

Effect of temperature and initial dibutyl sulfide concentration in chloroform on its oxidation rate by ozone

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Received 12 November 2007; received in revised form 21 December 2007; accepted 28 December 2007

Available online 12 January 2008

Abstract

A scheme of dibutyl sulfide (DBS) oxidation with ozone and generation of transitional products was determined in this study. The main identified intermediate product was dibutyl sulfoxide (DBSO), and the main end product of DBS oxidation was dibutyl sulfone (DBSO₂). It was determined that for three temperatures: 0, 10 and 20 °C there was certain initial DBS concentration for which half-times observed in experimental conditions were equal and independent from temperature. Generation of phosgene and water as by-products was confirmed for the reaction of DBS with ozone in chloroform. Results of the described study allowed to present generalized mechanism of sulfide oxidation with ozone.

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Keywords: Dibutyl sulfide; Oxidation; Chloroform; Ozone; Organic sulfur compounds; GC-AED; Reaction kinetics

1. Introduction

Composition of liquid industrial waste depends on a kind of production and contain, among others, sulfur compounds. The following branches of industry constitute the main source of organic sulfur compounds: petrochemical, paper and textile industry. The compounds are also present in liquid waste generated by food industry and in municipal wastes. Concentrations of organic sulfur compounds in liquid industrial waste can be significantly high. Water pollution with those compounds is especially noxious, for bacteria present in natural environment cause their degradation to, among others, hydrogen sulfide, which is a dangerous poison with unpleasant odor. Organic sulfur compounds contained in waste water can be rendered harmless using an oxidation method.

Using ozone for removal of organic pollutants from water is a common practice. Numerous studies of processes occurring under influence of ozone in aquatic environment have been

performed [1,2]. The main advantage of this method is that it does not involve necessity to remove the introduced oxidizer and products of its decomposition. Using ozone is pure and environment friendly approach to decontamination of sulfides and almost all other degradable organic pollutants. Ozone is the strongest available oxidizer (among oxygen compounds) with redox potential 2.07 V. There are only two other known unstable chemical mediums demonstrating higher potential, i.e. singlet oxygen (2.43 V) and hydroxyl radical (2.81 V). The main disadvantage of the ozone is that its production is still expensive and destruction of organic substances with ozone in water is not a cheap process. There are at least three other serious factors limiting (slowing down) oxidation with ozone in water.

- Currently existing technologies used for ozone production do not allow generation of high concentration of the compound (even if pure oxygen is used as a raw material for ozone generation). This is only partially disadvantage. Ozone at high concentration becomes very unstable and dangerous explosive and using it is not safe.
- Ozone is a very strong oxidizer, but its solubility in water is very low [3].

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- In aqueous phase there are various components, including some anions and cations, which react with ozone and cause additional consumption of the compound.

Laboratory trials of indirect oxidation using a double-phase systems: water–organic solvent have been undertaken in order to increase the rate of water pollution oxidation. Numerous organic pollutants are hydrophobic. Therefore it is easy to separate them from water using extraction with appropriate organic solvents. The separated chemicals concentrated in the solvents might be decomposed by ozonation more efficiently than in water. In order to increase the rate of removal of organic pollution from water a procedure of organic pollution extraction from water to an organic phase with appropriate solvent is more and more frequently used. In the next stage, the obtained solution is saturated with ozone in order to oxidize the components extracted from water. In some works fluorocarbon solvents FC40TM and FC77TM (3M Corp.) were successfully used [4,5]. The solvents are suitable for water purification because they show low toxicity, relatively low solubility in water, very low vapour pressure, and additionally—ozone dissolves in them very well and the resulting solutions are stable and dissolved ozone is not readily decomposed. Also various liquids with a structure of polydimethylsiloxanes were used in studies of processes taking place during destruction of organic compounds with ozone [6–8].

In this study we have decided to investigate processes taking place during oxidation of dibutyl sulfide (DBS) as a selected, model sulphide pollution in environment of chloroform. Other solvents were also taken into account, but preliminary studies indicated that among numerous selected organic solvents like: chloral, propionic acid, diethyl malonate, trichloroethylene, nitromethane, carbon tetrachloride, methanol, etc. [9], the rate of DBS oxidation with ozone in chloroform was the highest. Literature data [10,11] indicate that ozone solubility both in fluorocarbons and in polydimethylsiloxane solvent is approximately 10-times higher than in water, but ozone dissolves better in chloroform, which is confirmed by the value of Ostwald coefficient: polydimethylsiloxane—2.0, fluorocarbon FC77TM—2.0, chloroform—2.12 [11].

