Organic Chemistry

Reactions of chlorine dioxide with organic compounds

Selective oxidation of sulfides to sulfoxides by chlorine dioxide

A. V. Kutchin, S. A. Rubtsova,★ and I. V. Loginova

Institute of Chemistry, Komi Science Center, Ural Branch of the Russian Academy of Sciences,
48 ul. Pervomaiskaya, 167982 Syktyvkar, Russian Federation.
Fax: +7 (821 2) 43 6677. E-mail: chemi@ksc.komisc.ru

A novel method for the selective oxidation of various types of sulfides to sulfoxides using chlorine dioxide as the oxidant is proposed.

Key words: chlorine dioxide, selective oxidation, sulfides, sulfoxides.

Chlorine dioxide (ClO_2) is a readily available oxidant produced on an industrial scale. In our previous communications,[1—4] we demonstrated that the use of ClO_2 in organic synthesis is a convenient and promising technique. Chlorine dioxide is used in industry as an oxidant for treatment of potable water and for paper bleaching in pulp and paper plants.[5] However, the information on the use of ClO_2 in organic synthesis is scarce. There are few publications dealing with oxidation of amines,[6—8] phenols,[9,10] alkenes,[11] and carbonyl compounds.[5] It should be noted that before our studies, no data on the use of chlorine dioxide for sulfide oxidation have been available from the literature.

Therefore, it was of interest to study the reactivity of ClO_2 toward oxidation of sulfides. Previously,[2] we demonstrated the possibility of selective oxidation of lower (C_3, C_8) dialkyl sulfides to sulfoxides.

Sulfoxides are finding wide application as flotation reagents, extractants for rare metals, selective solvents, and biologically active compounds.[13,14] Sulfoxides can be prepared by oxidation of sulfides by various oxidants. A large number of suitable oxidants have been described; the most detailed discussion can be found in Refs. 13, 15, and 16. The preparation of sulfoxides from sulfides is performed using H_2O_2 in various media and in the presence of various catalytic additives; organic peroxy acids; hydroperoxides and (to a lesser extent) peroxides; various types of halogen-containing oxidants including free halogens; nitric acid and other nitrogen-containing oxidants; free oxygen; and other, more complex reagents. However, oxidation of sulfides also yields sulfones and for many of these oxidants, the reaction cannot be stopped at the step of sulfoxide formation. Although kinetic studies show that the first step of oxidation is usually much faster than the second one, noticeable impurities of sulfones, which are difficult to separate, are detected with many of these reagents; moreover, some of them are complex and not readily accessible.[13]

In this study, we present the results of oxidation of symmetrical and nonsymmetrical dialkyl, diaryl, and dibenzyl sulfides to sulfoxides with chlorine dioxide. Chlorine dioxide is a yellow-green gas with a pungent smell, readily soluble in water and some organic solvents (CCl_4, AcOEt). As an aqueous solution, chlorine dioxide is stable in the dark at room temperature for several weeks.

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According to published data, dioxide chlorine is toxic and explosive only in concentrated solutions or neat.[17]

Due to the ready solubility of ClO_2 in various media, oxidation can be carried out by an aqueous or organic solution (with a ClO_2 concentration of 3—5 g L^{-1}) or by bubbling a mixture of ClO_2 with air. The fact that sulfides are insoluble in water does not hamper the use of ClO_2 in aqueous solutions because ClO_2 readily passes from the aqueous phase to the organic one. Therefore, in oxidation by aqueous solutions of ClO_2, it makes virtually no difference whether or not the sulfide is dissolved in an organic solvent.

In order to optimize the conditions of preparation of sulfoxides, we studied oxidation of dipropyl sulfide by bubbling a mixture of chlorine dioxide with air using different sulfide/reagent molar ratios, temperatures, solvents, and reaction times.

$$\text{Pr}_2\text{S} \xrightarrow{\text{ClO}_2} \text{Pr}_2\text{SO} + \text{Pr}_2\text{SO}_2$$

The results are listed in Table 1.

A stoichiometric amount of the oxidant corresponding to a sulfide—ClO_2 molar ratio of 1 : 0.5 was found to be the optimum. In this case, the degree of sulfide conversion was 90—100%, the yield of the sulfoxide was 88—95%, and that of sulfone did not exceed 2—3%. The highest yield of a sulfoxide was achieved when CH_2Cl_2 or AcOEt were used as solvents or without a solvent. The optimum reaction temperature was 20 °C. At higher temperatures, the selectivity of sulfide oxidation decreases, while lower temperatures retard the reaction.

