

REVIEW ARTICLE

SULFOXIDES AND SULFONES: REVIEW

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(Received 27 December 2019) (Accepted 02 May 2022)

ABSTRACT

It has been established that sulfoxide with sulfones have distinct pharmacological effects. Commodity compounds like sulfoxide and sulfones find widespread use in many chemical disciplines. This is why organic chemists find the synthesis of sulfoxide and sulfones so interesting. In the process of oxidation, sulphides can transform into sulfoxides or sulfones. Comprehensive oxidation to the sulfones is significantly simpler than mild oxidation to the sulfoxide, but both can be achieved by the use of highly selective technologies.

Keywords: Oxidation, hydrogen peroxide, halogen derivatives, Green oxidation, electrochemical and photochemical oxidation

INTRODUCTION

Well over past 10 years, the study of organic sulfoxides has grown in the field of chemistry. This is because organic sulfoxides are used as building blocks to make many chemically as well as physiologically active compounds. Oxidation of sulphides, the major straight forward synthetic pathway to the latter, is the transition of sulfoxides to sulfone (Fig. 1)¹, which can be accomplished with a variety of reagents and oxidative processes. While many of these are useful, several of them lead to the over-oxidation of the related sulfones. Therefore, avoiding the formation of unwanted byproducts of oxidation requires carefully controlling the reaction's response setting, like time, the ratio of oxidants, and temperature. Unfortunately, this is frequently challenging to do, and there is still a large emphasis placed on the research and development of specific oxidants for this transition²⁻⁶.

Oxidation using hydrogen peroxide (H₂O₂)

Hydrogen peroxide's high oxygen content, low price and reliability in storage and operation make it a desirable oxidant for environmentally conscious businesses and

households⁷. Since just water is a byproduct, it has a negligible impact on the environment. Hydrogen peroxide (H₂O₂) is additional easily available than new oxidizing agents like peracids and hydroperoxides⁸.

Hydrogen peroxide (H₂O₂) is the most well known oxidizer of aromatic and aliphatic sulphides to the appropriate sulfoxides with a high yield⁹. When combined with a variety of catalysts and solvents and applied in neutral, acidic, or alkaline environments, it can produce a wide range of products.

The synthesis of sulfones from sulphide was examined when acoustic cavitations were present. The oxidant used was 30 percent hydrogen peroxide¹⁰. Sulfones yields were increased by a factor of five to six under optimal sonication compared to the more traditional method using mechanical agitation alone¹¹. Fig. 1 is a schematic depiction of the sulfoxide and sulfone synthesis in presence of hydrogen peroxide.

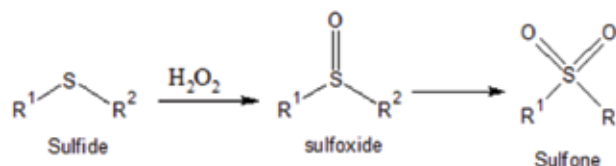


Fig. 1: Synthesis of sulfoxide and sulfone¹⁰

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At ambient temperature, the oxidizing agent hydrogen dioxide converts sulphide to sulfoxide in the presence of acetone or aqueous solution¹². Diisoamyl sulphoxide, Dibenzyl sulphoxide, 4, 4'-diethoxydiphenyl sulphoxide and 4, 4'- Diaminodiphenyl sulphoxide are prepared by this method^{13, 14}. Thioethers were converted into sulfoxide and sulfones in the presence of 30 % hydrogen peroxide, acetone, and glacial acetic acid¹⁵. 2, 4, 6-trichlorothiophenol was converted into 2, 4, 6, trichlorophenyl 2'-diethylamino- ethyl sulphoxide and 2, 4, 6-trichlorophenyl 2'-diethylamino- ethyl sulphone¹⁶. Sulfide is converted into sulfoxide in the presence of methanol as solvent and 30 % hydrogen peroxide¹⁷. At room temperature, ethylphenylsulfide was oxidized in the medium of hexafluoro-2-propanol with 30 % hydrogen peroxide. A good yield of ethylphenyl sulfoxide was obtained after 30 minutes, and a prolonged reaction did not convert the sulfoxide into sulfone¹⁸. In presence of phenol and 30 % hydrogen peroxide; the time necessary for the reaction was reduced with excellent yield¹⁹.

