

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23444620>

Rate of dibutylsulfide decomposition by ozonation and the O₃/H₂O₂ advanced oxidation process

ARTICLE *in* JOURNAL OF HAZARDOUS MATERIALS · SEPTEMBER 2008

Impact Factor: 4.53 · DOI: 10.1016/j.jhazmat.2008.09.049 · Source: PubMed

CITATIONS

10

READS

33

5 AUTHORS, INCLUDING:



[Stanisław Popiel](#)

Military University of Technology

29 PUBLICATIONS 155 CITATIONS

SEE PROFILE

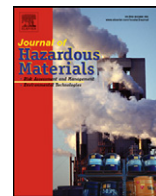


[Zygfryd Witkiewicz](#)

Military University of Technology

97 PUBLICATIONS 823 CITATIONS

SEE PROFILE



Rate of dibutylsulfide decomposition by ozonation and the O₃/H₂O₂ advanced oxidation process

Stanisław Popiel^{a,*}, Tomasz Nalepa^b, Dorota Dzierżak^a, Romuald Stankiewicz^c, Zygfryd Witkiewicz^{a,d}

^a Military University of Technology, Institute of Chemistry, 2 Kaliski Street, 00-908 Warsaw, Poland

^b Defence Department of Ministry of Economy, 3/5 Plac Trzech Krzyży, 00-507 Warsaw, Poland

^c University of Warsaw, Institute of Experimental Physics, 69 Hoża Street, 00-681 Warsaw, Poland

^d The Stanisław Staszic University of Arts and Sciences, 52 Wesola Street, 25-353 Kielce, Poland

ARTICLE INFO

Article history:

Received 25 June 2008

Received in revised form

12 September 2008

Accepted 15 September 2008

Available online 24 September 2008

Keywords:

Organic sulfur compounds

Dibutyl sulfide

Oxidation

Ozone

Hydrogen peroxide

GC–AED analysis

ABSTRACT

A process of dibutylsulfide (DBS) oxidation using advanced methods of oxidation with ozone and hydrogen peroxide was studied. It was demonstrated that depending on pH value there are two mechanisms of DBS oxidation present: ionic and radical. The ionic mechanism predominates in acidic environment and the radical mechanism predominates in alkaline environment. At high pH ozone stability decreases and hydrogen peroxide has a deciding effect on DBS oxidation rate. At pH 9, and at high concentration of hydrogen peroxide (ranging from 0.1 to 1 mol/L), a clear increase in DBS decomposition rate was observed. That was caused by production of hydroperoxide radicals in reaction of hydrogen peroxide and ozone. In solutions pH value of which is close to 2, the rate of DBS oxidation by ozone alone is slower than in a O₃/H₂O₂ system, regardless the H₂O₂ concentration. For higher H₂O₂ concentrations (ranging from 0.1 to 1 mol/L), regardless the pH value of the solution, oxidation in a O₃/H₂O₂ system is faster, compared to a situation in which ozone is a sole oxidizer. For H₂O₂ concentrations below 0.1 mol/L and when pH > 2 DBS oxidation in O₃/H₂O₂ system is slower compared to the situation in which ozone was the only oxidizer.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Organic sulfur compounds present in the natural environment are of biogenic (natural) and anthropogenic (human-related) origin. They involve various classes of chemical substances, from simple gaseous ones, such as volatile methanethiols or light alkyl sulfides, to complex ones, such as sulfur substituted polycyclic aromatic compounds. Those substances are present in air, water and soil, and in natural materials, such as crude oil, natural gas. They are formed in processes of biological material decomposition, organic compounds decomposition in waste waters, in composting facilities and waste dumps. Their presence is a source of odors emitted by waste water treatment plants and composting facilities. Organic sulfur compounds are also present in food, as natural substances, and are formed in course of thermal processing of food, influencing its taste and smell. They are also semi-products in industrial organic synthesis (for example of drugs). They participate in numerous natural processes. Dimethyl sulfide (DMS), emitted from oceans as a main sulfur compound, is responsible for formation of sulfate aerosols in upper atmosphere layers, constituting centers of con-

densation for water vapor and inducing atmospheric precipitation. Sulfur dioxide is formed when organic sulfur containing fossil fuels are burned. The compound is emitted to atmosphere. That is a very serious problem also for petrochemical industry. Sulfur compounds are toxic for various catalysts and cause corrosion of many installations [1,2]. Organic sulfur compounds, as by-products in various engineering processes, are emitted to atmosphere and sewage by refineries [3], cellulose and paper processing industry plants [4–6], artificial fiber production plants, tanneries and food industry. They are noxious odorants present in vicinity of the a/m facilities, and in high concentrations they are toxic. Therefore they have to be neutralized [7].

Volatile organic sulfur compounds participate in a cycle of sulfur transport from oceans and lands into the atmosphere [8]. Emission of sulfur compounds into atmosphere constitutes an air pollution and favors smog formation in urban areas, causes acid rains [9] and indirectly contributes to general climatic changes.

Natural volcanic processes, algae vegetation in the superficial layers of oceans, decomposition of organic matter in waters and on lands, and vegetative processes in plants and animals constitute main sources of sulfur compounds emission. Sulfates reduced by micro-organisms in assimilation and dissimilation processes are the main source of sulfur in water and soil [10]. During assimilative reduction a sulfate ion (SO₄^{2−}) becomes reduced via a set of enzy-

* Corresponding author. Tel.: +48 22 683 9097; fax: +48 22 683 9582.
E-mail address: spopiel@wat.edu.pl (S. Popiel).

Nomenclature

AOT	advanced oxidation technology
AOP	advanced oxidation process
CWA	chemical warfare agents
DBS	dibutyl sulfide
GC/AED	gas chromatography–atomic emission detector
GC/MS	gas chromatography–mass spectrometry
HO [−]	hydroxyl anion
HO [•]	hydroxyl radical
H ₂ O ₂	hydrogen peroxide
HO ₂ [−]	hydroperoxide anion
HO ₂ [•]	hydroperoxide radical
O ₃	ozone
O ₂ ^{•−}	superoxide anion radical
<i>r</i> _{O₃}	DBS oxidation rate with ozone
<i>r</i> _{O₃/H₂O₂}	DBA oxidation rate in a O ₃ /H ₂ O ₂ system
ROS	reactive oxygen species
<i>t</i> _{1/2} ^{O₃}	DBS half-life period for a system in which ozone was a sole oxidizer
<i>t</i> _{1/2} ^{O₃/H₂O₂}	DBS half-life period determined for a O ₃ /H ₂ O ₂ system

matic processes to a sulfhydryl form (R–SH). In this form, sulfur becomes incorporated into molecules of cysteine and methionine. During a dissimilation process, reducing bacteria—acting in anaerobic conditions, in hypoxic sediments in water bodies and soils reduce sulfates and sulfur oxides into hydrogen sulfide [11]. Numerous organic sulfur compounds originating in oceans and lands, become photochemically oxidized after getting into the atmosphere. The main products of this process are: dimethylsulfoxide, transformed into methylsulfonic acid, and sulfur dioxide, transformed into sulfur trioxide and sulfuric acid and its salts-sulfates. Methylsulfonic acid and sulfates constitute components of sulfate aerosols in atmosphere—becoming centers of condensation of water vapor and formation of clouds [12].

