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Nitrogen donor-controlled chemoselectivity of reaction in oxidation of sulfides with tetra-*n*-butylammonium hydrogen monopersulfate catalyzed by a partially β-brominated *meso*-tetraphenylporphyrinatomanganese(III) acetate: a clue to the nature of active oxidant

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Highly efficient and rapid oxidation of different sulfides to the corresponding sulfones with tetra-*n*- butylammonium hydrogen monopersulfate (TBAO) in the presence of catalytic amounts of $Mn(TPPBr_2)OAc$ at room temperature is reported. Contrary to other nitrogen donors, using 4-cyanopyridine as co-catalyst leads to an increase in the ratio of sulfoxide to sulfone in the products. Comparison of the chemoselectivity of reaction in the presence of different nitrogen donors as co-catalyst shows the involvement of a high-valent Mn-oxo species as well as the six-coordinate $Mn(TPPBr_2)(HSO_5)(B)$ (B = nitrogen donors) complex in sulfide oxidation reactions with TBAO.

Keywords: electron-deficient Mn(III) porphyrin; oxidation; tetra-*n*-butylammonium hydrogen monopersulfate; catalyst; sulfone

1. Introduction

The oxidation products of sulfur organic compounds, especially sulfones, are valuable synthetic intermediates for the preparation of biologically and chemically important compounds (*1, 2*). Also, they have been used as versatile intermediates in organic syntheses (*3*). In the Ramberg–Backlund reaction (*4*) and Julia olefination (*5, 6*), sulfones are converted to alkenes. A novel polyalkyl ether/polyaryl ether sulfone copolymer has been shown to be useful for producing a medical material to be used to contact the blood (*7*).

Polysulfone is widely used in food processing, electrical applications, medical instrumentation and trays for holding instruments during sterilization, chemical processing equipment, corrosion-resistant piping, tower packing, pump parts, filter modules and membranes (*8*).

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A group of compounds related to the sulfonamides have been used as antibacterial drugs. These drugs inhibit the growth of bacteria rather than killing the organisms (*8, 9*).

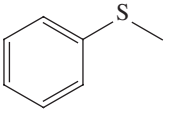
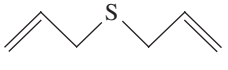
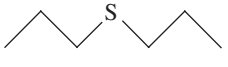
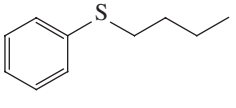
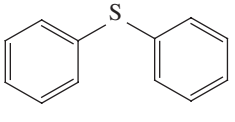
The three most important methods for the preparation of simple sulfones are oxidation of sulfides, alkylation of sulfinate salts and reactions of sulfonic acid derivatives. The oxidation of sulfides is an extremely useful and broadly applicable method for preparing sulfones. Goheen and Bennett (*10*) have reported the use of concentrated nitric acid for the preparation of simple dialkyl sulfones from the corresponding sulfides. Peracetic acid, generated *in situ* from hydrogen peroxide (*i.e.* 30% H_2O_2 in glacial acetic acid), is a very popular choice for this oxidation (*11*). Other forms of H_2O_2 useful for this reaction include the urea complex (*12*) and the bis(trimethylsilyl) derivative TMSOOTMS (*13*). Other oxidizing agents for this reaction are $KMnO_4$ (*14*), MnO_2 (*15*), $NaClO_4$ (*16*), *m*-chloroperbenzoic acid (MCPBA) (*17*), sodium metaperiodate (*18*), sodium perborate (*19*), etc. Oxone, as a safe and commercially available oxidant, has become widely accepted for the oxidation of sulfides to sulfones. Commercially available Oxone is a mixture of K_2SO_4, $KHSO_4$ and potassium hydrogen monopersulfate, $KHSO_5$. The tetrabutylammonium salt of Oxone has been also used for oxidation of sulfides [tetra-*n*-butylammonium hydrogen monopersulfate (TBAO)] (*20, 21*). We have recently reported the $Mn(TPPBr_2)OAc$-catalyzed oxidation of hydrocarbons with TBAO (*22*).

In the present work, highly efficient and chemoselective oxidation of sulfides to sulfones in the presence of the β-di-brominated *meso*-tetraphenylporphyrinatomanganese(III) acetate is reported.

