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Chromium (III) Catalyzed Selective Oxidation of Sulfides to Sulfoxides Using 30% H_2O_2

A. R. Supale · G. S. Gokavi

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Abstract Chromium (III) is used as an efficient, recyclable catalyst for selective oxidation of sulfides. The reactions were carried out in 60% acetonitrile (v/v) using 30% H_2O_2. Chromium (III) forms complex with sulfides which is then oxidized by H_2O_2 to form sulfoxides.

Keywords Homogeneous catalysis · Oxidation · Sulfides · Sulfoxides · Chromium (III) · H_2O_2

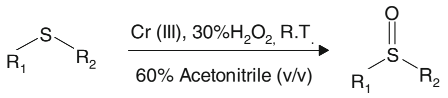
1 Introduction

In recent years interest in sulfoxide chemistry is increasing. Sulfoxides are the valuable intermediates in organic synthesis [1] and in formation of biological active molecules [2]. They play an important role as cardiotonic agents [3], antihypertensive [4], as well as vasodilators [5]. So various efforts have been made in development of new synthetic methods for sulfoxide synthesis [6–8]. Oxidation of sulfide is the simplest, straight and widely accepted for their synthesis. Various reagents and oxidative procedures are now available for their transformations [9–17]. But most of these reagents are not satisfactory for synthesis because of low content of effective oxygen, high cost and formation of unfavorable waste by-products. The major disadvantage of some of these processes is the over-oxidation into sulfone. So controlled method is necessary for sulfoxide preparation. Hydrogen peroxide is an ideal oxidant, having water as the only by-product with high oxygen content [18]. So it is an environmentally green reagent. The reaction between H_2O_2 and sulfide is slow; hence extensive studies have been made for development of new catalyst for their transformations [19–22]. It is advantageous to use water soluble catalyst for practical and industrial applications. If catalyst is soluble in organic solvents then its separation from product becomes difficult. Whereas, if it is soluble in aqueous medium, the separation becomes convenient leaving behind catalyst in aqueous phase, which can be recycled. Various reports are available on metal catalyzed transformation of sulfide with H_2O_2 [23–24]. But in many of these methods, metal catalyst cannot be recycled, so generation of heavy metal lost is occurred.

So still there is need of development of new catalyst which overcomes all these drawbacks. In this communication we report Chromium^{III} catalyzed selective oxidation of sulfide into sulfoxide using 30% H_2O_2 in 60% acetonitrile. The reaction takes place at room temperature as shown in Scheme 1.

2 Experimental

All the products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Spectrophotometric analysis was carried out by using Elico SL 177 spectrophotometer.



Scheme 1

Electronic supplementary material The online version of this article (doi:10.1007/s10562-008-9447-z) contains supplementary material, which is available to authorized users.

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Table 1 Effect of catalyst and oxidant variation on reaction[a]

Entry	Solvents	Catalyst (mol%)	H_2O_2 (mmol)	Isolated yield (%)	Time (h)
1	Acetonitrile	10	4	93	1.2
2	Acetonitrile	5	4	70	3
3	Acetonitrile	1	4	48	3.3
4	Acetonitrile	10	3	75	3
5	Acetonitrile	10	2	62	3.5
6	Acetonitrile	10	1	Trace	6
8	Acetonitrile	0	4	Trace	1.2
9	Acetone	10	4	70	4
10	Methanol	10	4	80	2.5
11	Ethanol	10	4	Trace	8
12	Water	10	4	–	24

[a] Reaction conditions: sulfide (1 mmol), H_2O_2 (4 mmol), Cr (III) (10 mol%) in 10 mL 60% acetonitrile (v/v) at room temperature

^{1}H NMR was recorded on Brukar Avance 300 MHz spectrometer. Melting and boiling points were determined on an open capillary and are uncorrected. Sulfides were purchased from Lancaster, chromic potassium sulphate was purchased from BDH chemicals. Acetonitrile, dichloromethane were purchased from SD Fine chemicals (Mumbai, India) and used without further purification. All yields refer to isolated yields.