Industrialization caused massive increase in quantity of burnt fuels of vegetable-origin, hard coal and crude oil. That caused increasing emission of sulfur dioxide into the atmosphere [1]. It is estimated that between the years 1850 and 2001 emission of the gas into the atmosphere increased 20-fold [13]. At present, anthropogenic emission of sulfur compounds exceeds natural emission of those compounds 3–4 times [14]. Major contributors to anthropogenic emission of sulfur compounds are: metallurgy, petrochemical industry, cellulose and paper processing and fiber production. Quantity of sulfur compounds originating from combustion of oil-derived fuels has been decreasing since the 70s of the 20th century. This is caused by introduction of an international convention limiting quantity of emitted pollutions by vehicles, and related to enforcement of new technologies of crude oil desulfurization. High emission of sulfur are noted for animal farms and waste water treatment plants. Waste water produced by refineries contain sulfides and thiols in concentrations up to mg/dm³ [15]. Cellulose and paper processing plants emit compounds such as: hydrogen sulfide, methanethiol (MeSH), DMS, and dimethyldisulfide (DMDS) [16].

Some organic sulfur compounds cause the following health effects: systemic, immunological, neurological, reproductive, genotoxic, and carcinogenic. Exposure to malodorous sulfur compounds leads to a considerable increase in the occurrence of ocular, respiratory, and neuropsychological symptoms [17]. Numerous organic sulfur compounds may accumulate in human, animal and vegetable tissues, and in bottoms of water bodies [18].

In the end of the 20th century intensive studies have been commenced on development of effective methods for the removal of toxic pollution occurring in water and waste water both in trace and relatively high concentrations. The resulting group of waste water processing methods was called the Advanced Oxidation Technology—AOT, and processes taking place during implementation of those methods are advanced oxidation processes—AOP. A common feature of all AOTs is that reactive oxygen species—ROS—are formed as a result of interaction of appropriate factors. ROS's produced in course of the advanced oxidation processes are characterized by high reactivity. Majority of them is also characterized by high efficiency of action towards numerous groups of organic compounds [19].

Two review papers [20,21] describe many aspects of waste water processing with AOT, but a problem of organic sulfur compounds removal is treated marginally there. Studies on application of AOT for the removal of organic pollutants both from waste water and from drinking water have been intensified during the last several decades. Some attention is also drawn to organic sulfur pollutants, including toxins [22–26].

The aim of this work was to study a process of dibutyl sulfide (DBS) destruction, as a selected organic sulfur compound, using a O₃/H₂O₂ system applied in the advanced oxidation technologies. Although DBS is relatively infrequent component of natural waters and waste waters, it was selected for model studies due to similarity of its structure to other dialkyl sulfides, including DMS, being a compound rather abundantly present in nature. DBS is a more attractive organic sulfur compound for studying, due to its significantly lower volatility compared to DMS. DBS is also frequently used in scientific experiments as a simulator of sulfur yperite (a chemical warfare agent) due to significant similarity of physical properties and structure between those two compounds [27,28].

2. Experimental

2.1. Equipment

Identification and quantitative analysis of chemical compounds formed as a result of DBS oxidation in buffer solutions was performed using a gas chromatograph HP 6890 from Hewlett Packard with atomic emission detector HP G2350A (GC–AED). Operation of the GC–AED was controlled by Chemstation HP 35920A software. The software was also used for data storage. The source of ozone was ozone generator OEM-15 from Ozone Advanced Systems (Sweden) with ozone production 1.5 g/h. A glass reactor with 600 mL capacity was used for sulfide oxidation.

2.2. Reagents

Dibutyl sulfide S(C₄H₉)₂, analytic grade (Fluka, Buchs, Switzerland) was used for the investigation. All the other reagents, namely: acetone, 30% hydrogen peroxide, methylene chloride, anhydrous magnesium sulfate, hexanol, sodium chloride, potassium iodide, hydrochloric acid, sodium thiosulfate, phosphoric acid, acetic acid, boric acid and sodium hydroxide—were obtained from Chempur company, Piekary Śląskie, Polska. All the substances were of analytic grade. Aqueous hydrogen peroxide solutions, pH 2, 5, 7, 9 and 12, were prepared by mixing aqueous 30% H₂O₂ (Chempur, Piekary Śląskie, Poland) with appropriate Britton–Robinson buffer solutions. Britton–Robinson buffers were prepared in a usual way, i.e. by mixing a solution of 0.04 mol/L phosphoric acid, 0.04 mol/L acetic acid, and 0.04 mol/L boric acid with the appropriate amount of 0.2 mol/L sodium hydroxide solution. Ozone was generated in OEM-15 generator from oxygen of 99.99% purity. Double distilled

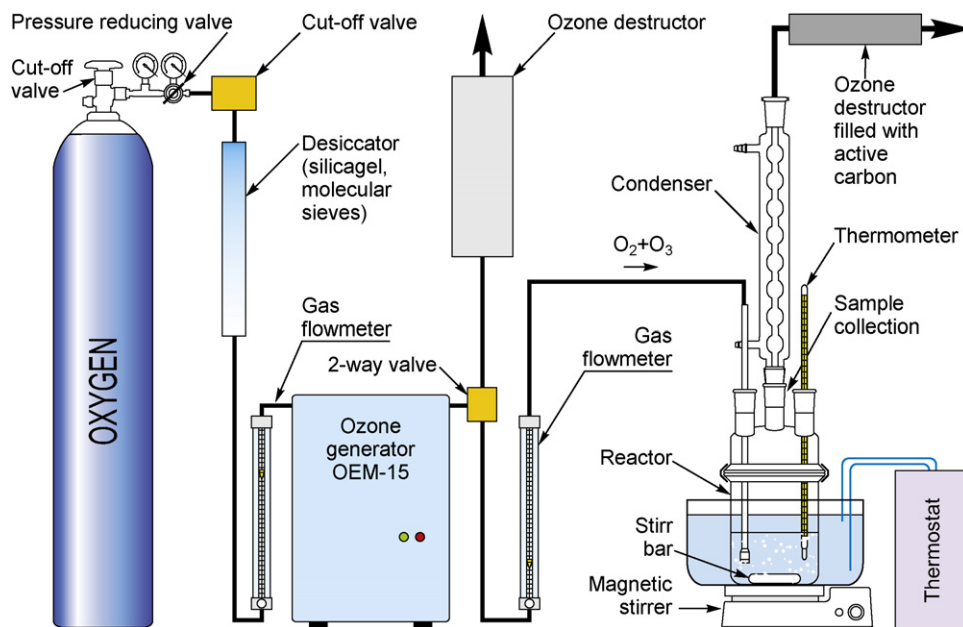


Fig. 1. Diagram of DBS oxidation system.

water was produced in a water still made of silica glass. To prepare derivatives from ozonation products of DBS ethyl iodide and acetonitrile (Chempur, Piekary Śląskie, Poland) were used.