The great significance of the oxidation of sulfides not only for the environment protection, but also for the straightforward synthesis of sulfoxides and sulfones directly from sulfides, both of which are important as commodity chemicals and, in some cases, as pharmaceuticals [12].

2. Experimental

2.1. Apparatus

Both quantitative analysis and identification of chemical compounds generated as a result of ozonation of chloroform-based solutions were performed using the HP 6890 gas chromatograph from Hewlett Packard. Software Chemstation HP 35920A was used for control of the chromatograph and for collection of measurement data. Ozone generator OEM-15 from Ozone Advanced Systems (Sweden) with ozone produc-

tion 1.5 g/h, and a glass reactor with 600 ml capacity were used for sulfide oxidation.

2.2. Reagents

Dibutyl sulfide (DBS) (Fluka, Buchs, Switzerland) dissolved in chloroform (Chempur, Piekary Śląskie, Poland) was used for the study. DBS and chloroform, were reagent grade and were used without further purification.

2.3. Oxidation of DBS

DBS oxidation was realized in a reactor controlled by a thermostat (Fig. 1). In the bottom part of the reactor there was a porous glass plate, through which a mixture of oxygen and ozone was passed. Magnetic stirrer was used for reagent mixing. 200 ml of chloroform was poured into the reactor, and a gas mixture O₂ + O₃ was initially passed through the liquid for 10 min in order to obtain a saturated solution. Then, still passing the O₂ + O₃ mixture through the reactor, a measured portion of DBS was added and measurement of reaction time started.

Oxidation of DBS with ozone in chloroform was carried out in temperatures 0, 10 and 20 °C, using various initial quantities of DBS (50, 100, 200 and 400 μL) in 200 mL of chloroform, obtaining DBS concentrations in chloroform equal: 1.4, 2.9, 5.7, and 11.5 mmol/L, respectively. Mixture of ozone and oxygen from a generator was passed through the DBS solution in chloroform. In case of all experiments, oxygen constantly flowed through the ozone generator with rate of 400 L/h. A stream of O₂ + O₃ mixture from the generator was divided into two parts: one part of the gas was directed into the reactor, and the other was directed to washers with potassium iodine, which were used for O₃ concentration control and then to ozone destructor, or directly to ozone destructor. During the experiments O₂ + O₃ mixture, containing 1.2 mg/L ozone in oxygen, flowed through the reactor at the rate of 200 L/h.

2.4. Sampling and preparing samples for analysis

Samples for analysis were collected from the reactor with a syringe after the following periods: 0.25, 0.5, 1, 1.5, 2, 3.5, 5, 10, 15, 20, 25, 30, 35, 40, 50 and 60 min. Collected samples of 100 μL each were placed in closed tubes. From there only 1 μL samples were collected with a Hamilton micro-syringe and dosed into the gas chromatograph. Oxidation in the same conditions was repeated three times, obtaining 3 results for each of the individual times. Those results were averaged.

2.5. Chromatographic analysis

Work parameters of the gas chromatograph coupled with atomic emission spectrometer were the following: temperature of a plasma cavity and transmission line 270 °C; injector temperature: 270 °C, split ratio: 10:1; time of solvent removal from the detector between 1 and 3.6 min; helium flowing at rate of 1 mL/min was a carrier gas. The following reaction gases were used: hydrogen, oxygen and methane–nitrogen mix-