3 General Procedure for Oxidation of Sulfide

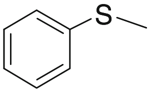
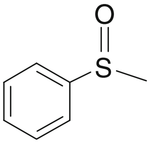
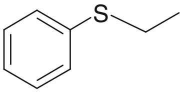
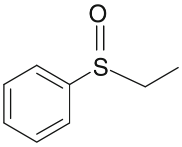
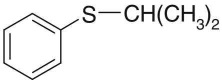
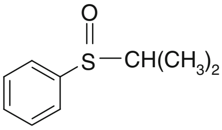
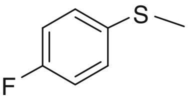
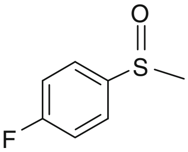
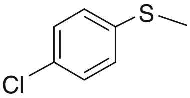
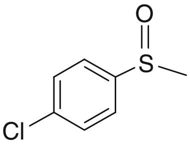
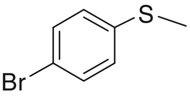
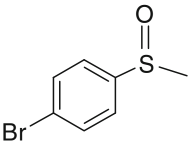
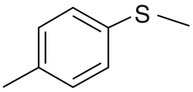
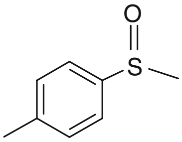
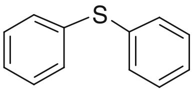
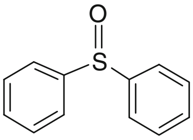
To an aqueous solution of acetonitrile (60% v/v) chromic potassium sulphate (10 mol%, 0.049 g) and methyl phenyl sulfide (1 mmol, 0.124 g) were added. The reaction mixture was stirred at room temperature, while stirring 30% H_2O_2 (4 mmol, 0.135 g) was added drop wise. The progress of the reaction was monitored by TLC. After completion of the reaction, the excess H_2O_2 was destroyed by 2 mL of sodium sulphite (3.0 mmol). The reaction mixture was treated with dichloromethane (2 × 20 mL). Organic layer was dried on anhydrous $MgSO_4$ and concentrated to get methyl phenyl sulfoxide (93% yield).

4 Results and Discussion

To study catalytic oxidation of sulfides mediated by chromium (III), methyl phenyl sulfide was chosen as a model compound and reaction conditions were optimized. Since solvent has pronounced effect on the reaction, it was carried out in various solvents and the results are tabulated in Table 1. Methanol and acetone gave moderate yield with comparatively greater reaction time where as ethanol was found to be a poor solvent. Acetonitrile (60% v/v) was found to be most effective solvent giving high yield with comparatively low reaction time and in its absence there was no reaction even after 24 h in only water. The yield and rate of the reaction were also found to be dependent on the concentration of the catalyst. For 1 mol% of the catalyst the yield was 48% in 200 min when it was increased to 10 mol%, reaction rate was enhanced and gave maximum yield of sulfoxide (93%). The rate of the reaction as well as yield of the product was also found to be dependent on the oxidant concentration. In absence of catalyst reaction afforded 60% yield after 24 h. The effect of oxidant and catalyst variation on the reaction rate and yield are tabulated in Table 1.

To study the scope of reaction, the series of sulfides having dialkyl, diaryl, alkyl-aryl groups were chosen and were subjected to oxidation reaction (Table 2). The overoxidation of sulfides into sulfone was not observed. It is clear from Table 2 that dialkyl sulfides afford sulfoxide in less time in comparison with Diaryl and alkyl-aryl sulfides. It is seen that substrates which having presence of electron donating group at p-position are more reactive, while electron withdrawing groups at p-position are less reactive. The Catalysis of hydrogen peroxide oxidations by metal ions involve [25] a radical mechanism, an ionic mechanism or ionic mechanism via formation of peroxide-Lewis acid complex. The catalyst, chromium (III), utilized in the present study is known for its substitution inertness. The oxidation of Cr (III) by hydrogen peroxide under normal conditions do not occur due to higher redox potential of the couple Cr (III)/Cr (VI) of 1.33 V which can be considerably reduced in presence of ligand forming complex with Cr (III). Such a complexed Cr (III) might be easily oxidized to its higher oxidation state. In order to understand any interaction between sulfide and Cr (III), the UV–VIS spectrophotometric examination of Cr (III), sulfide and their mixture was carried out. The UV–Visible spectrum of chromium (III) shows characteristic peaks at 415 and

