 1) and it demonstrated that the proper catalyst is a key factor to achieve good performance. Compared with simple molybdenum and tungsten compounds, such as sodium molybdate and sodium tungstate (entries 3 and 8), other polyoxometalates did not exhibit obvious predominance in the oxidation of thioanisole besides tetra-(tetraalkylammonium) octamolybdate. Moreover, the structure of the tetra-(tetraalkylammonium) cation and the α-,β-isomer of the octamolybdate anion of octamolybdate catalysts had less of an influence on activity and selectivity (entries 11 and 12).

Activity and efficiency of the catalyst

Because tetra-(tetraalkylammonium)octamolybdates showed excellent catalytic activity and efficiency in the oxidation of thioanisole, we investigated the influence of the ratio of substrate to catalyst (Table 4). When the ratio of substrate to catalyst increased, the reaction time increased accordingly, but the oxidation reaction still was steadily accomplished in a short time and the selectivity increased slightly. Even the ratio reached 10000:1, the reaction smoothly proceeded and provided phenyl methyl sulfoxide in 95% yield and >99% selectivity (entry 5).

Table 4 Influence of the ratio of substrate to catalyst[a]

Entry	S/C	Time (min)	Conversion (%)[b]	Yield (%)[b,c]	Selectivity (%)[b,c]
1	500/1	10	99	97	98
2	1000/1	20	>99	98	98
3	2000/1	30	98	97	99
4	5000/1	60	97	96	>99
5	10000/1	80	96	95	>99

[a] Reaction conditions: thioanisole/H_2O_2 (mol/mol) = 1/1; 0.005 mmol $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$; solvent: methanol; reaction temperature: 25 °C. [b] Determined by GC on the crude reaction mixture. [c] Yield = moles of SO/moles of substrate; selectivity = SO/(SO + SO_2).

Table 5 Recycling of catalyst in the oxidation of thioanisole

Run	Time (min)	Conversion (%)[b]	Yield (%)[b,c]	Selectivity (%)[b,c]	TOF (min^{-1})[d]
1	10	98	95	97	242
2	10	97	95	98	57
3	15	98	96	99	60
4	20	98	>96	99	43

[a] Reaction conditions: thioanisole/catalyst/H_2O_2 (mol/mol/mole) = 500:1:500; solvent: methanol; reaction temperature: 25 °C. [b] Determined by GC on the crude reaction mixture. [c] Yield = moles of SO/moles of substrate; selectivity = SO/(SO + SO_2). [d] The turnover frequencies (TOFs) of the catalyst were calculated over 2 min reaction time.

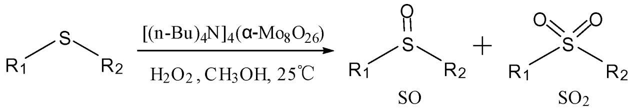
Recycling of the catalyst

The reusability of the catalyst was also investigated. After catalytic oxidation of thioanisole was completed with $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$ as a catalyst in 500 S/C ratios, ethyl acetate was added to the reaction mixture and the catalyst was self-precipitated. The catalyst was filtered, washed with ethyl acetate, and dried in vacuum at room temperature to recover with an average 78.2% yield. Four recycling experiments were carried out and the results are summarized in Table 5. Although the TOF values of the recovery catalysts decreased greatly compared to fresh catalyst, the reaction was completed within 20 min with comparatively high conversion and selectivity. It is noteworthy that no obvious decrease of the TOF values was observed for the successive uses of the recovery catalysts. The analysis of IR spectra showed that an obvious difference was found between the fresh and recovered catalysts, but no changes among the recovered catalysts especially in the region for the absorption characteristic of the Mo=O or Mo–O–Mo vibrations (see the ESI†).