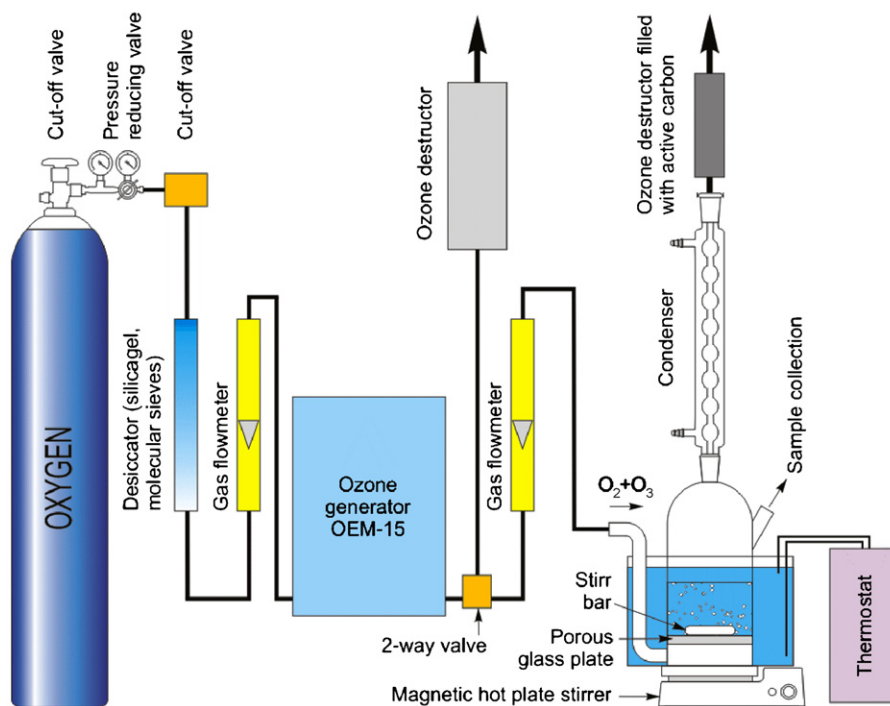


Fig. 1. Schematic of apparatus used for DBS oxidation.

ture (10% CH₄, 90% N₂). A capillary column HP-5 with 5% diphenylpolysiloxane and 95% dimethylpolysiloxane as a stationary phase was used for analysis of DBS and products of its oxidation. The column length was 30 m, internal diameter of 0.32 mm and stationary phase film thickness of 0.25 μm. The analysis was realized with programmed temperature: the column was heated from 70 to 270 °C at rate of 10 °C/min. The column was maintained for 5 min at the end temperature. Retention times and elemental compositions of the analyzed DBS oxidation products were compared to standards, allowing identification of the products. Quantitative analysis of the substrate and its oxidation products was performed using an absolute calibration method.

3. Results and discussion

Sample set of chromatograms illustrating changes in DBS and its oxidation products quantity during oxidation are presented in Fig. 2. In different temperatures of oxidation, besides DBS (6.6 min), the following oxidation products were present in the reaction mixture: dibutyl sulfoxide (10.58 min) dibutyl sulfone (11.2 min) and unidentified chemical compounds present in small quantities, with retention times of: 6.43, 6.88, 11.04, and 11.7 min.

Using another temperature program (the column was heated from 40 °C (5 min) to 270 °C (2 min) at rate of 20 °C/min) small amounts of phosgene were detected.

3.1. Determination of reaction rate

Percentage of DBS in reaction mixture comparing to the initial quantity of the compound for various oxidation times was

calculated based on the quantitative chromatographic analysis. As a result, curves of DBS quantity versus reaction time with ozone were determined. The obtained results are presented in Fig. 3. For the lowest DBS concentration of 1.4 mmol/L, concentration of the compound drops nearly to zero after 2 min of ozonation at 10 and 20 °C (Fig. 3a). At 0 °C DBS remains in chloroform for up to 5 min. At the double concentration of DBS—2.9 mmol/L, the course of the compound disappearing curves is almost identical to this for 0 and 10 °C, and DBS disappears from the reactor within 5 min. Reaction rate at 20 °C is higher, and DBS disappearance time decreases to 2 min (Fig. 3b).

For DBS concentration of 5.7 mmol/L (Fig. 3c) the course of temperature-related DBS concentration change is similar, and time of the compound disappearance is approximately 10 min. This shows similar effect of reaction temperature and ozone solubility in chloroform as a function of temperature on DBS disappearance rate. Further differentiation of effect of the above mentioned factors on DBS disappearance rate was illustrated in Fig. 3d. Analysis of data presented in Fig. 3 shows, that DBS disappearance rate for low concentrations (<2.9 mmol/L) clearly depends on temperature; and for higher concentrations a crucial role is played by ozone solubility.

Due to complexity and multi-stage character of mechanisms involved in DBS disappearance, making determination of the reaction rate constant impossible, DBS oxidation rate was determined using the half-life ($t_{1/2(\text{DBS})}$). In order to determine the $t_{1/2(\text{DBS})}$ value, experimental curves in Fig. 3 were linearly approximated, and equation factors and square correlation factor are presented in Table 1. DBS concentration changes (c_{DBS}) in time (t) are described by a linear equation: $c_{\text{DBS}} = A \times t + B$. Calculated DBS half-lives are presented in Table 2.