Table 2 Cr (III) catalyzed oxidation of sulfides into sulfoxides

Entry	Sulfide	Sulfoxide	Time (min)	Isolated yield (%)	MP or BP (°C)
1	$(CH_3(CH_2)_3)_2S$	$(CH_3(CH_2)_3)_2SO$	30	92	31[27]
2			72	93	32–34[28]
3			30	84	144–146 [28]
4			50	88	–
5			80	90	–
6			180	90	–
7			120	88	76 [28]
8			75	95	–
9			45	94	70 [29]

577 nm and their intensity increases considerably in presence of sulfide (Fig. 1) indicating complex formation. The absorbance of Cr (III) at 415 and 577 nm is due to ligand field band which increases considerably in presence of sulfide as a result of coordination [26] of S atom. Therefore, the mechanism involves a prior complex between the catalyst and the substrate which is oxidized by the oxidant as shown in Scheme 2. After completion of reaction the aqueous layer was concentrated to get catalyst back. It was washed with dichloromethane and further recycled for four times without loss in its activity as shown in Fig. 2.

$$R_1S\,R_2 + \mathrm{Cr\,(III)} \longrightarrow \mathrm{Complex} \qquad (1)$$

$$\mathrm{Complex} + H_2O_2 \longrightarrow R_1SOR_2 + H_2O + \mathrm{Cr\,(III)} \qquad (2)$$

Scheme 2

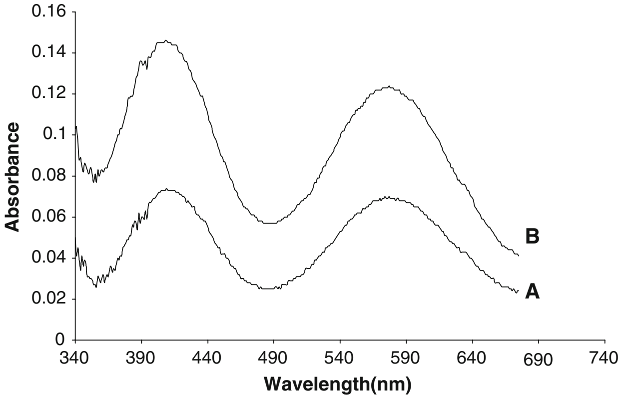


Fig. 1 Increase in absorbance due to complex formation. (A) 5 mL water + 7.5 mL acetonitrile + 35 mg chromic (III) potassium sulphate. (B) 5 mL water + 7.5 mL acetonitrile + 35 mg chromic (III) potassium sulphate + 0.10 mL methyl phenyl sulfide

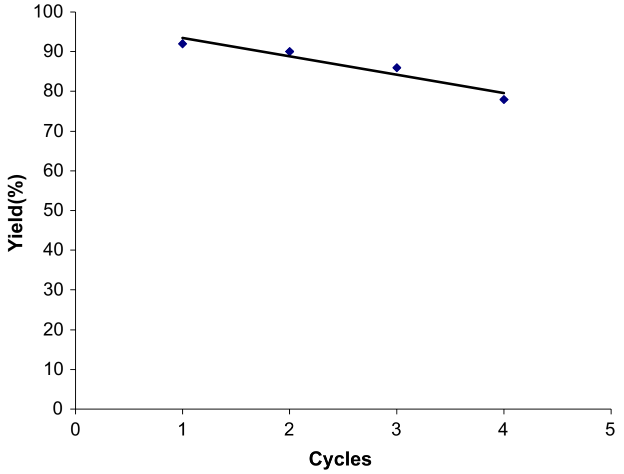


Fig. 2 Recyclibility of Cr (III)

5 Conclusion

The main advantage of this method is over-oxidation into sulfone is not occurring. The reagents used in this reaction are cheap and are easily available. The methodology is simple, economically viable, mild and selective affording high yields of sulfoxides after simple workup procedure. Chromium (III) found to be selective and recyclable catalyst in this transformation.