2. Results and discussion

Oxidation of various sulfides with TBAO in the presence of catalytic amounts of $Mn(TPPBr_2)OAc$ and ImH at room temperature gives the corresponding sulfones as the sole product (Table 1). There

Table 1. Oxidation of sulfides with TBAO catalyzed by $Mn(TPPBr_2)OAC$ in the presence of ImH in CH_2Cl_2 at room temperature.[a]

Entry	Substrate	Conversion %	Yield of sulfoxide (%)	Yield of sulfone (%)	Time (min)
1		100	–	100	2
2		100	–	100	2
3		100	18	82	2
4		97	7	90	2
5		90	20	70	2

Note: [a]The molar ratios for oxidant:sulfide:ImH:catalyst are 200:100:10:1.

is no substantial difference between the reactivity of sulfides carrying substituents with different electronic and steric properties. It may be rationalized in terms of the high reactivity of organic sulfides toward oxidation with different oxidants as well as the large size of the sulfur atom as the reaction center that reduces the steric effects of the substituents. However, the yield of sulfone is more sensible to the nature of substituents attached to the sulfur atom (compare 1 and 5). It seems that the first step of oxidation is accompanied with an increase in the steric hindrance around the reaction center and a decrease in reactivity of the sulfur atom.

2.1. *Co-catalytic effect of nitrogenous bases*

Four types of nitrogenous donors (Table 2) have been used in this study, including (i) σ and π-donor imidazole (entry 1), (ii) strong pure σ-donor amine (entry 2), (iii) weak π-donor pyridines (entries 3-5) and (iv) σ- and π-donor aminopyridine (entry 6). It is found that the strong π-donor imidazole is the best co-catalyst. Aminopyridines with π-donor ability are generally better than pyridines and amines (*23*).

Comparison of total conversions and the distribution of products in the presence of σ and/or π-donor axial bases clearly show that the use of weaker nitrogen donors essentially decreases the yield of sulfone relative to sulfoxide in the products. The second step of oxidation of sulfides seems to be more affected by the donor ability of axial bases. It seems that the strong σ- and π-nitrogen donors that facilitate the formation of high-valent Mn-oxo species direct the reaction toward the formation of sulfone as the major product (vide infra).

2.2. *Effect of co-catalyst/catalyst molar ratio*

Oxidation of methyl phenyl sulfide in the presence of various ratios of imidazole to catalyst mainly changes the ratio of sulfone to sulfoxide in the products rather than the total conversion (Table 3). This observation may also be explained on the basis of the high reactivity of organic sulfides toward oxidation reactions, which decreases the importance of electron donation from the axial base to the metal center on the catalytic activity of the metalloporphyrin. However, the second step of oxidation depends more strongly on the nature (Table 2) and concentration (Table 3) of the axial base so that the highest yield of sulfone relative to sulfoxide has been obtained with 10:1 ratio of ImH to catalyst. The addition of ImH beyond this ratio leads to a decrease in the ratio of sulfone to sulfoxide and the total conversion. This observation may be due to the formation of a six-coordinate inactive complex, *i.e.* $Mn(TPPBr_2)(ImH)_2$ (*24*).

Table 2. Oxidation of methyl phenyl sulfide with TBAO catalyzed by $Mn(TPPBr_2)OAc$ in the presence of different nitrogen donors in CH_2Cl_2 at room temperature.[a]

Entry	Axial ligand	Conversion (%)	Yield of sulfoxide (%)	Yield of sulfone (%)
1	ImH	100	0	100
2	2-EtImH	99	27	72
3	Et_2NH	92	21	71
4	Py	89	18	71
5	2-MePy	97	35	62
6	4-CNPy	86	46	40
7	2-NH_2Py	97	21	76
8	2,6-Cl_2Py	80	38	42
9	None	90	34	56

Note: [a]The molar ratios for oxidant:sulfide:ImH:catalyst are 200:100:10:1.

Table 3. Effect of various ImH/catalyst molar ratios on oxidation of methyl phenyl sulfide with TBAO in CH_2Cl_2 at room temperature.[a]

Entry	X[b]	Conversion %	Yield of sulfoxide (%)	Yield of sulfone (%)
1	0	90	34	56
2	5	95	32	63
3	10	100	0	100
4	20	91	15	76

Notes: [a]The molar ratios for oxidant:sulfide:ImH:catalyst are 200:100:X:1. [b]ImH/catalyst.

2.3. *Effect of the ratio of oxidant to sulfide*

The reaction was performed using different molar ratios of TBAO to methyl phenyl sulfide. The 2.0:1 ratio has been found to be the optimized one for the selective oxidation of the sulfide to methyl phenyl sulfone in the presence of a catalyst (Table 4).

2.4. *Proposed mechanism*

UV–VIS spectra of the reaction solution after the addition of TBAO (up to 2.5 h) show no observable change (Figure 1). The formation of a six-coordinate Mn(III) complex under reaction condition resulted in no detectable change of the Soret band (*23*).