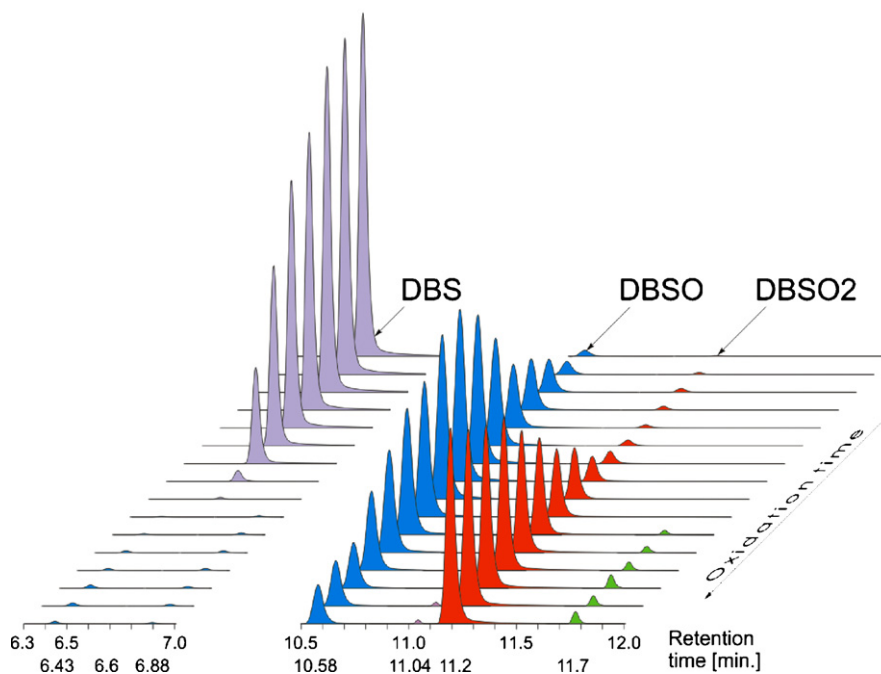


Fig. 2. A set of chromatograms obtained from sulfur channel of GC-AED during oxidation of DBS in concentration of 5.7 mmol/L in chloroform, at temperature 0 °C. Peaks with retention time of 6.6 min correspond to DBS; DBSO retention time is 10.58 min; and DBSO₂—11.2 min. Individual chromatograms show composition of a reaction solution at times: 0.25, 0.5, 1, 1.5, 2, 3.5, 5, 10, 15, 20, 25, 30, 35, 40, 50 and 60 min.

Relations between DBS half-life and temperature are characterized by total oxidation rate of the compound in given DBS concentration conditions, ozone content in oxygen, gas flow rate, gas pressure and temperature and the way the solution was mixed. Half-lives are important in those situations, when it is not possible to determine constant reaction rate in an unanimous way, or if we have to deal with several pathways of reaction occurring simultaneously, and especially in chemical engineering processes. Ozone solubility in chloroform and its stability decrease with increasing temperature, and DBS oxidation rate

increases with increasing temperature. Fig. 4 presents experimental results constituting a superposition of the following functions:

- (1) ozone solubility in chloroform;
- (2) ozone stability in solution;
- (3) DBS oxidation rate versus temperature.

In a dynamic system formed by mixture of oxygen and ozone flowing through a solution of dibutyl sulfide in chloroform some

