

Solid Silica-based Sulphonic Acid as an Efficient Green Catalyst for the Selective Oxidation of Sulphides to Sulphoxides using NaClO in Aqueous Media

Ali Amoozadeh* and Firouzeh Nemati

Department of Chemistry, Faculty of Science, Semnan University, Semnan, Iran.

Received 21 October 2008, revised 6 December 2008, accepted 7 January 2009.

ABSTRACT

A range of sulphides can be selectively oxidized to the corresponding sulphoxides in good yields using NaClO/silica sulphonic acid as an efficient and recyclable solid acid catalyst, in both water and 50/50 water/EtOH as solvents. The new method compares favourably with previous methods in the literature.

KEY WORDS

Silica sulphonic acid, heterogeneous catalyst, oxidation, sulphides, sulphoxides.

1. Introduction

Solid supported reagents are unique acid catalysts that have become popular over the last two decades. The activity and selectivity of a reagent dispersed on the surface of a solid support is improved as the effective surface area of the reagent is increased significantly, and hence the reagents are expected to perform more effectively than the individual reagents.¹ Low toxicity, moisture resistance, air tolerance and low prices are other common features that make the use of solid supported reagents attractive alternatives to conventional Lewis acids.

The oxidation of sulphides is an important method for the synthesis of sulphoxides, which are versatile intermediates in organic synthesis (usable for CC bond formation² and functional group transformations³ for the preparation of biologically and medically important compounds.)

Although many reagents are available for the oxidation of sulphides to sulphoxides⁴ the catalytic processes with environmentally benign oxidants have become increasingly important. Recently, hydrogen peroxide has been a very attractive 'green oxidant' offering the advantage that it is cheap, environmentally benign, readily available and produces only water as a by-product.⁵ The conventional methods suffer from some drawbacks such as: chlorohydrocarbon solvents or anhydrous H₂O₂ in ethanol⁶ are often used. Another disadvantage is the over-oxidation to sulphones as unwanted by-products.

It is further known that hypochlorous acid oxidation of certain sulphides leads to the corresponding sulphoxides⁷ most probably via the corresponding chlorosulphonium ion, as demonstrated by Johnson *et al.*⁸ in the oxidation of thianes with *tert*-butyl hypochlorite.^{1c} These types of oxidations are very much pH and solvent dependent, which also limits their use.

2. Results and Discussion

In continuation of our work on safe and environmentally friendly procedures for some important transformations,⁹ we wish to report an efficient, convenient and facile method for the selective oxidation of sulphides to sulphoxides using NaClO catalyzed by solid silica-based sulphonic acid under mild conditions. Silica-based sulphonic acid as a green and reusable

catalyst was prepared by the procedure used by Paul *et al.*¹⁰

To the best of our knowledge, there are no literature reports on the selective oxidation of sulphides to sulphoxides using silica sulphonic acid under these conditions. Oxidation of sulphides was performed at room temperature in the presence of 0.2 g of catalyst and NaClO (1 mmol) 5.84 % m/v as the oxidant or a mixture of H₂O/EtOH (50:50) as the solvent (Scheme 1).

In a typical general experimental procedure, a solution of sulphide and NaClO (both 1 mmol) in a 50:50 mixture of H₂O/EtOH in the presence of 0.2 g silica sulphonic acid was stirred for 25–65 min. This resulted in the formation of the corresponding sulphoxides without any over-oxidation and with good to excellent yields. In the case of water as solvent, vigorous stirring is necessary because the reaction mixture forms a suspension or emulsion with the sulphide in water. To study the scope of this procedure, a series of substituted sulphides including alkyl aryl sulphides and dialkyl sulphides was reacted according to optimized reaction conditions. The results are summarized in Table 1.