Table 4. Effect of various TBAO/sulfide molar ratios on oxidation of methyl phenyl sulfide in presence of ImH in CH_2Cl_2 at room temperature.[a]

X[b]	Conversion (%)	Yield of sulfoxide (%)	Yield of sulfone (%)
1.0	67	40	27
1.5	80	34	46
2.0	100	0	100

Notes: [a]The molar ratios for oxidant:sulfide:ImH:catalyst are X:100:10:1. [b]TBAO/sulfide.

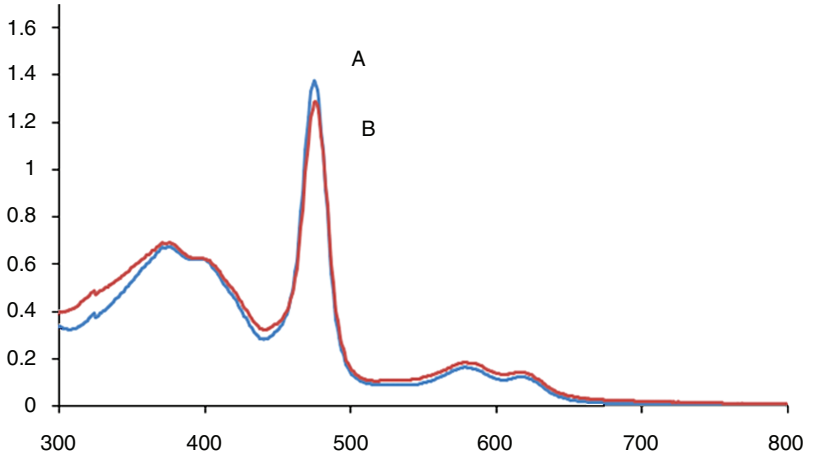


Figure 1. UV–VIS spectra of a solution of $Mn(TPPBr_2)OAc$ and methyl phenyl sulfide in CH_2Cl_2 in the presence of imidazole (a) 2 min after the addition of TBAO and (b) 2.5 h after the addition of TBAO.

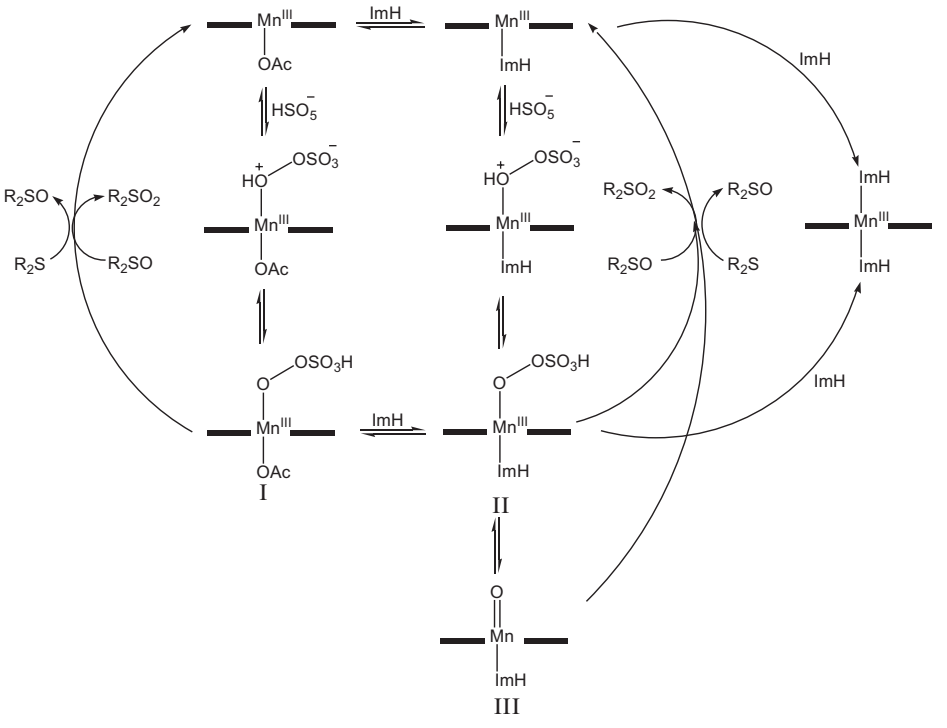


Figure 2. Proposed mechanism.

However, due to the high reactivity of sulfides toward oxidation with different oxidants, this observation cannot exclude the involvement of a high-valent Mn-oxo species.