This was also confirmed by the results of oxidation of diisobutyl sulfide with an aqueous solution of chlorine dioxide (Table 2).

$$\text{Bu}^i{}_2\text{S} \xrightarrow{\text{ClO}_2} \text{Bu}^i{}_2\text{SO} + \text{Bu}^i{}_2\text{SO}_2$$

Since no data on the oxidation of sulfides with chlorine dioxide in various media are available and the reactivity and the selectivity of the reagent can depend substantially on the nature of the solvent, we carried out oxidation of di(*p*-tolyl) sulfide by chlorine dioxide dissolved in AcOEt. Comparison of the oxidation by ClO_2 in water (method *1*) and in an organic solvent (method *3*) showed that, although the reaction in an organic solvent is faster, the yields and selectivities do not differ much for these two cases.

Table 1. Results of oxidation of Pr_2S by bubbling a mixture of ClO_2 with air

Molar ratio Pr_2S : ClO_2	T/°C	Time /min	Solvent	Yield (%)	
				Pr_2SO	Pr_2SO_2
1 : 0.5	20	60	—	95	2
1 : 0.5	20	60	CH_2Cl_2	95	2
1 : 0.75	20	60	CH_2Cl_2	61	38
1 : 1	20	60	CH_2Cl_2	45	55
1 : 2	20	60	CH_2Cl_2	19	81
1 : 0.5	20	120	CH_2Cl_2	75	24
1 : 0.5	10	60	CH_2Cl_2	36	—
1 : 0.5	20	60	CCl_4	88	3
1 : 0.5	20	60	C_6H_{14}	78	4
1 : 0.5	20	60	AcOEt	92	2
1 : 0.5	50	60	AcOEt	80	12
1 : 1	20	300	AcOEt	10	90
1 : 1	50	60	AcOEt	15	77

Table 2. Results of oxidation of $\text{Bu}^i{}_2\text{S}$ by an aqueous solution of ClO_2 (without a solvent)

Molar ratio $\text{Bu}^i{}_2\text{S}$: ClO_2	T/°C	Time /min	Yield (%)	
			$\text{Bu}^i{}_2\text{SO}$	$\text{Bu}^i{}_2\text{SO}_2$
1 : 0.5	20	60	95	3
1 : 1	20	60	61	38
1 : 1	50	60	9	91

Table 3. Oxidation of sulfides in sulfoxides

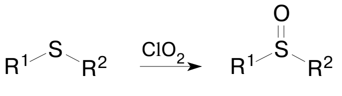
R^1	R^2	Oxidation method*	Yield** (%)	
			Sulfoxide	Sulfone
Pr	Pr	*1*	95	2
Pr	Pr	*2*	93	3
Bu^i	Bu^i	*1*	95	3
Bu^i	Bu^i	*2*	88	3
Me	Bu	*1*	91	2
n-C_8H_{17}	*n*-C_8H_{17}	*1*	92	3
n-C_8H_{17}	*n*-C_8H_{17}	*2*	89	3
Bn	Bn	*1*	96	3
p-Tol	*p*-Tol	*1*	94	2
p-Tol	*p*-Tol	*3*	94	3
p-BrC_6H_4	*p*-BrC_6H_4	*1*	98	2
p-BrC_6H_4	*p*-BrC_6H_4	*2*	97	—

* Experimental conditions: 20 °C, molar ratio sulfide : ClO_2 = 1 : 0.5; aqueous ClO_2 (method *1*), gaseous ClO_2 (method *2*), and a solution of ClO_2 in AcOEt (method *3*) were used.

** Preparative yields of sulfoxide and sulfone after silica gel chromatography are given.

The results of sulfide oxidation to sulfoxides are listed in Table 3.

Thus, a new method for the oxidation of sulfides to sulfoxides has been developed; this method can be recommended for synthetic practice.