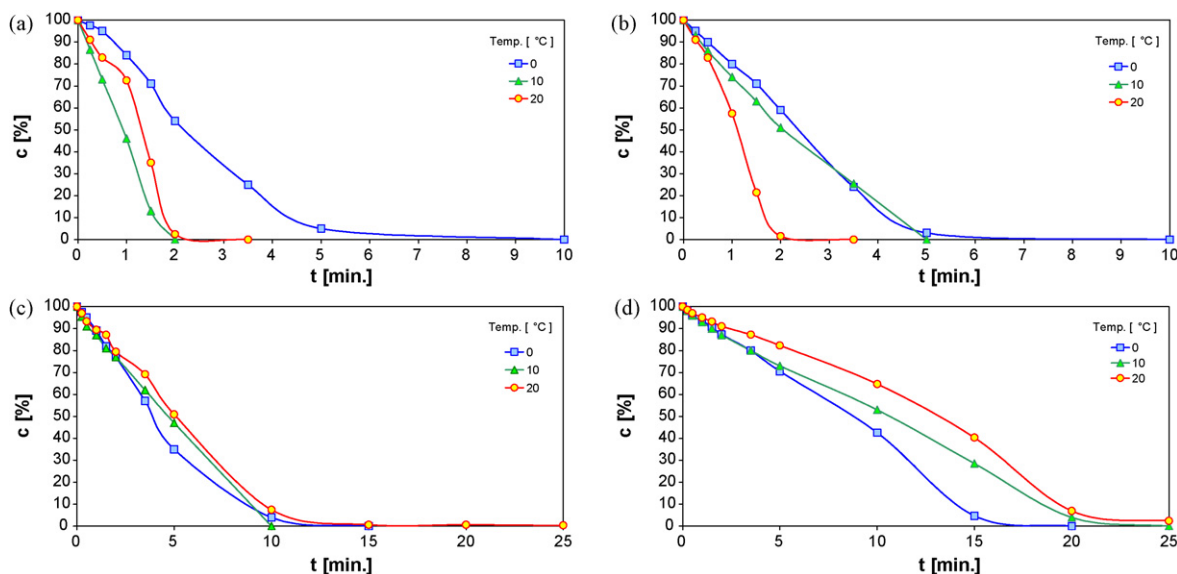


Fig. 3. DBS concentration change during a reaction with ozone for various initial concentrations ($C_{0[DBS]} = 1.4$ mmol/L (a), 2.9 mmol/L (b), 5.7 mmol/L (c) and 11.5 mmol/L (d) at various temperatures.

Table 1
Parameters of linear equations ($c_{\text{DBS}} = A \times t + B$) approximating curves of DBS disappearance

T (°C)	$C_{0[\text{DBS}]}$ (mmol/L)	A	B	R^2
0	1.4	-20.333	101.380	0.986
	2.9	-20.063	99.734	0.995
	5.7	-10.072	97.300	0.971
	11.5	-6.152	100.150	0.996
10	1.4	-57.517	101.090	0.998
	2.9	-19.853	95.685	0.991
	5.7	-9.817	97.072	0.998
	11.5	-4.669	97.890	0.998
20	1.4	-47.747	105.770	0.956
	2.9	-51.564	104.160	0.989
	5.7	-9.217	99.188	0.997
	11.5	-4.116	100.260	0.986

Table 2
List of DBS half-lives for its different initial concentrations and oxidation temperatures

$C_{0[\text{DBS}]}$ (mmol/L)	$t_{1/2}$ (s)		
	0 °C	10 °C	20 °C
1.4	2.53	0.89	1.17
2.9	2.48	2.30	1.05
5.7	4.70	4.79	5.34
11.5	8.15	10.26	12.21

regularities can be seen despite complexity of the occurring processes. And namely: for low initial DBS concentrations (1.4 and 2.9 mmol/L) slight increase of DBS disappearance rate at 20 °C is noted ($t_{1/2}$ decrease), comparing to the rate determined for 0 °C. The highest DBS destruction rate is observed for initial concentration of DBS of 1.4 mmol/L at 10 °C. This is influenced by combined effect of three factors: (1) quantity of ozone dissolved in CHCl_3 , introduced up to the state of saturation, is high enough to ensure oxidation of majority of DBS molecules; (2) ozone solubility in CHCl_3 , decreasing with increasing temperature, is still high, and (3) increasing effect of temperature on the reaction rate.

In case of 2.9 mmol/L DBS solution at 10 °C, DBS destruction rate did not change with temperature increasing from 0 to 10 °C. This means that temperature-mediated increase of

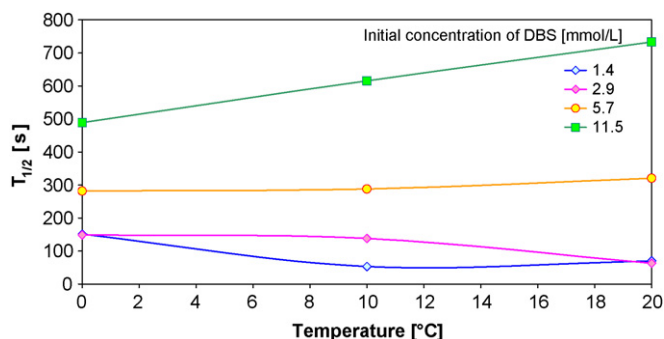


Fig. 4. Relation between DBS half-life and temperature for various initial concentrations.