Good σ- and π-nitrogen donors facilitate the formation of high-valent Mn-oxo species in reaction conditions (*23, 25*). The observed unusual behavior of 4-cyanopyridine may be evidence for the existence of an equilibrium between a six-coordinate Mn(III) species (Figure 2, **I**) and a high-valent Mn-oxo (Figure 2, **III**) species (Figure 2) that shifts toward the six-coordinate moiety in the presence of 4-cyanopyridine. The comparison of 4-amninopyridine, pyridine and 4-cyanopyridine (entries 4, 6 and 7, Table 2) clearly reveals the importance of 4-cyano group on the chemoselectivity of the reaction. It is observed that 4-cyanopyridine, as a weaker σ- and π-donor (or possibly a π-acceptor) relative to pyridine and 4-aminopyridine, shifts the reaction toward the formation of sulfoxide. In accordance with this point, using 2,6-dichloropyridine (Table 2, entry 8) mainly affects the yield of sulfone but has little effect on sulfoxide. It is suggested that the lower ratios of **III** to **II** decrease the yield of sulfone relative to sulfoxide due to the lower reactivity of **II** with respect to **III** (*26*). It may be observed from Table 2 (entries 6 and 9) that the presence of 4-cyanopyridine has little effect on total conversion.

3. Conclusion

In summary, the distribution of oxidation products of sulfides with TBAO in the presence of the partially brominated Mn(TPPBr$_2$)OAc was found to be controlled by the electronic properties of nitrogenous donors; 4-cyanopyridine shifts the reaction toward the formation of sulfoxide as the major product. The distribution of products seems to provide a clue to the nature of active oxidants in the metalloporphyrin-catalyzed oxidation of sulfides with different oxygen donors.

4. Experimental

^{1}H NMR spectra were obtained in $CDCl_3$ solutions with a BRUKER FT-NMR 250 (250 MHz) spectrometer. The residual $CHCl_3$ in conventional 99.8 at% $CDCl_3$ gives a signal at $\delta = 7.26$ ppm, which was used for the calibration of the chemical shift scale. The electronic absorption spectra were recorded on a double-beam spectrophotometer (Shimadzu, UV-240) in CH_2Cl_2. The reaction products were analyzed by gas chromatography using a HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m $\times$ 320 μm $\times$ 0.25 μm) and a flame-ionization detector.

Chemicals were purchased from Merck or Fluka chemical companies. The free base *meso*-tetraphenylporphyrin was prepared and purified as reported previously (*27*). *n*-Bu_4NHSO_5 was prepared according to the literature (*28*).

4.1. *Preparation of H_2TPPBr_2*

β-Di-brominated *meso*-tetraphenylporphyrin (H_2TPPBr_2) was prepared from H_2TPP and freshly recrystalized *N*-bromosuccinimide (NBS) according to the method reported by Bhyrappa and coworkers (*29*) with some modification. H_2TPP (300 mg, 0.49 mmol) was dissolved in $CHCl_3$ (80 ml). To this solution, freshly recrystallized NBS (180 mg, 0.98 mmol) was added. The reaction mixture was stirred for 48 h in darkness and then $CHCl_3$ was evaporated to dryness. The residue was washed with methanol (2 $\times$ 20 ml) to remove any soluble succinimide impurities. UV–VIS (CH_2Cl_2): λ_{max} (nm): 423, 519, 594, 650. ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 8.64–8.78 (m, 6H, β-pyrrole), 8.07–8.20 (m, 8, *o*-phenyl), 7.72–7.75 (m, 12, *m*- and *p*-phenyl).

4.2. *Preparation of Mn(TPPBr$_2$)OAc*

Mn($TPPBr_2$)OAc was prepared and purified according to the previously reported method (*30*). H_2TPPBr_2 (110 mg, 0.13 mmol) was dissolved in a minimum amount of methanol and then 30 ml chloroform was added. $Mn(OAc)_2 \cdot 4H_2O$ (250 mg, 1.04 mmol) was added to the reaction mixture and refluxed for a period of 4.5 h. UV–VIS (CH_2Cl_2): λ_{max} (nm): 375, 475, 583 and 619.

4.3. *General oxidation procedure*

Stock solutions of the catalyst (0.003 M) and nitrogenous bases (0.5 M) were prepared in CH_2Cl_2. In a 10 ml round-bottom flask, the reagents were added in the following order: sulfide (0.3 mmol), catalyst (0.003 mmol, 1.0 ml), nitrogenous bases (0.03 mmol, 60 μl). TBAO (0.6 mmol, 0.247 g) was then added to the reaction solution at 25 °C. The reaction solutions were analyzed immediately by GC after stirring for 2 min.