2.3. DBS oxidation

DBS oxidation was realized in a system presented in Fig. 1. Oxygen from a cylinder, after passing through a reducing valve, flowed at the rate of 700 L/h through a desiccator containing molecular sieves and silicagel, and then through a flowmeter to a OEM-15 ozone generator. An outflowing stream of O_3/O_2 was separated in a two-way valve. One stream was directed to an ozone destructor, and the other was directed, via flowmeter, to a glass reactor equipped with a thermostat. A mixture of oxygen and ozone was passed through glass tube with plate made of porous glass sinter at the end. Magnetic stirrer was used for mixing of reagents, and water thermostat maintained stable temperature in the reactor. 195 mL of B–R buffer was poured into the reactor, and O_3/O_2 mixture was passed through it for 15 min, in order to obtain a saturated solution. Analogous procedure was applied for a mixture of B–R buffer with hydrogen peroxide. During the study, a mixture of O_3/O_2 gases in quantity of 50 L/h, with 2 mg/L ozone content in oxygen, was passing through the reactor. Then 50 μ L of DBS dissolved in 5 mL acetone was added and reaction time was measured. Choice of acetone as a solvent for DBS is justified by low susceptibility of the solvent to ozone oxidation [29]. Oxygen with ozone flowing out of the reactor was directed to a reflux condenser, and then into an ozone destructor. The main ozone destructor was consisted of a tower filled with cotton wool, and the other column filled with activated coal. Both wool and active coal were periodically exchanged. To ensure complete safety, the ozone generator and the reactor, where DBS oxidation took place, were placed under a ventilating hood.

DBS oxidation with ozone and hydrogen peroxide in Britton–Robinson buffer and with ozone alone was realized at 10 °C. Oxidation of DBS in concentration of 1.4 mmol/L (50 μ L DBS/5 mL acetone/195 mL buffer) was realized with the following concentrations of hydrogen peroxide: 0, 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} , 1 mol/L, and B–R buffers with the following pH values: 2, 5, 7, 9 and 12, investigating synergic effect of both oxidizing factors.

3. Sampling and preparation of samples for analysis

After 1, 2, 3, 5, 10, 20, 30, 40 and 60 min, from the reactor where DBS was oxidized, 2 mL of solution was collected with a syringe. Collected samples were placed in closed tubes, to which 2 mL of methylene chloride, 10 μ L of chromatographic standard (0.5 mL hexanol in 10 mL acetone) and 100 mg NaCl were added, and the whole content was shaken for 1 min. After aqueous and organic phases become separated, 1.5 mL of the organic phase was pipetted into a tube and 1 mL of 10% KI aqueous solution was added. The mixture was acidified with two drops of HCl, and again shaken for 1 min. The procedure caused reduction of residual hydrogen peroxide in the extract. Then, three drops of concentrated, 1 mol/L aqueous solution of sodium thiosulfate were added to reduce the liberated iodine. After discoloration of the solution, organic phase was pipetted into another tube and dried with anhydrous magnesium sulfate. 1 μ L samples of extract decanted over the $MgSO_4$ sediment were collected with a Hamilton micro-syringe and used for chromatographic analysis.

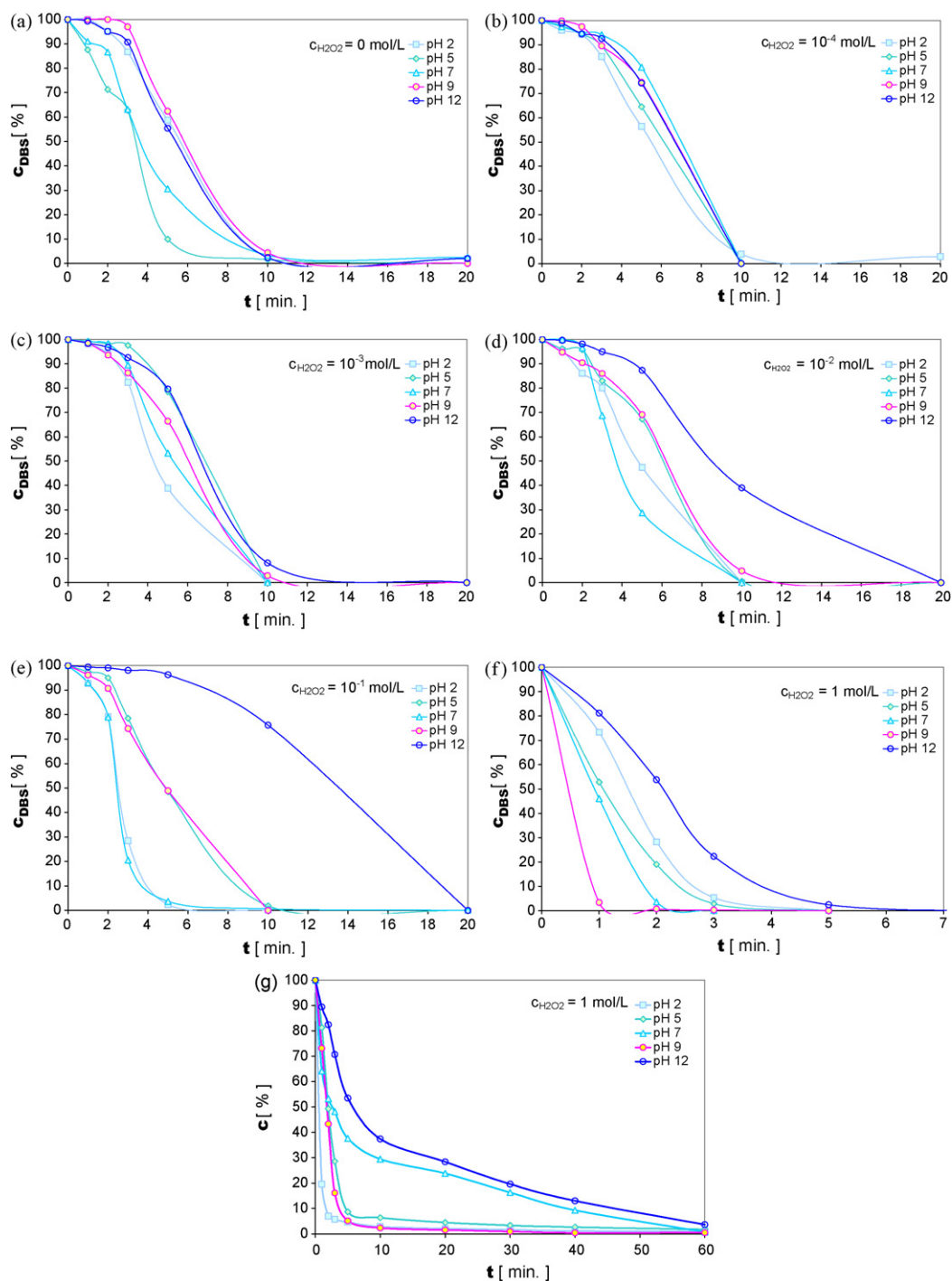
Synthesis of different acids as products of DBS oxidation by ozone in water was confirmed in the following way. After 1 h of ozonation of DBS solution, collected samples were derivatized in ion-exchange column, according to procedure described by Verner [30]. In our research ion-exchange resin Dowex® 1 \times 2 was used as an ion-exchanger. All acids collected in ion-exchange column were derivatized using mixture of acetonitrile and ethyl iodide (instead of acetone/methyl iodide as applied in [30]).

