

Oxidation of Thiols to Disulfides by Oxygen in Presence of Cobalt(II) and Manganese(II) Salts of 4-Aminobenzoic Acid Supported on Silica Gel

Mohammed M. Hashemi* and **Zahed Karimi-Jaberi**

Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516,
Tehran, Iran

Received July 3, 2003; accepted (revised) July 16, 2003
Published online October 20, 2003 © Springer-Verlag 2003

Summary. A mixture of cobalt(II) and manganese(II) salts of 4-aminobenzoic acid supported on silica gel catalyses the oxidation of thiols to disulfides in the presence of oxygen or air.

Keywords. Oxidation; Thiols; Disulfides; Manganese; Cobalt; Silica gel.

Introduction

Disulfides play important roles in biological and chemical processes [1]. Oxidation of thiols is the most exploited method for disulfide synthesis mainly because a large number of thiols are commercially available or are easily synthesized. Reagents such as cerium(IV) salts [2], permanganates [3], transition metal oxides [4], chromium peroxide [5], sodium perborate [6], ferric chloride [7], sodium chlorite [8], nitric oxide [9], dinitrogen tetroxide copper nitrate complex [10], and halogens [11] among others have been utilized for oxidation of thiols to disulfides.

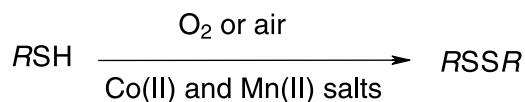
The increasing environmental concern surrounding the use of toxic and dangerous oxidants has impelled organic chemists to develop catalytic oxidation methodologies using molecular oxygen as primary oxidant. In this context catalytic oxidation of thiols to disulfides by molecular oxygen using basic alumina [12], Fe(III)/NaI [13], and cobalt phthalocyanine [14] as catalysts have been reported.

* Corresponding author. E-mail: mhashemi@sharif.edu

Results and Discussion

During the course of our systematic study on the catalytic oxidation of organic compounds with molecular oxygen, we have recently developed a heterogeneous catalytic method based on Co(II) and Mn(II) salts of 4-aminobenzoic acid supported on silica gel for oxidation of allylic and benzylic alcohols to their corresponding carbonyl compounds [15], aromatization of 1,4-dihydropyridines to pyridine derivatives [16], oxidation of phenols to quinones [17], and oxidative deprotection of acetals and ketals [18]. Here we report this method for the oxidation of thiols to disulfides.

The catalysts are easily prepared by the following method: silica gel is heated in a pyrolysis apparatus at 260°C and at 20 mm Hg until 5.7% of water are lost. 4-Aminobenzoic acid is then treated with the activated silica gel. The reaction of the acid bonded to the silica gel with sodium hydrogen carbonate affords the sodium salt of the acid, which is then converted to the cobalt and manganese salts using cobalt and manganese chloride solution [15–19]. The results of oxidation of thiols to disulfides by oxygen or air in the presence of this catalyst are summarized in Scheme 1 and Table 1. The catalyst is recovered in each experiment *via* simple



Scheme 1

Table 1. Oxidation of thiols to disulfides with oxygen or air catalysed by Co(II) and Mn(II) salts

Entry	R	O ₂		Air	
		Time/h	Yield/% ^a	Time/h	Yield/% ^a
1	C ₆ H ₅ CH ₂	1	94	5	83
2	C ₆ H ₅	1	96	5	83
3	<i>n</i> -C ₈ H ₁₇	2	88	9	69
4	<i>p</i> -MeC ₆ H ₄	1	95	5	82
5	<i>p</i> -ClC ₆ H ₄	1	95	5	79
6	<i>n</i> -C ₄ H ₉	2	89	10	66

^a Isolated yields

Table 2. Reusability of the catalyst for the oxidation of benzyl mercaptane to dibenzyl disulfide

Experiment ^a	Yield/%
1 st	94
2 nd	91
3 rd	90
4 th	88

^a All experiments were carried out at the same conditions using O₂

filtration and dried at 135°C for 4 hours after which it can be reused (Table 2). The greatest advantages of this procedure arise from the employment of molecular oxygen or air and from reusability of the catalyst.

Experimental

Products were characterized by comparison of their physical and spectroscopic data with those of authentic samples. All yields refer to isolated products after column chromatography. IR and NMR spectra were recorded on Perkin Elmer 781 and Bruker DPX500 instruments. The progress of the reaction was monitored by TLC. Co(II) and Mn(II) salts of 4-aminobenzoic acid supported on silica gel were prepared according to Hashemi *et al.* [15–19].

Typical Procedure for the Oxidation of Thiols to Disulfides

To a stirred solution of 110 mg of thiophenol (1 mmol) in 25 cm³ of *n*-hexane was added 0.46 g of supported Co salt (0.5 mmol Co) and 0.45 g of Mn salt (0.5 mmol Mn). The reaction mixture was refluxed for 1 h while oxygen was bubbled through the solution at a rate of 15 cm³/min. The reaction mixture was cooled to room temperature and then filtered to recover the solid material (Co and Mn salts). The solid material was washed with 20 cm³ of *n*-hexane. The solvent was evaporated and the product was purified by column chromatography (*n*-hexane) on silica gel. The pure diphenyl disulfide was obtained in 96% yield (105 mg, mp 59–61°C, Ref. [10] 58–61°C). This experiment was also repeated using air instead of oxygen at a rate of 40 cm³/min (see Table 1).

References

- [1] Jocelyn PC (1977) *Biochemistry of the Thiol Groups*. Academic Press, New York
- [2] Firouzabadi H, Iranpoor N, Parham HA (1984) *Synth Commun* **14**: 717
- [3] a) Firouzabadi H, Naderi M, Sardarian A, Vessal M (1983) *Synth Commun* **13**: 611; b) Noureldin NA, Caldwell M, Hendry J, Lee DG (1998) *Synthesis* 1587
- [4] Wallace TJ (1966) *J Org Chem* **31**: 1217
- [5] Firouzabadi H, Iranpoor N, Kiaeezadeh F, Toofan J (1986) *Tetrahedron* **42**: 719
- [6] Mc Killop A, Koyuncu D (1990) *Tetrahedron Lett* **31**: 5007
- [7] Ramesha AR, Chandrasekaran S (1994) *J Org Chem* **59**: 1354
- [8] Ramadas K, Srinivasan N (1995) *Synth Commun* **25**: 227
- [9] Pryor WA, Church DF, Gorindan CK, Crank G (1982) *J Org Chem* **47**: 156
- [10] Iranpoor N, Firouzabadi H, Zolfigol MA (1998) *Synth Commun* **28**: 367
- [11] a) Wu X, Rieke RD (1996) *Synth Commun* **26**: 191; b) Ali MH, McDermott M (2002) *Tetrahedron Lett* **43**: 6271
- [12] Liu KT, Tong YC (1978) *Synthesis* 664
- [13] Iranpoor N, Zeynizadeh B (1994) *Synthesis* 49
- [14] Rao TV, Rao KN, Jain SL, Sain B (2002) *Synth Commun* **32**: 1151
- [15] Hashemi MM, Ghazanfari D (1995) *Iran J Chem Chem Eng* **13**: 77
- [16] Hashemi MM, Beni YA (1998) *J Sci I R I* **9**: 237
- [17] Hashemi MM, Beni YA (1998) *J Chem Research (S)* 138
- [18] Hashemi MM, Kalantari F (2000) *Synth Commun* **30**: 1857
- [19] Hashemi MM, Ahmadibeni Y (2003) *Monatsh Chem* **134**: 411