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References

(1) Clark, E.; *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 23; Wiley: New York, 1997.
(2) Page, P., Ed. *Organosulfur Chemistry I & II*; Springer: Berlin, 1999.
(3) Simpkins, N.S. *Sulphones in Organic Synthesis*; Pergamon Press: Oxford, 1993.

(4) Ramberg, L.; Backlund, B. *Ark. Chim*., *Mineral Geol.* **1940,** *27,* 1–50.
(5) Julia, M.; Paris, J.-M. *Tetrahedron Lett.* **1973,** *14,* 4833–4836.
(6) Kocienski, P. J.; Lythgoe, B.; Ruston, S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 829–834.
(7) Kuwahara, H.; Kawaguchi, T.; Ohmori, S.; Matsumura, S. US Patent 6166168 – Application of Sulfone, Ketone and Ester Containing Polyalkyl Ether Units to Medical Materials. US Patent Issued on 26 December, 2000.
(8) Considine, D.M. Ed., *Van Nostrand's Scientific Encyclopedia*, Vol. 2; Van Nostrand Reinhold: New York, 1989.
(9) Roth, H.J.; Kleemann, A. *Pharmaceutical Chemistry*; Ellis Horwood Ltd: Chichester, 1988.
(10) Goheen, D.W.; Bennet, C.F. *J. Org. Chem.* **1961,** *26,* 1331–1333.
(11) Balaji, T.; Reddy, D.B.; *Bull. Chem. Soc. Jpn.* **1979,** *52,* 3434–3437.
(12) Cooper, M.S.; Heaney, H.; Newbold, A.J.; Sanderson, W.R. *Synlett* **1990,** *9,* 533–535.
(13) Kocienski, P.; Todd, M. *J. Chem. Soc., Cem. Commun.* **1982,** 1078–1079.
(14) Gokel, G.W.; Gerdes, H.M.; Dishong, D.M. *J. Org. Chem.* **1980,** *45,* 3634–3639.
(15) Edwards, D.; Stenlake, J.B. *J. Chem. Soc.* **1954,** 3272–3274.
(16) Khurana, J.M.; Panda, A.K.; Ray, A.; Gogia, A. *Org. Prep. Proc. Int.* **1996,** *28,* 234–237.
(17) Durst, T. *J. Am. Chem. Soc.* **1969,** 91, 1034–1035.
(18) Johnson, C.R.; Keiser, J.E. *Org. Synth. Coll.* **1973,** *5,* 791–795.
(19) McKillop, A.; Tarbin, J.A. *Tetrahedron Lett.* **1983,** *24,* 1505–1508.
(20) Iranpoor, N.; Mohajer, D.; Rezaeifard, A.R. *Tetrahedron Lett.* **2004,** *45,* 3811–3815.
(21) Ghaemi, A.; Rayati, S.; Zakavi, S.; Safari, N. *Appl. Catal. A: Gen.* **2009,** *353,* 154–159.
(22) Rayati, S.; Zakavi, S.; Noroozi, V.; Motlagh, S.H. *Catal. Commun.* **2008,** *10,* 221–226.
(23) Mohajer, D.; Karimipour, G.; Bagherzadeh, M. *New J. Chem.* **2004,** *28,* 740–747.
(24) Mohajer, D.; Sadeghian, L. *J. Mol. Catal. A: Chem.* **2007,** *272,* 191–197.
(25) Nam, W.; Jin, S.W.; Lim, M.H.; Ryu, J.Y.; Kim, C. *Inorg. Chem.* **2002,** *41,* 3647–3652.
(26) Nam, W. *Acc. Chem. Res.* **2007,** *40,* 522–531.
(27) Adler, A.D.; Longo, F.R.; Finarelli, J.D.; Goldmacher, J. Asour, J.; Korsakoff, L. *J. Org. Chem.* **1967,** *32,* 476.
(28) Mohajer, D.; Rezaeifard, A.R. *Tetrahedron Lett.* **2002,** *43,* 1881–1884.
(29) Kumar, P.K.; Bhyrappa, P.; Varghese, B. *Tetrahedron Lett.* **2003,** *44,* 4849–4851.
(30) Nascimento, E.; Silva, G.; Caetano, F.A.; Fernandez, M.A.M.; Silva, D.C.; Carvalho, M.E.M.D.; Parnaut, J.M.; Reboucas, J.S.; Idemori, Y.M. *J. Inorg. Biochem.* **2005,** *99,* 1193–1204.