4. Chromatographic analysis

Parameters of operation of a gas chromatograph coupled with an atomic emission spectrometer were the following: plasma cavity and transfer line temperature 270 °C; feeder temperature: 27 °C, stream divider: 10:1; time for solvent removal from a detector from 1 to 3.6 min; carrier gas was helium flowing at the rate of 1 mL/min. The following reaction gases were used: hydrogen, oxygen and methane–nitrogen mixture (10% CH_4 , 90% N_2). A capillary column HP-5 with 5% diphenyl- and 95% dimethylpolysiloxane as a stationary phase was used for the analysis of DBS and products

Table 1Relation between DBS half-life and pH value of the solution, and H_2O_2 concentration.

pH	O ₃ [H ₂ O ₂] = 0	O ₃ /H ₂ O ₂ (mol/L)										H ₂ O ₂ [O ₃] = 0
		0.0001		0.001		0.01		0.1		1		
		t _{1/2} (min)		t _{1/2} (min)		t _{1/2} (min)		t _{1/2} (min)		t _{1/2} (min)		t _{1/2} (min)
2	5.62	5.49↓	−0.13	3.84↓	−1.65	4.78↑	0.94	2.51↓	−2.27	1.51↓	−1	0.62
5	3.40	6.13↑	2.73	7.59↑	1.46	6.06↓	−1.53	4.90↓	−1.16	1.07↓	−3.83	1.96
7	3.60	7.00↑	3.4	5.86↓	−1.14	3.70↓	−2.16	2.44↓	−1.26	0.92↓	−1.52	2.64
9	5.81	6.72↑	0.91	6.16↓	−0.56	6.20↑	0.04	4.92↓	−1.28	0.43↓	−4.49	1.76
12	5.39	6.69↑	1.3	6.98↑	0.29	8.50↑	1.52	13.56↑	5.06	2.12↓	−11.44	6.08

↑↓—denotes increase and decrease of $t_{1/2}$ and $\Delta t_{1/2}$ —difference of DBS half-life periods for two subsequent H_2O_2 concentrations.**Fig. 2.** Kinetics of DBS disappearance during its ozonation (a), and in $\text{O}_3/\text{H}_2\text{O}_2$ system for selected H_2O_2 concentrations (b) 10^{-4} mol/L, (c) 10^{-3} mol/L, (d) 10^{-2} mol/L, (e) 10^{-1} mol/L, (f) 1 mol/L, and for oxidation with common H_2O_2 at selected pH values of a solution (g).

of its oxidation. Length of the column was 30 m, internal diameter 0.32 mm and stationary phase film thickness 0.25 μm . The analysis was carried with programmed temperature: the column was heated from 70 to 270 $^{\circ}\text{C}$ at the rate of 10 $^{\circ}\text{C}/\text{min}$. The column was maintained for 5 min at the end temperature.

Derivatized acids synthesized during ozonation of DBS in water–acetone solution were analyzed using *TRB-Sulfur* column from *Teknokroma*, Spain (stationary phase: 100% dimethylpolysiloksan). Length of the column was 30 m, internal diameter 0.32 mm and stationary phase film thickness 4 μm .

The analysis was carried with programmed temperature: the chromatographic column was maintained for 5 min at the temperature 45 $^{\circ}\text{C}$, and afterwards heated to 250 $^{\circ}\text{C}$ at the rate of 5 $^{\circ}\text{C}/\text{min}$. The column was maintained for 5 min at the end temperature.

5. Results and discussion

Results of measurements of DBS concentration during the oxidation reaction and time, hydrogen ions concentration (pH) and H_2O_2 concentration are presented in Fig. 2, and values of DBS half-life $t_{1/2}$ in Table 1.

DBS loss during oxidation with ozone and without hydrogen peroxide is presented in Fig. 2a. DBS half-lives at pH 2, 9 and 12 are similar (Table 1). At pH 5 and 7 DBS oxidation takes place at rate approximately 40% faster compared to the previous three values.

After introduction of hydrogen peroxide in concentration of 10^{-4} mol/L to the buffer solution, equalization of the reaction rate for all pH values was observed (Fig. 2b). $t_{1/2}$ times for all pH, except for pH 2, were extended compared to oxidation with ozone alone.

H_2O_2 concentration increase up to the value of 10^{-3} mol/L caused occurrence of slight differences in reaction rates (Fig. 2c). Differences were the following: at pH 2, 7 and 9 – reaction rates increased, and at pH 5 and 12 they decreased compared to corresponding rates for H_2O_2 concentration of 10^{-4} mol/L.

Increasing H_2O_2 concentration up to 10^{-2} mol/L caused clear slowing down of the reaction rate at pH 12 by 20%, and at pH 2 by 24% (Fig. 2d). For pH 9 the reaction rate did not change, but at pH 5 and 7 it increased by 20 and 37% compared to analogous concentrations for H_2O_2 concentration of 10^{-3} mol/L.

At the H_2O_2 concentration of 0.1 mol/L (Fig. 2e) clear increase in the reaction rate was observed compared to reaction rates for H_2O_2 concentration of 10^{-2} mol/L: for pH 2 by 47%, for pH 5 by 19%, for pH 7 by 34% and for pH 9 by 21%, and for pH 12 the reaction rate was lower by 60%.

Hydrogen peroxide concentration change from 1 to 0.1 mol/L caused over twofold reduction of DBS half-lives from 10 to 5 min and below (compare Fig. 2e and f). DBS half-lives for H_2O_2 concentration of 1 mol/L decrease with increasing pH: for pH 2 by 40%, for pH 5 by 78%, for pH 7 by 62%, for pH 9 by 91% and for pH 12 by 84%, reaching minimal value for pH 9 (0.43 min). For pH 12, at H_2O_2 concentration of 1 mol/L, $t_{1/2}$ of DBS loss is 2.12 min and is the longest, compared to other times for other pH values. Correlation with data obtained in the study is visible here [31].

In case of using H_2O_2 alone, in concentration of 1 mol/L (Fig. 2g) for DBS oxidation it was observed that at pH < 12 its disappearance rate was much higher compared to oxidation with ozone. Half-life of the compound become reduced: for pH 2–9.06-fold, for pH 5–1.73-fold, for pH 7–1.36-fold, for pH 9–3.30-fold, and for pH 12 the reaction was 0.89-fold slower. Conclusion drawn from that observation is obvious: DBS oxidation with H_2O_2 as an oxidizer and at pH < 12 is much more effective compared to oxidation with ozone alone or in $\text{O}_3/\text{H}_2\text{O}_2$ system.