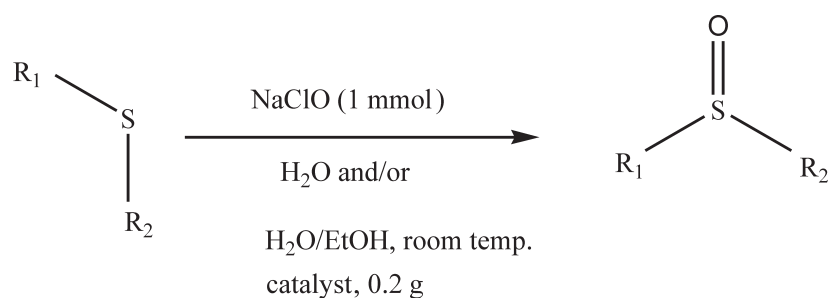
The process is devoid of sulphone formation, a by-product common to most other peroxide-based oxidations. These oxidations exhibited striking solvent effects. It was found that the reaction rates were very slow in chloroform and dichloromethane, but increased dramatically in H₂O/EtOH mixture. Table 2 compares the efficiency of our method with the efficiency of other results in the oxidation of sulphides.

The possible mechanism for the oxidation of sulphide to the corresponding sulphoxide using NaClO in the presence of silica sulphonic acid is outlined in Scheme 2.

It is interesting to note (see Table 1) that for protected 2-phenylthio-3-aminocyclohexanols (entries 9 and 10) only one diastereomer was observed. Note that the sulphur atom is chiral.^{16,17} Based on the literature,^{24,25} it is expected that the neighbouring hydroxyl group stabilizes one of the conformations.¹⁶

In conclusion, a fast and exclusive generation of various sulphoxides from the corresponding sulphides was achieved using silica sulphonic acid/NaClO in EtOH/H₂O. The reaction is highly selective and efficient. The use of a reusable catalyst, the exceptionally fast reaction rate, the absence of a need for control

* To whom correspondence should be addressed. E-mail: aliamoozadeh@yahoo.com



Scheme 1

of temperature and no formation of over-oxidized products make this protocol an attractive alternative to the existing methodologies.

3. Experimental Section

3.1. General Procedure

A solution of sulphide (1 mmol) and dilute NaClO (1 mmol, 1.25 mL) (5.84 % m/v) in water or a mixture of H₂O/EtOH (50:50) (10 mL) and silica sulphonylic acid (0.1 g, 1.2 mol % of HSO₃) was stirred vigorously for an appropriate time (25–65 min). After completion of the reaction (monitored by TLC) the mixture was filtered to separate the catalyst. The organic products were then extracted with diethyl ether (4 × 5 mL). The ether layer was washed with 2 mL of water and dried over MgSO₄. The organic

solvent was removed under reduced pressure to give the corresponding pure sulphoxide (Table 1). The sulphoxide from entries 9 (R_i = 0.14; diethyl ether/hexane, 75/25) and 10 (R_i = 0.25; diethyl ether/hexane, 75/25) were separated and purified by flash chromatography as oily products.

All compounds were identified by their IR and ¹H NMR spectral data.

3.2. Preparation and Recycling of Silica Sulphonylic Acid

Silica sulphonylic acid was prepared according to the procedure of Paul *et al.*¹¹ The catalyst was separated from the reaction mixture and washed with EtOH and dried at 100 °C for 24 h and recycled. The oxidation reaction of diethylsulphane was repeated with recycled catalyst and the yields were found to remain approximately 90 % for three cycles.

Table 1 Oxidation of sulphides to sulphoxides using NaClO/silica sulphonylic acid in the presence of H₂O or H₂O/EtOH as solvent at room temperature.

Entry	R ₁	R ₂	Time/min	M.p. or b.p./°C found (reported)	Yield/% ^a	Yield/% ^b
1	Ph	Me	25	30–31 (30–30.5) ¹¹	62	85
2	Ph	Et	30	144–145 (146) ¹²	70	94
3	Ph	Ph	50	70–71 (72–73) ¹¹	75	93
4	Ph	Bn	40	43–44 ¹² (43–45)	78	95
5	Et	Et	35	101–103 (103–106) ¹³	70	95
6	n-Bu	n-Bu	35	29–31 (29–32) ¹¹	60	82
7	n-Pr	n-Pr	40	24–25 (24.5–25.5) ¹⁴	65	88
8	Ph		25	153–154 (154–155) ¹⁵	73	92
9 ^c	Ph		65	Only one diastereomer ¹⁶	70	85
10 ^c	Ph		65	Only one diastereomer ¹⁶	72	85