Selective oxidation of different sulfides

Tetra-(tetraalkylammonium)octamolybdate catalysts could be applicable to the oxidation of various sulfides including dialkyl sulfides, cyclic sulfide, benzylalkyl sulfide, substituted arylalkyl and dialkyl sulfides bearing different functional groups with 30% aqueous hydrogen peroxide as oxidant and the results are given in Table 6. Just like the oxidation of thioanisole, excellent catalytic activity and selectivity were obtained for all tested sulfides. Especially, in the oxidation of dialkyl sulfides bearing other active functional groups, such as the hydroxyl group, ketone, carboxylic acid ester, nitrile, and C=C bonds (entries 1–5), the functional groups were tolerated including the hydroxyl group and C=C bonds that were easy to be oxidized (entry 1 and 5).[21] In the oxidation of benzyl methyl sulfide (entry 8), no oxidation was observed at the benzylic C–H bonds. For the oxidation of various phenyl-ring substituted thioanisoles to corresponding sulfoxides, the electronic nature and the position of the substituents had less of an effect on the selectivity of the reaction (entries 11–15), but the presence of an electron-withdrawing substituent or 2-position bulky group on the phenyl

Table 6 Oxidation of sulfides to sulfoxides with H_2O_2 catalyzed by tetra-(tetraalkylammonium)octamolybdate[a]

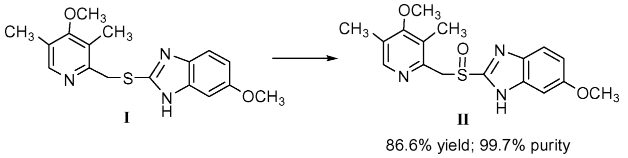


Entry	R_1	R_2	time (min)	Conversion (%)[b]	Yield (%)[b,c,d]	Selectivity (%)[b,c]
1	CH_3	CH_2CH_2OH	8	>99	98(98)	99
2	CH_3	CH_2COCH_3	25	99	98(97)	99
3	CH_3	CH_2CN	120	100	98	98
4	CH_3	$CH_2CH_2COOCH_3$	15	100	97	97
5	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	30	100	96	96
6[e]	$(CH_2)_4$		10	100	100	100
7[e]	CH_3	$CH(CH_3)CH_2CH_3$	15	100	99	99
8	$C_6H_5CH_2$	CH_3	10	100	99(98)	99
9	C_6H_5	CH_3	20	>99	98(97)	98
10	C_6H_5	CH_2CH_3	60	100	97(95)	97
11	2-Cl-C_6H_5	CH_3	240	99	99(98)	100
12	4-Cl-C_6H_5	CH_3	50	>99	97(96)	98
13	4-$CH_3OC_6H_4$	CH_3	25	100	98(97)	98
14	4-$NO_2C_6H_4$	CH_3	150	99	94(92)	95
15	4-$CH_3C_6H_4$	CH_3	25	100	98(96)	98

[a] Reaction conditions: 2.5 mmol of sulfide; 2.5 mmol H_2O_2; 0.0025 mmol $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$; 4 ml of methanol; reaction temperature: 25 °C. [b] Determined by GC or ^1H NMR using an internal standard technique on the crude reaction mixture. [c] Yield = moles of SO/moles of substrate; selectivity = SO/(SO + SO_2). [d] Data in parentheses was the isolated yield. [e] Reaction temperature: 15 °C.

ring required a longer reaction time to complete the reaction (entries 11 and 14).

The present catalytic system was also applied to the oxidation of the sulfide (**I**) to produce well-known antiulcer drug, omeprazole (**II**) in 86.6% yield and 99.7% purity (Scheme 1).[22,23]



Scheme 1 Reaction conditions: $I/H_2O_2/NEt_3/[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26}) = 400:420:40:1$, 30% aqueous H_2O_2, isopropanol, 0 °C, 55 h.

Experimental

Preparation of $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$[24]

Dihydrate sodium molybdate (12.220 g, 0.05 mol) was dissolved into 30 ml of water and the solution was acidified with aqueous HCl (6 mol/l) to pH 4.5. After stirring for 1 h, $(n\text{-}C_4H_9)_4NCl$ (8.0 g, 0.0282 mol) was added to the solution and stirred for 4 h. The precipitate was filtered and thoroughly washed successively with water, absolute ethanol, acetone, and diethyl ether. The white solid was dried in vacuum at room temperature to give $[(n\text{-}C_4H_9)_4N]_4(\alpha\text{-}Mo_8O_{26})$ (10.200 g) in 75.8% yield. Anal. Calcd. for $[(n\text{-}C_4H_9)N]_4(\alpha\text{-}Mo_8O_{26})$: C, 35.69%; H, 6.75%; N, 2.60%. Found: C, 35.47%; H, 6.78%; N, 2.60%. ^{1}H-NMR (d^6-DMSO, 300 MHz), δ (ppm) 0.94 (t, $J = 7.5$ Hz, 3H × 4), 1.26–1.38 (m, 2H × 4), 1.52–1.62 (m, 2H × 4), 3.17 (t, $J = 8.6$ Hz, 2H × 4). IR spectrum (KBr, cm^{-1}): 2961, 2938, 2872, 1633, 1481, 1460, 1379, 1345, 1149, 1104, 1053, 1025, 934, 921, 910, 872, 848, 807, 730, 712, 662, 555, 521, 409, 370, 311.