Observed relationships are related to presence of two mechanisms of DBS oxidation with ozone, depending on H_2O_2

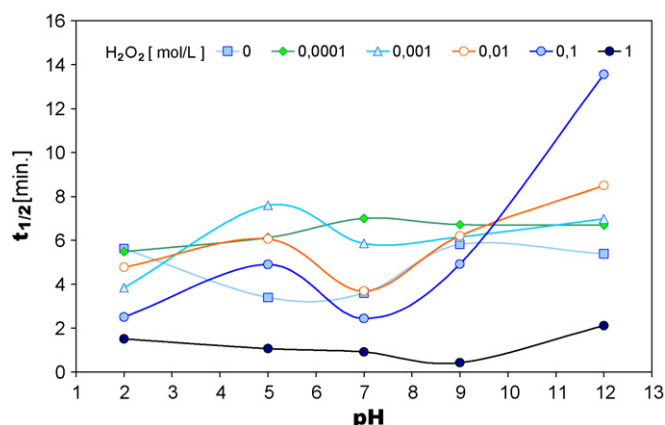


Fig. 3. Changes in DBS half-life in $\text{O}_3/\text{H}_2\text{O}_2$ system, depending on pH of a solution and H_2O_2 concentration. Solutions with selected H_2O_2 concentrations were used, and definite pH values of reaction solutions were obtained using Britton–Robinson buffers.

concentration and pH of the reaction medium. Summary of relationship between DBS half-lives and pH of a solution and H_2O_2 concentration is presented in Fig. 3.

It was observed that at pH 2, DBS oxidation rate in the $\text{O}_3/\text{H}_2\text{O}_2$ system was higher for all H_2O_2 concentrations compared to DBS oxidation with ozone alone. pH value increase from 2 to 5 causes reduction in DBS disappearance rate for H_2O_2 concentrations ranging between 0.0001 and 0.1 mol/L, and in the same pH range oxidation rate with ozone alone (without H_2O_2) rises.

At pH 7 a clear increase in DBS disappearance rate was noted for the $\text{O}_3/\text{H}_2\text{O}_2$ system, compared to the rate at pH 5, for H_2O_2 concentrations: 0.001, 0.01 and 0.1 mol/L; and slight reduction of the rate for H_2O_2 in concentration of 0.0001 mol/L. DBS disappearance rates in the $\text{O}_3/\text{H}_2\text{O}_2$ system for H_2O_2 concentration of 0.1 mol/L at pH 2, 7 and 9 are higher compared to DBS disappearance rate during oxidation with ozone alone (without addition of H_2O_2) for the same pH values. Only if pH value is close to 5 or 12, the relationship is opposite, and oxidation is much faster for ozone alone, without H_2O_2 addition compared to oxidation in the $\text{O}_3/\text{H}_2\text{O}_2$ system. Effect of H_2O_2 concentration on DBS disappearance rate was the following: when H_2O_2 concentration was 1 mol/L, the reaction rate was the highest, compared to rates noted for other applied H_2O_2 concentrations, and reached the maximal value at pH 9. It should be noted that similar courses of curves for H_2O_2 concentrations falling within the range of 0.001–0.1 mol/L suggest existence of similar mechanisms of DBS oxidation reaction. Addition of a small quantity of H_2O_2 (0.0001 mol/L) reduced DBS disappearance rate, compared to the disappearance rate measured for DBS oxidation with ozone alone, for all applied pH values. Those observations are consistent with results of previously published studies on effect of $\text{H}_2\text{O}_2/\text{O}_3$ molar ratio on efficiency of oxidation processes [32–34].

Attempting to determine DBS oxidation rate in the $\text{O}_3/\text{H}_2\text{O}_2$ system in relation to oxidation rate with ozone alone, determined DBS half-lives for the system in which ozone was the sole oxidizer were divided by corresponding values of half-life determined for the $\text{O}_3/\text{H}_2\text{O}_2$ system, and results are presented in Fig. 4.

As the value $[t_{1/2}^{\text{O}_3}]^{-1}$ is proportional to DBS oxidation rate in the oxidizing system, in which ozone is a sole oxidizer, and value $[t_{1/2}^{\text{O}_3/\text{H}_2\text{O}_2}]^{-1}$ is proportional to DBS oxidation rate in the $\text{O}_3/\text{H}_2\text{O}_2$ system, result of division of those values in the order mentioned above provides an approximate ratio of DBS oxidation rate in the system, in which ozone alone is used as an oxidizer and its oxidation rate in the $\text{O}_3/\text{H}_2\text{O}_2$ system. That is presented in the following

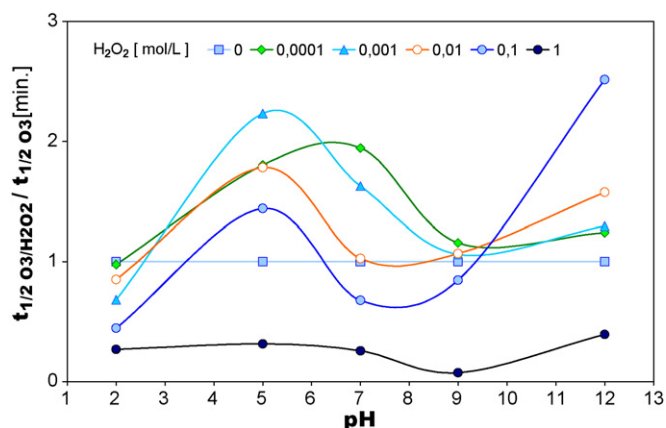


Fig. 4. DBS half-life changes in the O_3/H_2O_2 system in relation to changes in the system containing ozone, without addition of H_2O_2 . Numbers given in the legend describe initial concentration of H_2O_2 . pH value of all solution was buffered using Britton–Robinson buffers.

relationship:

$$\frac{r_{O_3}}{r_{O_3/H_2O_2}} \approx \frac{[t_{1/2}^{O_3}]^{-1}}{[t_{1/2}^{O_3/H_2O_2}]^{-1}} = \frac{t_{1/2}^{O_3/H_2O_2}}{t_{1/2}^{O_3}}$$

So $t_{1/2}^{O_3/H_2O_2}/[t_{1/2}^{O_3}]$ ratio is approximately equal to the ratio of DBS oxidation in the system, in which ozone alone is used, to DBS oxidation rate in the O_3/H_2O_2 system.

Particular attention should be paid to a horizontal line obtained for the concentration $[H_2O_2]=0$. The line was obtained dividing $t_{1/2}^{O_3}$ values by the same values obtained respectively for subsequent pH, obtaining the result value of one every time. The line is of importance for understanding of processes taking place during DBS oxidation in the O_3/H_2O_2 system, compared to processes taking place in the system containing ozone alone as a oxidizing factor ($[H_2O_2]=0$). Graph points lying over the line corresponding to $[H_2O_2]=0$ are characterized by the fact that oxidation rate with O_3 alone is higher than oxidation rate in the O_3/H_2O_2 system; and points located below the line correspond to the situation, in which oxidation rate in the O_3/H_2O_2 system is higher than in the situation in which ozone is a sole oxidizer of DBS. Using this figure it may be stated that if hydrogen peroxide concentration is in the range $0.1 < [H_2O_2] < 1$ mol/L, for almost all pH values of the solution, DBS oxidation is faster in the O_3/H_2O_2 system, compared to O_3 alone. Only for pH 5 (approximately), and when $pH > 9$, for lower H_2O_2 concentrations (range $0.1 < [H_2O_2] < 1$ mol/L), DBS oxidation rate in the system using ozone alone becomes higher than in the O_3/H_2O_2 system. For pH 2, regardless the hydrogen peroxide concentration, oxidation rate in the O_3/H_2O_2 system is higher compared to the situation, in which ozone is the sole DBS oxidizer.