Table 3
DBS destruction reaction rate constants for its different initial concentrations and oxidation temperatures

$C_{0[\text{DBS}]}$ (mmol/L)	k_1 (s^{-1})		
	0 °C	10 °C	20 °C
1.4	0.3957	1.1258	0.8561
2.9	0.4034	0.4346	0.9521
5.7	0.2129	0.2086	0.1873
11.5	0.1227	0.0975	0.0819

reaction rate was compensated by relatively lower quantity of dissolved ozone. In case of DBS solutions with concentrations 5.7 and 11.5 mmol/L this trend is even more pronounced. Quantity of pre-dissolved ozone in chloroform plays lesser role, and ozone transport from gaseous phase to liquid phase is insufficient in relation to quantity of DBS molecules present in solution. Gaseous bubbles of oxygen with ozone passing through a porous barrier in the reactor travel several centimeters through the liquid phase of chloroform and leaves the environment of reaction. Time of a bubble contact with liquid is short, below 1 s, and ozone content in oxygen at the level of 1%. Transport of ozone molecules from gaseous phase and rate of their dissolution in chloroform takes place on a spherical interface between the bubble and liquid. Only small part of 1% of ozone contained in an oxygen bubble will be able to dissolve in chloroform. As a result we observe decreasing reaction rate with increasing DBS concentration in chloroform and with temperature.

DBS destruction reaction rate constant values in relation to initial concentration and temperature are presented in Table 3. They include all constituent reactions and factors determining DBS oxidation process and range between 0.08 and 1.13 s^{-1} , characterizing DBS destruction in the presented conditions as moderately slow.

Data presented in Table 3 indicate that the fastest are DBS oxidation reactions occurring for low initial concentrations (1.4 and 2.9 mmol/L). For higher initial concentrations (5.7 and 11.5 mmol/L) the reaction rate was lower and independent from temperature. In that case there was an additional drop of the reaction rate constants with increasing DBS concentration in chloroform. This is connected with decreasing ozone solubility in chloroform with increasing temperature. Further more ozone solubility decrease is a consequence of increasing concentration of semi-products and final products of DBS oxidation in chloroform.

Graphs presented in Fig. 5 show relationships between DBS destruction reaction rate constants and DBS concentration and temperature. For DBS concentrations below 5 mmol/L destruction rate increases with increasing temperature, which is related to concentration of dissolved ozone. For DBS concentrations over 5 mmol/L destruction rate is reversely proportional to temperature.

A characteristic feature of the relations presented in the graph is intersection of the three functions within the area corresponding to DBS initial concentration of approximately 5.5 mmol/L. DBS destruction rate for initial concentrations close to 5.5 mmol/L (at intersection of lines) does not depend on

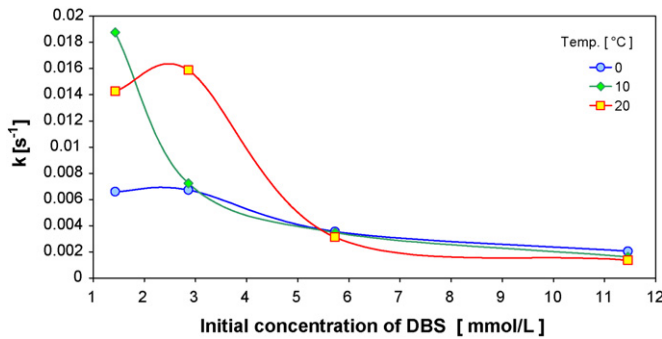


Fig. 5. Relationship between DBS destruction reaction rate constant and initial concentration and temperature.

temperature. This means that DBS destruction rate is mainly influenced by transport of ozone from gaseous phase to liquid phase, determined by ozone concentration dissolved in chloroform in saturation state.

DBS oxidation rate constant in relation to temperature and DBS initial concentration vary greatly, from the minimal value of 0.0819 (20 °C, 11.5 mmol/L) to maximal 1.1258 (10 °C, 1.4 mmol/L), which is 13.7-times. Variable conditions of oxidation process caused change in DBS destruction rate by more than one order of magnitude.

DBS undergoes oxidation to sulfoxide as semi-product, and then finally to sulfone according to the following kinetic reaction:



An attempt was made to adapt kinetic equations of successive reactions to experimental values. Rate constants k_1 were adopted in first approximation based on values calculated from linear approximation of measurement points (from Table 3).