Experimental

Reaction mixtures were analyzed by GLC using a Chrom-5 chromatograph with a flame ionization detector (3 × 3000 mm column, SKTFT-50 supported on Chromaton-N-AW-DMCS as the stationary phase, helium as the carrier gas), linear temperature programming in the 50—250 °C range with a heating rate of 6 grad min^{-1}. Authentic samples of sulfides, sulfoxides, and sulfones were used as reference standards. IR spectra were recorded on a Specord M 80 instrument for CCl_4 solutions with a layer thickness of 0.2 mm or for KBr pellets in the region of 400—4000 cm^{-1}. NMR spectra were recorded on Tesla BS-467-A (60 MHz) and Tesla BS-567 (100 MHz) spectrometers in CCl_4 or $CDCl_3$ using HMDS as the internal standard. Elemental analysis was carried out using an EA 1110 CHNS-O automated analyzer. Melting points were determined in an open capillary.

The dipropyl, diisobutyl, and dioctyl sulfides used in the work were commercial preparations. The solvents were purified by distillation.

The authentic sulfoxides and sulfones were prepared by known procedures.[18,19]

Preparation of sulfoxides (general procedure).[18] An equimolar amount of a 30% solution of H_2O_2 was added dropwise with stirring at 20 °C to a sulfide (0.05 mol) in 30 mL of Ac_2O. The reaction time was 20—24 h. Acetic anhydride was evaporated *in vacuo* from the reaction mixture and the remaining sulfoxide was either distilled or recrystallized from EtOH.

Preparation of sulfones (general procedure).[19] A sulfide (0.01 mol) in 30 mL of glacial AcOH was placed in a flask equipped with a stirrer and dropping funnel. Then an excess (0.025—0.03 mol) of a 30% solution of H_2O_2 was added with stirring and ice cooling. The reaction mixture was stirred on a water bath for 2 h at 50—60 °C, poured onto crushed ice, and extracted with ether. The ethereal extract was washed with a saturated solution of $NaHCO_3$ and water and dried with Na_2SO_4. After evaporation of the solvent, the sulfone was recrystallized from a mixture of hexane with ether (2 : 1).

Characteristics of the authentic samples of sulfones are presented below.

Di(*n*-propyl) sulfone, m.p. 30 °C (*cf.* Ref. 20: m.p. 29—30 °C). IR, ν/cm^{-1} (KBr): 1120—1160, 1270—1320 (O=S=O).

Di(*n*-octyl) sulfone, m.p. 76 °C (*cf.* Ref. 21: m.p. 76—77 °C). IR, ν/cm^{-1} (KBr): 1120—1160, 1270—1320 (O=S=O).

Di(*p*-tolyl) sulfone, m.p. 79—80 °C (*cf.* Ref. 22: m.p. 80 °C). IR, ν/cm^{-1} (KBr): 1120—1160, 1270—1320 (O=S=O).

Di(isobutyl) sulfone, m.p. 18 °C (*cf.* Ref. 23: m.p. 17 °C). Found (%): C, 53.88; H, 10.02; S, 17.82. $C_8H_{18}O_2S$. Calculated (%): C, 53.93; H, 10.11; S, 17.92. IR, ν/cm^{-1} (CCl_4): 1120—1160, 1270—1320 (O=S=O).

Butyl methyl sulfone. Found (%): C, 44.01; H, 8.93; S, 23.67. $C_5H_{12}O_2S$. Calculated (%): C, 44.12; H, 8.82; S, 23.53. IR, ν/cm^{-1} (CCl_4): 1120—1160, 1270—1320 (O=S=O).

Dibenzyl sulfone, m.p. 149 °C (*cf.* Ref. 24: m.p. 150 °C). IR, ν/cm^{-1} (KBr): 1120—1160, 1270—1320 (O=S=O).

***p,p´*-Dibromodiphenyl sulfone,** m.p. 167 °C (*cf.* Ref. 25: m.p. 168 °C). IR, ν/cm^{-1} (KBr): 1120—1160, 1270—1320 (O=S=O).

Oxidation of sulfides was carried out using chlorine dioxide as an aqueous solution with a concentration of 4—5 g L^{-1} prepared by an industrial technology at the Syktyvkar LPK joint-stock company. The oxidation by gaseous ClO_2 implies the use of a ClO_2—air mixture. This mixture was prepared by bubbling air through an aqueous solution of chlorine dioxide; the amount of chlorine dioxide was calculated from the initial ClO_2 concentration in the aqueous solution. A solution of ClO_2 in AcOEt was prepared by carrying chlorine dioxide with a slow flow of air from an aqueous solution into AcOEt cooled to 0 °C. The concentration of chlorine dioxide was determined in all cases by a known procedure.[26]