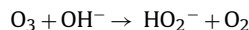
For H_2O_2 concentrations ranging from 0.0001 to 0.1 mol/L, similar shape of curves is observed for pH values ranging between 2 and 9. Over the value of pH 9 no uniform course of curves of relationship of the $t_{1/2}^{O_3/H_2O_2}/[t_{1/2}^{O_3}]$ ratio and DBS half-life and pH value of the solution is observed. This behavior may be explained by presence of various mechanisms of DBS oxidation, depending on H_2O_2 concentration, when pH of the solution is over 9.

Considering the rate of DBS reaction with ozone in relation to pH value, it is important to take solubility and stability of O_3 as $f(pH)$ into account. Ozone stability in acidic solutions is high enough that its concentration does not change even after increasing tempera-

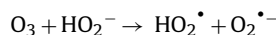
ture from 10 to 30 °C [35]. Ozone stability in solutions with higher pH decreases proportionally to the pH value at stable temperature [36].

In the study [37] a sequence of free radical reactions determining ozone decomposition in aqueous solutions was established. It is presented in Table 2.

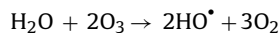
In case of introduction of hydrogen peroxide into the solution, with increasing concentration and above some limiting concentration, a reaction with OH^\bullet radical dominates, which is much faster and less selective compared to other oxidizing factors. Rising H_2O_2 concentration speeds up the rate of ozone decomposition initiated by hydroxide ions. The reaction is slow and leads to formation of hydroperoxide ions [38]



Hydroperoxide ions are also formed in an equally slow reaction of H_2O_2 dissociation. Fast reaction of hydroperoxide anion with ozone yields hydroperoxide radicals and ozonide anion radicals [38]



Rate of the a/m reactions increases with increasing pH of the solution. Overall, in a reaction of one molecule of H_2O_2 and two molecules of ozone, two HO^\bullet radicals are formed according to the following reaction [39,40]:



That explains significant synergic effect of increasing DBS decomposition reaction rate at pH 9 and at high H_2O_2 concentration (1 mol/L) (Fig. 2f).

DBS oxidation with ozone in aqueous solution proceeds according to the ionic mechanism at low pH 2. In alkaline medium, however, participation of the radical mechanism in oxidation processes increases with increasing pH. After exceeding value pH 9 there is a significant drop in reaction rate related to decreased ozone stability (ozone decomposition at high pH does not lead to formation of the HO^\bullet radical).

Ozonation of organic sulfides was also investigated by other authors [41–43]. In all cases the only isolated products were sulfoxides and/or sulfones, albeit Barnard noticed [43] that dibutyl sulfone obtained as row product of dibutyl sulfide oxidation smelled like aldehyde and butyric acid. Firstly, it is known from experimental data presented by Bailey [42], that sulfur atom in sulfide molecule as well as carbon atom in side chain of molecule undergo oxidation, in contrary to results obtained by other researchers. Secondly, oxidation of side chain is the main reaction only in aprotic solvents (e.g. carbohydrates). Thirdly, more protic solvent gives lower contribution of ozone reaction with side chain. Fourthly, the lower temperature of reaction—the lower contribution of ozone attack on side chain of DBS. Schematic diagram of DBS oxidation reactions by ozone in water is presented in Fig. 5. It is worth to notice that when sulfide oxidation follows mechanism of path 1, sulfur atom in sulfide is oxidized without oxidation of side chain. Oxidation of sulfide side chain using ozone starts from

Table 2
Ozone decomposition reactions.

Reaction	Rate constant k ($M^{-1} s^{-1}$)	Stage
$O_3 + H_2O \rightarrow 2HO^\bullet + O_2$	10^{-4}	Initiation
$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^\bullet$	70	Propagation
$O_3 + OH^\bullet \rightarrow O_2 + HO_2^\bullet$	2×10^9	
$O_3 + HO_2^\bullet \rightarrow 2O_2 + HO^\bullet$	1.6×10^9	
$2HO_2^\bullet \rightarrow O_2 + H_2O_2$	8.3×10^5	Conclusion

detachment of proton from carbon atom in α position and can proceed along three different paths (2, 3 and 4). Path 2 is analogous to sulfide oxidation mechanism by singlet oxygen [44]. Analyzing oxidation products of DBS buthyl hydrosulphide was not detected. It does not mean that path 2 is preferred, but that buthyl hydrosulphide synthesized according to mechanisms of paths 3 and 4 undergoes subsequent oxidation by ozone to butanesulphinic acid. At present we cannot estimate the probability of each reaction path and which one is the most likely. Assuming that oxidation of sulfide side chains (paths 2, 3 and 4) leads to creation of acids, we verified which acids are synthesized during ozonation of DBS in water. For this purpose sample of DBS in water–acetone solution was ozonized for 1 h. In the next step all acids were separated in ion-exchange column, and later derivatized according to the procedure described by Verner [30]. Results of chromatographic analysis of derivatized acids were presented in Fig. 6. They confirm that dibutyl sulfide in water environment is oxidized by ozone mainly to dibutyl sulfoxide and subsequently to dibutyl sulfone (reaction path 1). Moreover, only small amounts of butanesulphinic and much lower amounts of butanesulphonic acids were detected. Besides butyric acid is observed in amount of similar to amounts of sulphinic and sulphonic acids together, and propionic and acetic acids in very low amounts. The amount of obtained formic acid is comparable to amount of oxidation products of side chain of DBS. Only small amount of formic acid could come from oxidation of acetone (~1%), present in solution, and used for dissolving of DBS in water.

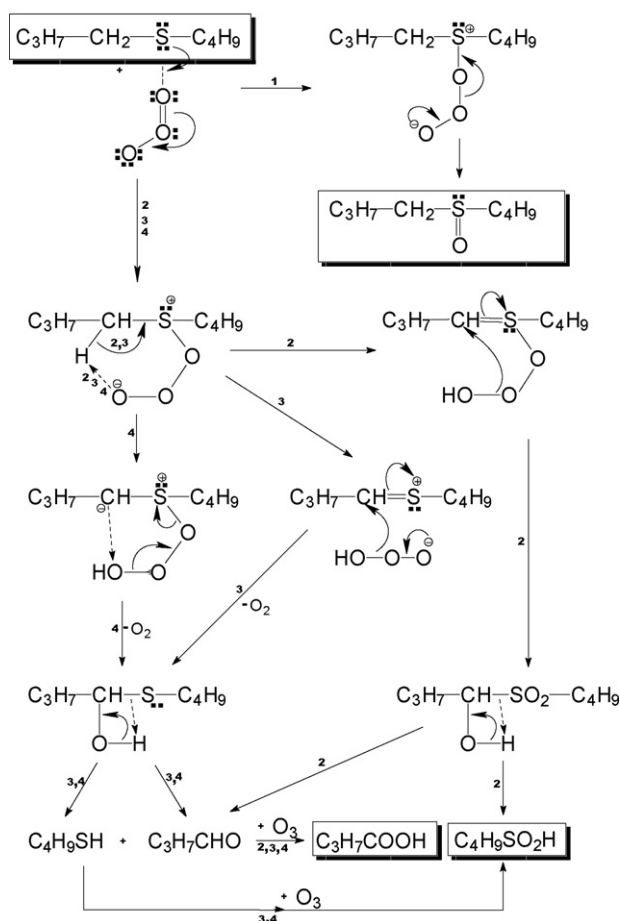


Fig. 5. Diagram of DBS oxidation reactions by ozone in water.