Kinetic equations for [DBS], [DBSO] and [DBSO₂] for complex primary kinetics are the following:

$$\begin{aligned} \frac{d[\text{DBS}]}{dt} &= -k_1[\text{DBS}] \\ \frac{d[\text{DBSO}]}{dt} &= k_1[\text{DBS}] - k_2[\text{DBSO}] \\ \frac{d[\text{DBSO}_2]}{dt} &= k_2[\text{DBSO}] \end{aligned}$$

Assuming boundary conditions:

$$[\text{DBS}] = [\text{DBS}]_0, \quad [\text{DBSO}] = 0, \quad [\text{DBSO}_2] = 0 \quad \text{for } t = 0$$

we have a kinetic equation for [DBS]:

$$\begin{aligned} [\text{DBS}] &= [\text{DBS}]_0 e^{-k_1 t} \\ \frac{d[\text{DBSO}]}{dt} + k_2[\text{DBSO}] &= k_1[\text{DBS}]_0 e^{-k_1 t} \\ [\text{DBSO}] &= \frac{k_1[\text{DBS}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \end{aligned}$$

Taking the law of conservation of mass into account

$$[\text{DBS}] + [\text{DBSO}] + [\text{DBSO}_2] = [\text{DBS}]_0$$

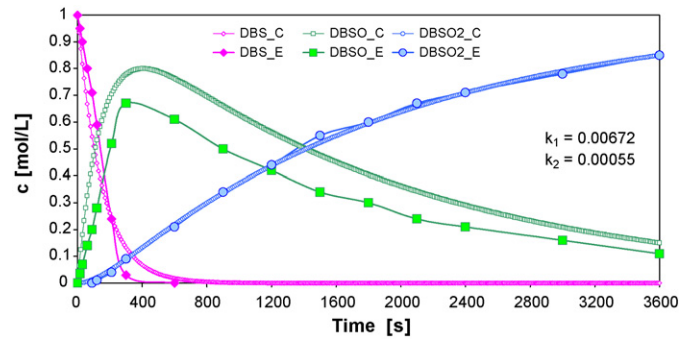


Fig. 6. Example of comparison of experimental data and calculated values for DBS oxidation to DBSO and subsequent formation of DBSO₂ ($Q_{(\text{O}_2+\text{O}_3)} = 200 \text{ L/min}$, $t = 0^\circ \text{C}$, $C_{0[\text{DBS}]} = 2.9 \text{ mmol/L}$). Denotation: DBS_C, a curve of DBS destruction calculated from a primary reaction kinetics equation; DBSO_C, a curve of sulfoxide generation and destruction; DBSO₂_C, a curve of sulfone generation; DBS_E, DBSO_E and DBSO₂_E regard experimental conditions.

and placing equations for [DBS] and [DBSO] we obtain:

$$[\text{DBSO}_2] = [\text{DBS}]_0 \left(1 - \frac{k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right)$$

This way the final equations for DBS, DBSO and DBSO₂ concentration in relation to time were achieved. The equations were used for calculation of a model run of the above mentioned reactions for all DBS concentrations and temperatures.

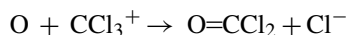
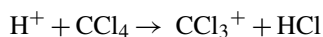
Adaptation of theoretical curves to experimental values proves to be poor. One of the reactions is presented in Fig. 6. Lack of precise matching of theoretical curves to experimental ones is a result of complexity of the reaction system and of the fact that there is not a single primary reaction going on according to equilibrium conditions, but at least several simultaneous and successive reactions in condition of a dynamic equilibrium and decreasing yield, leading to formation of transition and by-products in small quantities. Making an attempt to adapt the curves to experimental results we knew that the adaptation will not be perfect, or even good. However, we wanted to learn the discrepancy between the assumed simple theoretical model and experimental data. The obtained analytical function describe experimental values in an approximate manner for: $Q_{(\text{O}_2+\text{O}_3)} = 200 \text{ L/h}$, $T = \{0.10, \text{ and } 20^\circ \text{C}\}$ and $C_{0[\text{DBS}]} = \{1.4, 2.9, 5.7 \text{ and } 11.5 \text{ mmol/L}\}$. This approach allowed obtaining approximate dibutyl sulfone generation rate constants k_2 .

Comparing curves obtained from theoretical equations with experimental curves we can note that DBS undergoes slower destruction on the preliminary stage, than it would be expected based on the kinetic equation of a primary reaction. After destruction of approximately 75% of DBS, the reaction rate increases, in case of all samples and irrespective the initial concentration and temperature. This is visible in Fig. 6 as intersecting theoretical and experimental curves of DBS destruction.

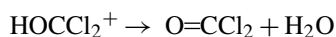
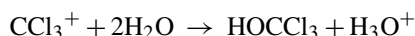
Generation of phosgene and water as by-products was noted in the DBS oxidation in chloroform solution, according to the following reaction (in the absence of water):



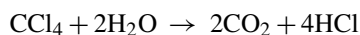
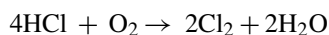
The destruction of CHCl_3 in absence of water and wide range of temperatures [13] leads to transitive CCl_4 formation. In the next step carbon tetrachloride is oxidized by atomic oxygen (from decomposition of ozone) producing phosgene.