In the absence of organic solvents and halogens, 30 % hydrogen peroxide can convert diphenyl sulphide into sulfoxide and sulfone. The most effective catalysts for this reaction were sodium tungstate, phenylphosphonic acid, and methyltrioctylammonium hydrogen sulphate, respectively²⁰. Sulfones and sulfoxides were synthesized from anhydrous hydrogen peroxide in tert-butyl alcohol catalyzed by vanadium pentoxide sulphide²¹. Catalyst bisacetylacetonato-oxovanadium was utilized to oxidize p-chlorophenyl methyl sulphide, also aryl methyl sulphide oxidation in ethanol at ambient temperature²². To create p-chlorophenyl methyl sulphoxide, hydrogen peroxide is used in the oxidation of p-chlorophenyl methyl sulphide, dioxane as well as dioxaneethanol containing catalytic amounts of bisacetylacetonato oxovanadium²³. The equivalent sulfoxide can be obtained by oxidising diphenyl sulphide with hydrogen peroxide, methanol, and a small amount of sodium metavanadate as a catalyst²⁴. Oxidizing sulphides with tellurium dioxide and hydrogen peroxide proved to be an extremely effective and discerning reagent. An excessive amount of oxidation is prevented²⁵.

Zirconium tetrachloride exists, thus, it is well known that hydrogen peroxide is an effectual solvent for the room-temperature conversion of sulphides into sulfoxides and sulfones²⁶. With a cheap poly(amidoamine) catalyst and a first-generation linked phosphomolybdate hybrid, oxides of sulphur were converted to sulfoxides and sulfones. Extensive testing revealed that reusing the catalyst was possible²⁷. Without monitoring the potential sulfoxide oxidation consequence, ethyl acetate was neatly

transformed to the sulfone using urea-hydrogen peroxide and phthalic anhydride²⁸.

Oxidation using halogen oxide derivatives

Halogen reacts with organic sulphides to form halosulfonium salts, which are hydrolyzed in the presence of water to form sulfoxide²⁹. Lower dialkyl sulphides were oxidized directly to sulfone, whereas higher sulphides were oxidized to sulfoxides³⁰ amount of sodium metaperiodate was reported for selective sulfoxidation³¹. For the specific oxidation of sulphides to sulfoxides, sodium hypochlorite can be used as an oxidant, and 2, 2, 6, 6-tetramethylpiperidyl-1-oxy connected metalloporphyrines be capable as used as catalysts³². It has become clear that iodosobenzene is a powerful oxidizing agent for converting unsaturated or receptive sulphides into sulfoxides^{33, 34}. The oxidant catalyst combination of iodoxybenzoic acid (IBX) and tetraethyl ammonium bromide is effective in the chemoselective oxidation of various sulphides³⁵.

Sodium bromide is used as a desizing agent in the textile industry³⁶. It has been reported that sodium bromide is used in the oxidation of sulphides and alcohol. Mild conditions resulted in the oxidation of sodium bromide sulphides to sulfoxide³⁷. It has been observed that o-iodoxybenzoic acid and tetraethyl ammonium bromide can catalyze the chemoselective oxidation of sulphides³⁸. In 30 % hydrogen peroxide in acetonitrile, it has been found that silica bromide is an effective catalyst again for oxidation process of sulphides towards sulfoxides and sulfones³⁹. High yield of alkyl alkynyl sulfones can be created and through photoinduced reaction of potassium alkyltrifluoroborate, sulphur dioxide, and alkynyl bromide in the presence of visible light at ambient temperature⁴⁰. This process can take place at 60-140°C temperature.

In presence of iodosobenzene, the catalyst benzeneseleninic acid converts sulphides to sulfoxides by ligand coupling on the iodine atom⁴¹. Over oxidation was prevented during the conversion of thioanisoles and allylic sulphides to sulfoxides. Under the influence of visible light, carbonyl ruthenium porphyrin complexes act as effective oxidation catalysts⁴².

Oxidation using nitrogen oxide derivatives

The first oxidising agent utilised to transform sulphides into sulfoxides was nitric acid⁴³. Nitric acid oxidizes dibenzylsulfide to dibenzylsulfoxide⁴⁴. Gold halides catalyze the oxidation of sulphides by the phase-transfer process. Organic sulphides are treated with nitromethane, tetrabutylammonium hydroxide, and chloroauric acid in catalytic amounts and aqueous nitric

acid⁴⁵. The rapid response of H₂O₂ through HNO₂ in acidic medium produces peroxyxynitrous acid ONOOH, a potent oxidant along with an unhinged isomer of HNO₃. ONOOH sulfoxidizes sulfides R₂S in minutes if they are present. This process is faster than ONOOH to HNO₃ decay, allowing for the rapid production of sulfoxides with H₂O₂⁴⁶. At low temperatures (-76°C), aralkyl and dialkyl sulphides respond quickly with acetyl as well as benzoyl nitrates to produce sulfoxides in high yield⁴⁷. Dialkyl, aryl, and diaryl sulphides in methylene chloride treated with nitronium hexafluorophosphate at -78° gave excellent yields of sulfoxides⁴⁸. Significant yields of sulfoxides were achieved from the pretreatment of dialkyl and diaryl sulphides using thallium (III) nitrate (2.2 equivalents) with chloroform-acetic acid (3: 1) at ambient temperature. Sulfones were discovered to be produced exclusively in chloroform-acetic anhydride reactions (3:1)⁴⁹.