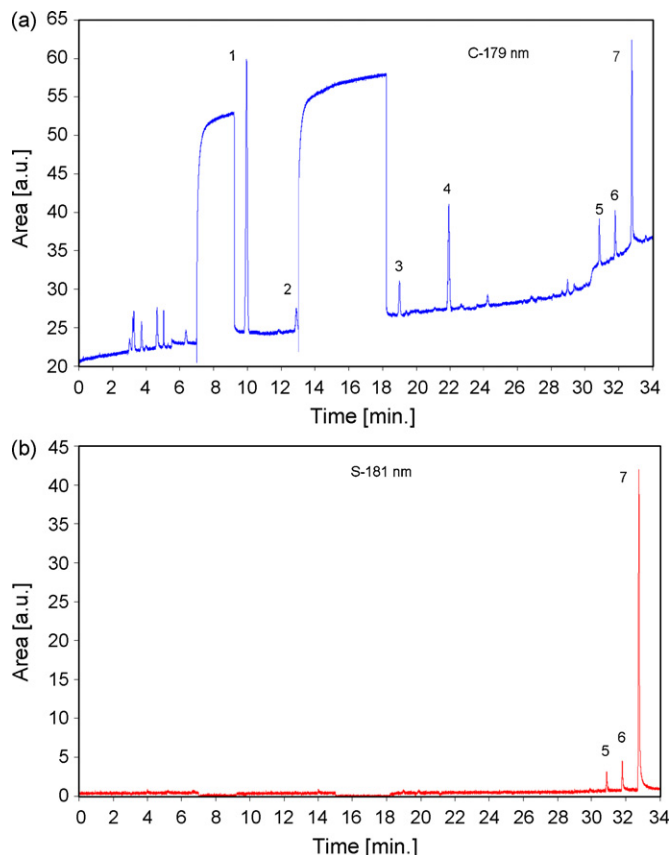


Fig. 6. Chromatograms of derivatized acids obtained as DBS oxidation products in water–acetone solution (a) detection at carbon emission line C-179 nm and (b) detection at sulfur emission line S-181 nm. Description of products: (1) ethyl ester of formic acid, (2) ethyl ester of acetic acid, (3) ethyl ester of propionic acid, (4) ethyl ester of butyric acid, (5) unidentified compound, (6) ethyl ester of butanesulphonic acid and (7) ethyl ester of butanesulphinic acid.

6. Conclusions

Studies of dibutyl sulfide decomposition with ozone in environment of hydrogen peroxide and depending on pH indicate that:

- With increasing H_2O_2 concentration for DBS oxidation at various pH, two predominating reaction mechanisms may be differentiated: ionic and radical.
- The ionic mechanism dominates in acidic environment, at $\text{pH} < 3$; contribution of the radical mechanism increases with increasing pH value, reaching its maximum at pH 9.
- At $\text{pH} > 9$ stability of ozone becomes decreased at fast rate, and hydrogen peroxide has a deciding effect on DBS oxidation.
- Small (0–0.1 mol/L) addition of H_2O_2 to aqueous solution of DBS (in presence of 2.5% acetone) slows down decomposition of the compound with ozone. Increasing H_2O_2 concentration from 0.1 to 1 mol/L causes significant increase in DBS oxidation rate (regardless the pH).
- Significant synergic effect of DBS decomposition rate rise at pH 9, for high concentration of 1 mol/L H_2O_2 is a result of a reaction of hydrogen peroxide with ozone, forming additional molecules of hydroperoxide radicals.
- Dibutyl sulfide in water environment is oxidized by ozone mainly to dibutyl sulfoxide and subsequently to dibutyl sulfone. Detected amounts of butanesulphinic and butyric acids are one order of magnitude lower than main products. Oxidation of aliphatic side

chain of DBS in protic solvent proceeds in much lower extent. Other acids occur in vestigial amounts.

Acknowledgements

- This work was supported by the Ministry of Sciences and High Education, Grant No. 3 T09D 024 29 for the period of 2005–2008.
- The authors wish to thank JAS GmbH (Moers, Germany, Website www.jas.de) for its kind, reliable and competent assistance during usage and maintenance of a gas chromatography with atomic emission detector)