Oxidation by an aqueous solution of ClO_2 (method *1*). An aqueous solution (5 g L^{-1}) of ClO_2 (48 mL, 3.5 mmol) was added with stirring at 20 °C over a period of 60 min to a solution of Pr_2S (0.84 g, 7 mmol) in 5 mL of AcOEt. Then the reaction mixture was extracted with chloroform. The solvent was evaporated to give 0.92 g (97%) of an oxidized product containing, according to GLC, 95% sulfoxide and 2% sulfone. The major product was distilled *in vacuo*, b.p. 81 °C (2 Torr) (*cf.* Ref. 27). Found (%): C, 53.69; H, 10.56; S, 23.97. $C_6H_{14}OS$. Calculated (%): C, 53.69; H, 10.51; S, 23.88. IR, ν/cm^{-1} (CCl_4): 1050 (S=O). ^1H NMR ($CDCl_3$), δ: 1.10 (t, 6 H, 2 CH_3, J = 7.0 Hz); 1.85 (m, 4 H, 2 CH_2); 2.68 (m, 4 H, 2 CH_2S).

Oxidation by gaseous ClO_2 (method *2*). A mixture of air with chlorine dioxide (prepared from 100 mL of an aqueous solution containing 4 g L^{-1} of ClO_2) was bubbled through a solution of di(*n*-octyl) sulfide (4.25 g, 16 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 2 h at 20 °C. The solvent was evaporated to give after silica gel chromatography (eluent — benzene—EtOH (4 : 1)) 4.0 g (89%) of sulfoxide as white crystals, m.p. 69 °C (*cf.* Ref. 21: m.p. 70 °C). Found (%): C, 70.24; H, 12.35; S, 11.82. $C_{16}H_{34}OS$. Calculated (%): C, 70.01; H, 12.48; S, 11.68. IR, ν/cm^{-1} (CCl_4): 1050 (S=O). ^1H NMR ($CDCl_3$), δ: 0.85 (t, 6 H, 2 CH_3, J = 7.0 Hz); 1.24 (m, 16 H, 8 CH_2); 1.41 (m, 4 H, 2 CH_2); 1.73 (m, 4 H, 2 CH_2); 2.61 (m, 4 H, 2 CH_2S).

Oxidation of ClO_2 dissolved in an organic solvent (method *3*). Ethyl acetate (25 mL) containing 3 g L^{-1} (1.15 mmol) of ClO_2 (prepared from 18 mL of an aqueous solution containing 4.2 g L^{-1} of ClO_2) was added with stirring to a solution of di(*p*-tolyl) sulfide (0.50 g, 2.3 mmol) in AcOEt (5 mL). The reaction mixture was stirred for 3 h at 20 °C (to complete decoloration). The solvent was evaporated to give after silica gel chromatography (eluent — benzene—EtOH (4 : 1)) 0.52 g (94%) of di(*p*-tolyl) sulfoxide, m.p. 89 °C (*cf.* Ref. 22: m.p. 92 °C). Found (%): C, 73.18; H, 6.30; S, 13.82. $C_{14}H_{14}OS$. Calculated (%): C, 73.01; H, 6.13; S, 13.92.

The following compounds were prepared in a similar way (the yields and purity characteristics are listed in Table 3).

Diisobutyl sulfoxide. Found (%): C, 59.41; H, 11.27; S, 19.89. $C_8H_{18}OS$. Calculated (%): C, 59.21; H, 11.18; S, 19.75. IR, ν/cm^{-1} (CCl_4): 1050 (S=O).

Butyl methyl sulfoxide. Found C, 50.22; H, 10.31; S, 26.45. $C_5H_{12}OS$. Calculated (%): C, 49.96; H, 10.06; S, 26.67. IR, ν/cm^{-1} (CCl_4): 1050 (S=O).

Dibenzyl sulfoxide. Found (%): C, 73.12; H, 6.31; S, 13.73. $C_{14}H_{14}OS$. Calculated (%): C, 73.01; H, 6.13; S, 13.91. IR, ν/cm^{-1} (CCl_4): 1050 (S=O).

***p,p'*-Dibromodiphenyl sulfoxide,** m.p. 148 °C (*cf.* Ref. 28: m.p. 152 °C). Found (%): C, 40.25; H, 2.08; S, 8.94. $C_{12}H_8Br_2OS$. Calculated (%): C, 40.03; H, 2.24; S, 8.91. IR, ν/cm^{-1} (CCl_4): 1050 (S=O).

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