Under very mild circumstances, ceric ammonium nitrate⁵⁰ is a proficient solvent for conversion of diaryl sulphides into the consequent sulfoxides⁵¹. Cerium (IV) salts are used as a catalyst in conjunction with a cooxidant (BrO_i) to reuse previously used cerium (III) ions in a recycling process. The oxidation of dialkyl sulphide can also be accomplished using this catalytic method⁵². Creating trans-1,4-dithiane a-disulfoxide requires a specific set of conditions, nitrous oxide fumes were introduced during the oxidation process^{53,54}. For the purpose of converting methyl phenyl sulphide into the equivalent sulfoxide, dinitrogen tetroxide was combined with carbon tetrachloride⁵⁵. Liquid dinitrogen tetroxide quickly oxidises alkyl sulphides to sulfoxides without the production of sulfones⁵⁶. The oxidation of bis(chloromethyl) sulfide with dinitrogen tetroxide is possible if the synthesis of N₂O₃ is avoided through scavenging the reaction mixture with oxygen⁵⁷.

Oxidation using oxygen, ozone

Sulfides can be selectively oxidised with molecular oxygen in a solvent-controlled reaction that does not involve any metals or additives⁵⁸. Peroxides could be produced from the reaction of ethers with molecular oxygen in its ground state. Using bis (2-ethoxyethyl) ether, bis (2-methoxyethyl) ether as well as bis (2-butoxyethyl) ether, peroxide was created. Catalyst sulfones are produced when this peroxide is available⁵⁹. Ozonolysis is the simplest scheme for the synthesis of sulfoxides and sulfones⁶⁰. Oxidation is carried out in hydroxylic and aprotic solvents⁶¹. Mixed metal oxides supported on gamma alumina, copper oxide, manganese oxide, chromium oxide, molybdenum oxide, and ozone are used to catalyse the gas-phase oxidation of dimethyl sulphide⁶².

Complete conversion of dimethyl sulphide into sulfoxide and sulfones was achieved in the presence of vanadia/tatania catalyst⁶³. It has been reported that molecular oxygen catalyzed selective oxidation of sulphides to sulfoxides using oxygen acceptor Ru(TPP)Cl (ruthenium (III) meso-tetraphenylporphyrin chloride)⁶⁴. For sulphur mustard, a possible chemical warfare agent, a simple and effective oxidative decontamination approach was developed. In a controlled manner, ozone gas oxidises sulphur mustard to produce its harmless sulfoxide counterpart⁶⁵.

Oxidation using peracids

Chromic acid is used to oxidize sulfides⁶⁶. The method is improved by using pyridine instead of chromic acid⁶⁷. To create S-monoxide from a cephalosporin, chromic anhydride as well as sulfuric acid is used⁶⁸. Peroxymonosulfuric acid along with its salts has been utilized to prepare certain sulfoxides⁶⁹. When optically active peracids were used to oxidize asymmetric sulphides, optically active sulfoxides were formed⁷⁰.

Electrochemical oxidation

The continuous-flow microreactor was used to study the electrochemical oxidation of thioethers and thiols⁷¹. Anodic oxidation of aliphatic sulphides was carried out by cyclic voltammetry along with controlled potential electrolysis. Dimethyl sulphide in acetonitrile is converted into sulfone⁷². Under electrochemical conditions, diaryl sulphides and aryl alkyl sulphides are oxidised to the corresponding sulfoxides and sulfones⁷³.

Oxidation in chiral solvents

o-(Methylthio) benzoic acid and chiral peroxy-acids produce diastereomeric sulphoxides⁷⁴. In order to create sulfoxides, sulphides are oxidised asymmetrically with tert-butyl hydroperoxide and a titanium complex catalyst⁷⁵. An asymmetric oxidation that uses R-(+) binaphthol like a chiral auxiliary is responsible for catalysing the sulfoxide oxidation reaction, resulting in high chemical yield and good enantiomeric excess⁷⁶. Asymmetric sulphide oxidation by acid-promoted oxidation yields solely sulfoxides when chiral N-alkyl oxaziridines are used as reagents^{77, 78}.