References

- [1] J.A. Zahn, A.A. DiSpirito, Y.S. Do, B.E. Brooks, E.E. Cooper, J.L. Hatfield, Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent, *J. Environ. Qual.* 30 (2001) 624–634.
- [2] I. Devai, R.D. DeLaune, Emission of reduced malodorous sulfur gases from wastewater treatment plants, *Water Environ. Res.* 71 (1999) 203–207.
- [3] E. Smet, P. Lens, H. Van Langenhove, Treatment of waste gases contaminated with odorous sulfur compounds, *Crit. Rev. Environ. Sci. Technol.* 28 (1998) 89.
- [4] J.J.K. Jaakkola, V. Vilkkä, O. Marttila, P. Jappinen, T. Haahtela, The South Karelia air pollution study: the effects of malodorous sulfur compounds from pulp mills on respiratory and other symptoms, *Am. Rev. Respir. Dis.* 142 (1990) 1344–1350.
- [5] J.J.K. Jaakkola, K. Partti-Pellinen, O. Marttila, P. Miettinen, V. Vilkkä, T. Haahtela, The South Karelia air pollution study: changes in respiratory health in relation to emission reduction of malodorous sulfur compounds from pulp mills, *Arch. Environ. Health* 54 (1999) 254–263.
- [6] O. Marttila, J.J.K. Jaakkola, K. Partti-Pellinen, V. Vilkkä, T. Haahtela, South, Karelia air pollution study: daily symptom intensity in relation to exposure levels of malodorous sulfur compounds from pulp mills, *Environ. Res.* 71 (1996) 122–127.
- [7] I. Devai, R.D. Delaune, Effectiveness of selected chemicals for controlling emission of malodorous sulfur gases in sewage sludge, *Environ. Technol.* 23 (2002) 319–329.
- [8] M.O. Andreae, T.W. Andreae, D. Meyerdierks, C. Thiel, Marine sulfur cycling and the atmospheric aerosol over the springtime North Atlantic, *Chemosphere* 52 (2003) 1321–1343.
- [9] U. Siniarovina, M. Engardt, High-resolution model simulations of anthropogenic sulfate and sulfur dioxide in Southeast Asia, *Atmos. Environ.* 39 (2005) 2021–2034.
- [10] J. Dippell, W. Jaeschke, A comparison between natural and anthropogenic emissions of the reduced sulfur compounds H_2S , COS, and CS₂ in a tropical industrialized region, *J. Atmos. Chem.* 25 (1996) 251–270.
- [11] I. Devai, R.D. Delaune, Emissions of reduced gaseous sulfur compounds from wastewater sludge: redox effects, *Environ. Eng. Sci.* 17 (2000) 1–8.
- [12] H. Berresheim, F.L. Eisele, D.J. Tanner, L.M. McInnes, D.C. Ramsey-Bell, D.S. Covert, Atmospheric sulfur chemistry and cloud condensation nuclei (CCN) concentrations over the northeastern Pacific coast, *J. Geophys. Res.* 98 (1993) 12701–12711.
- [13] P. Brimbelcombe, C. Hammer, H. Rhode, A. Ryaboshapko, C.F. Boutron, Evolution of the Global Biogeochemical Sulfur Cycle, SCOPE, vol. 39, John Wiley and Sons, Chichester, UK, 1989, pp. 77–81.
- [14] F.J. Zhao, J.S. Knights, Z.Y. Hu, S.P. McGrath, Stable sulfur isotope ratio indicates long-term changes in sulfur deposition in the Broadbalk experiment since 1845, *J. Environ. Qual.* 32 (2003) 33–39.
- [15] A.P. Bianchi, M.S. Varney, J. Phillips, Analysis of volatile organic compounds in estuarine sediments using dynamic headspace and gas chromatography–mass spectrometry, *J. Chromatogr.* 542 (1991) 413–450.
- [16] J.C.M. Bordado, J.F.P. Gomes, Characterisation of non-condensable sulfur containing gases from Kraft pulp mills, *Chemosphere* 44 (2001) 1011–1016.
- [17] T. Haahtela, O. Marttila, V. Vikka, P. Jappinen, J.J.K. Jaakkola, The South Karelia air pollution study: acute health effects of malodorous sulfur air pollutants released by a pulp mill, *Am. J. Public Health* 82 (1992) 603–605.
- [18] T.E. Higgins, M.M. Halmann, Photodegradation of Water Pollutants, CRC Press, London, 1995, ISBN: 0849324599.
- [19] S. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment, Iwa Publishing, London, 2004.
- [20] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501.
- [21] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. II. Hybrid methods, *Adv. Environ. Res.* 8 (2004) 553.
- [22] Y. Lee, C. Lee, J. Yoon, Kinetics and mechanisms of DMSO (dimethylsulfoxide) degradation by UV/H_2O_2 process, *Water Res.* 38 (2004) 2579.
- [23] A.V. Vorontsov, L. Davydov, E.P. Reddy, C. Lion, E.N. Savinov, P.G. Smirniotis, Routes of photocatalytic destruction of chemical warfare agent simulants, *New J. Chem.* 26 (2002) 732–744.
- [24] A.V. Vorontsov, C. Lion, E.N. Savinov, P.G. Smirniotis, Pathways of photocatalytic gas phase destruction of HD simulant 2-chloroethyl ethyl sulfide, *J. Catal.* 220 (2003) 414–423.
- [25] M.H. Habibi, H. Vosooghian, Photocatalytic degradation of some organic sulfides as environmental pollutants using titanium dioxide suspension, *J. Photochem. Photobiol. A* 174 (2005) 45–52.
- [26] G.-M. Zuo, Z.-X. Cheng, G.-W. Li, L.-Y. Wang, T. Miao, Photoassisted reaction of sulfur mustard under UV light irradiation, *Environ. Sci. Technol.* 39 (2005) 8742–8746.
- [27] C.R. Clark, J.R. Smith, M.L. Shih, Development of an in vitro screening method for evaluating decontamination of sulfur mustard by reactive dermal formulations, *J. Appl. Toxicol.* 19 (1999) S77–S81.
- [28] C.A. Sanders, M. Rodriguez Jr., E. Greenbaum, Stand-off tissue-based biosensors for the detection of chemical warfare agents using photosynthetic fluorescence induction, *Biosens. Bioelectron.* 16 (2001) 439–446.
- [29] J. De Laat, H. Gallard, S. Ancelin, B. Legube, Comparative Study of The Oxidation of Atrazine and Acetone by H_2O_2/UV , $Fe(III)/UV$, $Fe(III)/H_2O_2/UV$ and $Fe(II)$ or $Fe(III)/H_2O_2$, *Chemosphere* 39 (15) (1999) 2693–2706.
- [30] P. Verner, F. Pehal, Ion-exchange extractive alkylation of organic acids, *J. Chromatogr.: Biomed. Appl.* 382 (1986) 232–236.
- [31] R. Battino (Ed.), Solubility Data Series, vol. 7, Oxygen and Ozone, Pergamon Press, Oxford, 1981.
- [32] A. Laplanche, M.T. Orta De Velasquez, V. Boisson, N. Martin, G. Martin, Modulation of micropollutant removal in drinking water treatment by ozonation or advanced oxidation processes (O_3/H_2O_2), *Ozone Sci. Eng.* 17 (1995) 97–117.
- [33] T.A. Tuhkanen, The effect of preozonation, ozone/hydrogen peroxide treatment, and nanofiltration on the removal of organic matter from drinking water, *Ozone Sci. Eng.* 16 (5) (1994) 367–383.
- [34] N. Karpel Vel Leitiner, A.-L. Papaihou, J.-P. Croué, J. Peyrot, M. Dore, Oxidation of methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) by ozone and combined ozone/hydrogen peroxide, *Ozone Sci. Eng.* 16 (1994) 41–54.
- [35] R. Battino (Ed.), Solubility Data Series, vol. 7, Oxygen and Ozone, Pergamon Press, Oxford, 1981, p. 490.
- [36] M. Horvath, L. Bilitzky, J. Huttner, Ozone, Akademia Kiado, Budapest, 1985.
- [37] Y. Qiu, Kinetic and mass transfer studies of the reactions between dichlorophenols and ozone in liquid–liquid and gas–liquid systems, Ph.D. Thesis, Mississippi State University 1999.
- [38] J. Stachelin, J. Hoigne, Decomposition of ozone in water: rate of oxidation by hydroxide ions had hydrogen peroxide, *Environ. Sci. Technol.* 16 (1982) 676–681.
- [39] M.B. Venta, C.H. Castro, L.A.F. García, A.L. Marzo, E.V. Lorenzo, C.Á. Álvarez, Effect of O_3/H_2O_2 molar concentration ratio at different pH values on cyclophosphamide degradation, *J. Water Supply: Res. Technol.—AQUA* 54 (2005) 403–410.
- [40] A. Safarzadeh-Amiri, O_3/H_2O_2 treatment of methyl-tert-butyl ether (MTBE) in contaminated waters, *Water Res.* 35 (2001) 3706–3714.
- [41] Q.E. Thompson, Ozone oxidation of nucleophilic substances, *J. Am. Chem. Soc.* 83 (1961) 845–851.
- [42] P.S. Bailey, A.-I.Y. Khashab, Ozonation of nucleophiles. 7. Dibenzyl sulfides, *J. Org. Chem.* 43 (1978) 675–678.
- [43] D. Barnard, Oxidation of organic sulphides. Part IX. The reaction of ozone with organic sulphur compounds, *J. Chem. Soc.* (1957) 4547–4555.
- [44] E.L. Clennan, A. Pace, Advances in singlet oxygen chemistry, *Tetrahedron* 61 (2005) 6665–6691.