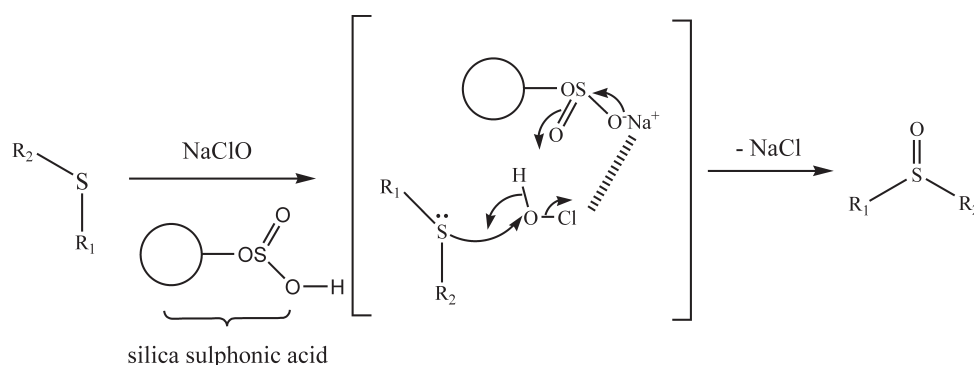
^a Isolated yield in water.

^b Isolated yield in 50/50 H₂O/EtOH.

^c The starting material was prepared according to ref. 17.

Table 2 Comparison of results using silica sulphonic acid with those obtained by other workers using diphenylsulphane.

Catalyst	Conditions	Time/min	Yield/%	Ref.
Silica sulphonic acid	H ₂ O/room temp.	50	75	–
	H ₂ O/EtOH/room temp.		93	
Silica sulphuric acid	CH ₃ CN/room temp.	360	95	19
Mn(III) complex	CH ₃ COOH/room temp.	35	91	20
VO(acac) ₂	CH ₃ CN/reflux	720	74	21
cis-[MoO ₂ (phox) ₂]/UHP ^a	CH ₂ Cl ₂ /CH ₃ OH/room temp.	20	58	22
CeEPBSS3 ^b /NaBrO ₃	CH ₃ CN/H ₂ O/room temp.	180	97	23

^a cis-Dioxo-bis[2-(20-hydroxyphenyl)-oxazolinato]molybdenum(VI) complex/urea hydrogen peroxide.^b Immobilized cerium alkyl phosphonate.**Scheme 2**

Acknowledgement

We thank the Department of Chemistry of Semnan University for supporting this work