Microbiological oxidation

Aspergillus niger was tested for its ability to oxidise biotin to S-oxide. After the matching sulphide was microbiologically oxidised by two distinct fungi, optically pure R- and S-configured P-tolymethyl sulfoxides were recovered^{79, 80}. *Cunninghamella echinulata* MK40 has

recently looked at the possibility of producing a proton pump inhibitor through the process of microbiological synthesis by enantioselectively oxidizing a sulphide to its equivalent sulfoxide⁸¹. *Pseudomonas putida* strains have been shown to preferentially produce (*R*)- or (*S*)-configured chiral sulfoxides from corresponding sulphides, with no confirmation of sulfone formation. Comparable outcomes were achieved with a clone (pKST11) of *Escherichia coli* containing the toluene dioxygenase (Tod) C1 C2 B and A genes⁸². Multiple methionine sulfoxide reductase genes have been discovered in *Staphylococcus aureus*⁸³.

Enzymatic oxidation

Rat liver homogenates were used to examine the microsomal fraction's enzymatic oxidation of thiocarboxylic acids to sulfoxides. To function at its best, this system needed NADPH and oxygen supplementation and a pH of 7.4⁸⁴. Since then, researchers have delved deeply into the topic of sulphide oxidation by enzymes. Hepatic microsomes isolated from phenobarbital-treated rabbits were found to be superior to nonenzymatic oxidation in the enzymatic oxygenation of different diaryl, alkyl, and aryl alkyl sulphides to corresponding sulfoxides⁸⁵. *E. coli* enzymes reduce methionine sulfoxide residues in ribosomal protein L12. The purified enzyme also reduces methionine sulfoxide, which is found in oxidizing [Met] enkephalin⁸⁶.

Alkyl sulphides, sulfoxides, including sulfones were oxidised using rabbit liver microsome-isolated cytochrome P-450 or a reconstituted system⁸⁷. Alkyl sulphides with a more acidic -hydrogen were more readily S-dealkylated and describes the enantioselective sulfoxidation reactions using three Baeyer-Villiger monooxygenases to make chiral heteroaryl, cyclohexyl, and alkyl sulfoxides (BVMOs)⁸⁸.

Green oxidation organic compounds

Ultrasonication is the advanced approach used to synthesize sulfoxides⁸⁹. Hydrogen peroxide oxidises poly (ethylene glycol) dimethylether, as a consequence of which, an effective method for the oxidation of sulphides to sulfoxides with high selectivity is produced. This approach does not require the use of any catalyst⁹⁰. Iron (III) bromide and its complexes with solid cyclodextrin or DMSO are effective chemoselective sulfoxidation catalysts^{91,92}. In the absence of a solvent, alkyl, aryl, and cyclic sulphides can be converted to their corresponding sulfoxides through the use of microwave thermolysis in conjunction with iron (III) nitrate impregnated on clayfen⁹³.

Under microwave irradiation, organic inorganic hybrids produced from lacunary polyoxotungstates

were tested as H₂O₂ oxidation catalysts⁹⁴. Selective oxidation of sulphides by n-butyltriphenylphosphonium dichromate was carried out to create sulfoxides and sulfones with aluminium chloride in solution and microwave irradiation⁹⁵. An inquiry into the oxidation of sulphides in an environmentally acceptable and chemoselective manner utilizing sodium perborate as well as sodium percarbonate was carried out. The oxidant can be sodium perborate or percarbonate, and the reaction media can be solvent-free or water. Irradiation by microwaves or the heat generated by more conventional means is the source of energy⁹⁶. The use of oxone in the manufacture of sulphoxide has the drawback of requiring excessive equivalents of oxone, inorganic substrates such as montmorillonite and alumina, and thermal or MW activation. This is a disadvantageous combination⁹⁷⁻¹⁰⁰.

CONCLUSION

Due to the versatile nature of sulfoxides and sulfones, they have great importance in the chemical and polymer industries. The scientific literature describes a variety of distinct pathways that can be taken to arrive at sulfoxides and sulfones; however, the oxidation of sulfoxides is the one that makes the most sense. Use of hydrogen peroxide for oxidation is easy and inexpensive. Ozone is a newer option for the oxidation reaction. It's a reliable, a technique that may be scaled up for the selective oxidative conversion of sulphides into their corresponding sulfoxides or sulfones. Additionally, microbiological and environmentally friendly synthesis methods can be used to oxidize sulphides.

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