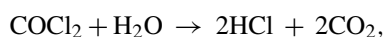
As an effect of increasing amount of water in solution the role of a new mechanism of oxidation and phosgene synthesis becomes dominating:



Hydrochloride being by-product of oxidation of carbon tetrachloride in the next stage creates water, chloride and carbon dioxide.



Phosgene is a very toxic gas very well soluble in chloroform and that is why it could be easily detected. Phosgene easily undergoes reaction of hydrolysis:



and because of that reason it does not threaten the environment [14,15].

Sulfine and sulfone acids and water formed during ozonation can catalyze DBS destruction. Water molecules, reacting with atomic oxygen formed as a result of ozone decomposition, create a highly reactive hydroxyl radical [16]:



The other reason for increased DBS destruction reaction rate could be presence of protons, formed as a result of acid dissociation, having a crucial influence on formation of water molecules, with a very fast, transient stage of hydroxyl radicals formation, with much higher oxidation capacity comparing to ozone. Increase of real DBS oxidation rate in relation to the oxidation rate calculated for kinetics of a primary reaction is

connected with presence of free protons originating from dissociated molecules of acids, which causes separation of an oxygen atom from a molecule of ozone and generation of a hydroxyl radical OH^\bullet , which considerably speeds up oxidation reactions at all stages. An experiment of DBS ozonation in chloroform solvent with a slight addition of sulfuric acid confirmed this thesis. Presence of dissociated protons really increases the rate of DBS destruction reaction.

In all graphs of calculated data fitted to experimental ones, shift of the experimental curve down for sulfoxide formation DBSO_M in relation to the calculated curve DBSO_C is observed. Consent between experimental and calculated curves for sulfone DBSO_2 formation is much better. As a result of fit of calculated to measured data, values of constants k_1 and k_2 were calculated with some approximation. They are listed in Table 4.

The set of data presented above indicates that based on the conditions, k_2 values are 4.5- to 17-times lower than k_1 . Differences between calculated and experimental results obtained for low DBS concentrations indicate clearly presence of other products from side reaction pathways. Only in the case of a solution with the highest DBS concentration and the temperature 0°C , the amount of by-products is minimal and approximation of real results with kinetic equations for creation of an intermediate and end product in the model of subsequent reactions shows the best correlation.

3.2. Mechanisms of sulfide oxidation with ozone

Ozone molecules attack sulfur atoms in sulfide molecule with their positive poles, and oxidation of the molecule starts according to an electrophilic mechanism. This is due to the fact that the positive charge of an ozone molecule is clearly localized at one place within the molecule, and the negative charge is partially delocalized, and therefore much weaker. On the other hand, sulfur atoms in sulfide molecules have partial negative charge, which is due to stronger electronegativity of the sulfur atom comparing to electronegativity of carbon atoms. This negative charge at the sulfur atom is twice bigger (its absolute value) than uniformly distributed positive charges localized at carbon atoms located in direct neighborhood, on both sides of the sulfur atom. As a result of sulfide oxidation with ozone according to the electrophilic mechanism a corresponding sulfoxide is formed according to the Eq. (1). Further oxidation of sulfoxide with ozone is difficult, for negative charge at ozone molecules is clearly delocalized (and therefore weaker than the analogous positive charge accumulated at ozone molecule), and a positive charge localized at the sulfur

Table 4
Reaction rate constants k_1 and k_2 in relation to DBS initial concentration and temperature

$C_{0[\text{DBS}]}$ (mmol/L)	0 °C			10 °C			20 °C		
	k_1 (s ⁻¹)	k_2 (s ⁻¹)	k_1/k_2	k_1 (s ⁻¹)	k_2 (s ⁻¹)	k_1/k_2	k_1 (s ⁻¹)	k_2 (s ⁻¹)	k_1/k_2
1.4	0.0066	0.00082	8.05	0.01876	0.0011	17.05	0.01427	0.002	7.14
2.9	0.00672	0.00055	12.22	0.00724	0.0008	9.05	0.01587	0.002	7.94
5.7	0.00355	0.00045	7.89	0.00348	0.00049	7.10	0.00312	0.00069	4.52
11.5	0.00204	0.0003	6.80	0.00162	0.00027	6.00	0.00136	0.0003	4.53

Acknowledgement

This work was supported by the Ministry of Sciences and High Education, Grant No. 3 T09D 024 29 for the period of 2005–2008.

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