References

- A. Corma and H. Garcia, *Adv. Synth. Catal.*, 2006, **348**, 1391–1412.
- (a) M. C. Careno, M. Ribagorda and G.H. Poster, *Angew. Chem. Int. Ed. Engl.*, 2002, **41**, 2753–2755; (b) J.P. Marino, M.S. McClure, D.P. Holub, J.V. Comasseto and F.C. Tucci, *J. Am. Chem. Soc.*, 2002, **124**, 1664–1668; (c) M.R. Acocella, M.A. De Rosa Massa, L. Palombi, R. Villano and A. Scettri, *Tetrahedron*, 2005, **61**, 4091–4097; (d) S. E. Martín and L.I. Rossi, *Tetrahedron Lett.*, 2001, **42**, 7147–7151.
- B.M. Trost, *Chem. Rev.*, 1978, **78**, 363–382.
- (a) G. Agnihotri and A.K. Misra, *Tetrahedron Lett.*, 2005, **46**, 8113–8116; (b) V.G. Shukla, P.D. Salgaonkar and K.G. Akamanchi, *J. Org. Chem.*, 2003, **68**, 5422–5425; (c) A.R. Hajipour, S.E. Mallakpour and H. Adibi, *J. Org. Chem.*, 2002, **67**, 8666–8668; (d) S.E. Martin and L.I. Rossi, *Tetrahedron Lett.*, 2001, **42**, 7147–7151; (e) B. Pelotier, M.S. Anson, I.B. Campbell, S.J.F. Macdonald, G. Priem and R.F.W. Jackson, *Synlett*, 2002, 1055–1061; (f) F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri and G. Sartori, *J. Mol. Catal. A: Chem.*, 2008, **286**, 124–127; (g) N. Iranpoor, H. Firouzabadi and A.R. Pournali, *Synlett*, 2004, 347–349; (h) H. Veisi, *Synlett*, 2007, 2607–2608; (i) B. Karimi and D. Zareyee, *J. Iran. Chem. Soc.*, 2008, **5**, s103-s107; (j) M.A. Zolfigol, K. Amani, A. Ghorbani-Choghamarani, M. Hajjami, R. Ayazi-Nasrabadi and S. Jafari, *Catal. Commun.*, 2008, **9**, 1739–1744; (k) K. Amani, M.A. Zolfigol, A. Ghorbani-Choghamarani and M. Hajjami, *Monatsh. Chem.*, 2008, **139**, 895–899.
- K. Kaczorowska, Z. Kolarska, K. Mitka and P. Kowalski, *Tetrahedron*, 2005, **61**, 8315–8327.
- R. Noyori, M. Aoki and K. Sato, *Chem. Commun.*, 2003, 1977–1986.
- L.S.S. Réamonn and W.I. O’Sullivan, *J. Chem. Soc., Chem. Commun.*, 1976, 1012–1013.
- (a) C.R. Johnson and D.J. McCants, *J. Am. Chem. Soc.*, 1965, **87**, 1109–1114; (b) C.R. Johnson and J.J. Rigau, *J. Am. Chem. Soc.*, 1969, **91**, 5398–5399.
- (a) M.A. Bigdeli, F. Nemati and G. H. Mahdavinia, *Tetrahedron Lett.*, 2007, **48**, 6801–6804; (b) M.A. Bigdeli, M.M. Heravi and F. Nemati, *Synth. Commun.*, 2007, 2225–2230; (c) M.A. Bigdeli, H. Dostmohammadi, G.H. Mahdavinia and F. Nemati, *J. Heterocyclic Chem.*, 2008, **45**, 1203–1205; (d) M.A. Bigdeli, M.M. Heravi, F. Nemati and G.H. Mahdavinia, *Arkivoc*, 2008, 243–248.
- R. Gupta, S. Paul and R. Gupta, *J. Mol. Catal. A: Chem.*, 2007, **266**, 50–54.
- K. Sato, M. Hyodo, M. Aoki, X. Q. Zheng and R. Noyori, *Tetrahedron*, 2001, **57**, 2469–2476.
- J.I.G. Cadogan, S.V. Levy, G. Pattenden, R.A. Raphael and C.W. Rees (eds.), *Dictionary of Organic Compounds*, 6th edn., Chapman and Hall, London, 1996.
- R.C. Weast (ed.), *Handbook of Chemistry and Physics*, 70th edn., CRC Press, Boca Raton, FL, USA, 1989–1990.
- S.J. Searles and H.Y. Hays, *J. Org. Chem.*, 1958, **23**, 2028–2029.
- T. Kageyama, Y. Ueno and M. Okawara, *Synthesis*, 1983, 815–816.
- A. Amoozadeh and F. Nemati, *Phosphorus, Sulfur and Silicon*, DOI10.1080/10426500802529226
- D. Gravel, A. Amoozadeh and Y. Wang, *Tetrahedron Lett.*, 1998, **39**, 8039–8042.
- R.S. Glass, W.N. Setzer, U.D.G. Parbhu and G.S. Wilson, *Tetrahedron Lett.*, 1982, **23**, 2335–2338.
- A. Shaabani and A.H. Rezayan, *Catal. Commun.*, 2007, **8**, 1112–1116.
- F. Hosseinpour and H. Golchoubian, *Tetrahedron Lett.*, 2006, **47**, 5195–5197.
- K.L. Prasanth and H. Maheswaran, *J. Mol. Catal. A: Chem.*, 2007, **268**, 45–49.
- M. Bagherzadeh, L. Tahsini, R. Latifi, A. Ellern and L.K. Woo, *Inorg. Chim. Acta*, 2008, **361**, 2019–2024.
- M. Al-Hashimi, G. Roy, A.C. Sullivan and J.R.H. Wilson, *Tetrahedron Lett.*, 2005, **46**, 4365–4368.
- O. De Lucchi, V. Lucchini, C. Marchioro, G. Valle and G. Modena, *J. Org. Chem.*, 1986, **51**, 1457–1466.
- A. Hirschon, J.T. Doi and W.K. Musker, *J. Am. Chem. Soc.*, 1982, **104**, 725–730.