References

1. (a) Drabowicz J, Kielbasinski P, Mikolaiczyk M (1994) Synthesis of sulfoxides. Wiley, New York; (b) Holland HL (1998) Chem Rev 88:473
2. (a) Carreno MC (1995) Chem Rev 95:1717; (b) Patai S, Rapport Z (1994) Synthesis of sulfones, sulfoxides and cyclic sulfides. J. Wiley, Chichester
3. Parsons WJ, Ramkumar V, Stiles GL (1988) Mol Pharmacol 34:37
4. Kotelanski B, Grozmann RJ, Cohn JN (1973) Clin Pharmacol Ther 14:427
5. Padmanabhan S, Lavin RC, Durant GJ (2000) Tetrahedron: Asymmetry 11:195
6. Olah GA, Marinez ER, Prakash GKS (1999) Synlett 9:1397
7. Mahamuni NN, Gogate PR, Pandit AB (2007) Tetrahedron Lett 14:195
8. Laali KK, Nagvekar DS (1991) J Org Chem 56:1867
9. Drust T (1969) J Am Chem Soc 91:1034
10. Ozanne-Beaudenon A, Quideau S (2006) Tetrahedron Lett 47:5869
11. Ganesan TK, Rajagopal S, Bharathy JB (2000) Tetrahedron 56:5885
12. Brinksma J, Crois R, Feringa BL, Donnoli MI, Rosini C (2001) Tetrahedron Lett 42:4049
13. Quallich GJ, Lackey JW (1990) Tetrahedron Lett 31:3685
14. Zhou XT, Ji HB, Cheng Z, Xu JC, Pei LX, Wang LF (2007) Bioorg Med Chem Lett 17:4650
15. del Rio RE, Wang B, Achab S, Bohe L (2007) Organ Lett 9:2265
16. Maayan G, Popovitz-Biro R, Neumann R (2006) J Am Chem Soc 128:4968
17. Kantam ML, Neelima B, Reddy CV, Chaudhuri MK, Dehury SK (2004) Catal Lett 5:19
18. (a) Sato K, Aoki M, Noyori R (1998) Science 281:1646; (b) Brink GT, Arends IWC, Sheldon RA (2000) Science 287:1636
19. Prasanth KL, Maheswaran H (2007) J Mol Catal A: Chem 268:45
20. Imada Y, Ohno T, Naota T (2007) Tetrahedron Lett 48:937
21. Bryliakov KP, Evgenil PT (2007) J Mol Catal A: Chem 264:280
22. Choi S, Yand JD, Ji M, Choi H, Kee M, Ahn KH, Byenon SH, Baik W, Koo S (2001) J Org Chem 66:8192
23. Mateucci M, Bhalay G, Bradley M (2003) Org Lett 5:235
24. Sato K, Hyodo M, Aoki M, Zheng X-Qi, Noyori R (2001) Tetrahedron 57:2469
25. Ogata Y, Sawaki Y (1986) Organic synthesis by oxidation with metal compounds, In: Mijs WJ, de Jonge CRHI (eds) Plenum Press, New York, p 840
26. (a) Teresa AM, Mederos A, Gili P, Dominguez S, Hernadez-Molina R, Lorenzo P, Lorena AM, Brito F, Otero A, Gabriela CM (2004) Chem Spec Bioavail 16:45; (b) de Meester P, Hodgson DJ, Freeman HC, Moore CJ (1977) Inorg Chem 16:1494
27. Searls SJ, Hays HY (1958) J Org Chem 23:2028
28. (a) Dictionary of organic compounds, 6th edn. Chapman Hall, London (1966); (b) Shaabani A, Rahmati A, Farhangi E (2006) J Sulf Chem 27:287
29. Orito K, Hatakeyama T, Takco M, Suginoma H (1995) Synthesis 1357