Preparation of $[(n\text{-}C_4H_9)(\pi\text{-}C_5H_5N)]_4(\beta\text{-}Mo_8O_{26})$[25]

A mixture of 12% dilute hydrogen chloride (9.5 ml, 0.038 mol) and an aqueous solution of dihydrate sodium molybdate (6.11 g, 0.025 mol) was dropwise added into 50 ml of aqueous solution of n-butylpyridinium chloride (8.233 g, 0.047 mol) under stirring at 70 °C. After continuously stirring for 25 minutes, the resulted white precipitate was filtered, washed successively with water and diethyl ether, and dried in vacuum at room temperature to give $[(n\text{-}C_4H_9)(\pi\text{-}C_5H_5N)]_4(\beta\text{-}Mo_8O_{26})$ (2.559 g) in 47.4% yield. Anal. Calcd. for $[(n\text{-}C_4H_9)(\pi\text{-}C_5H_5N)]_4(\beta\text{-}Mo_8O_{26})$: C, 25.02%; H, 3.27%; N, 3.24%. Found: C, 24.85%; H, 3.31%; N, 3.36%. ^{1}H-NMR (d^6-DMSO, 300 MHz), δ (ppm) 0.91 (t, $J = 7.6$ Hz, 3H), 1.26–1.33 (m, 2H), 1.85–1.95 (m, 2H), 4.62 (t, $J = 7.5$ Hz, 2H), 8.16 (t, $J = 7.3$ Hz, 2H), 8.61 (t, $J = 7.9$ Hz, 1H), 9.11 (d, $J = 5.6$ Hz, 2H). IR spectrum (KBr, cm^{-1}): 3127, 3079, 3061, 2956, 2931, 2868, 1631, 1579, 1496, 1484, 1462, 1435, 1376, 1321, 1215, 1174, 941, 935, 912, 897, 837, 766, 713, 683, 664, 644, 573, 554, 520, 473, 449, 408, 366, 290.

General procedure for the oxidation of sulfides

At room temperature, 0.005 mmol of catalyst and 2.5 mmol of sulfide were added into a 15 cm-height and 2.5 cm-diameter round tube and 4 ml of solvent was added. After the reaction solution was stirred for 2 minutes, 30% aqueous hydrogen peroxide (2.5 mmol) was dropwise added into the solution under stirring. The progress of the reaction was monitored by TLC. After completion of the reaction, a small amount of sodium thiosulfate was introduced into the reaction solution in order to eliminate the unreactive H_2O_2. Then 10 ml of ethyl acetate (or methanol) was added to the reaction mixtures to self-precipitate the catalyst, and the catalyst was separated by filtration. The solvent was removed under reduced pressure and the crude products were analyzed by gas chromatography or ^{1}H NMR with dimethyl maleate or bromobenzene as internal standard. The further purification of sulfoxides was performed by flash chromatography (ethyl acetate/hexane or ethyl acetate/methanol) on silica gel.

Conclusions

In summary, the oxidation of various sulfides to sulfoxides catalyzed by tetra-(tetraalkylammonium)octamolybdates was achieved by using 30% aqueous hydrogen peroxide as oxidant in high ratio of substrate to catalyst (up to 10000:1) and short reaction time with excellent selectivity (95–100%). It is noteworthy that actively functional groups, including hydroxyl group and C=C bonds that were easy to be oxidized,[21] were tolerated in the oxidation. In addition, the preparation of the catalysts was simple and convenient, and they could be easily recovered with simple self-precipitation and filtration after reaction and showed high activity and selectivity even after being used four times. Moreover, the present catalytic system is cheap, safe, reproductive, easy to handle and environmentally benign. In addition to mild reaction conditions, the catalytic procedure provides a green alternative because it involves recyclable pollution-free polyoxomolybdate catalysts, halogen-free solvent and a green oxidant.

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