Investigation of DBS electro-oxidation reaction in the aqueous-organic solution of LiClO$_4$

Witold Darlewski [a], Stanisław Popiel [a,*], Tomasz Nalepa [b], Waldemar Gromotowicz [c], Rafał Szewczyk [d], Romuald Stankiewicz [e]

[a] Military University of Technology, Institute of Chemistry, Kaliskiego Street 2, 00-908 Warszawa, Poland
[b] Department of Defense Affairs of the Ministry of Economy, Plac Trzech Krzyży 3/5, 00-507 Warszawa, Poland
[c] Warsaw Pharmaceutical Plant "Polfa" S.A., Karolkowa Street 22/24, 01-207 Warszawa, Poland
[d] Department of Biology and Environment Protection, University of Łódź, Pilarskiego Street 14/16, 90-231 Łódź, Poland
[e] Warsaw University, Department of Physics, Hoża Street 69, 00-681 Warszawa, Poland

ARTICLE INFO

ABSTRACT

A process of dibutyl sulphide (DBS) electro-oxidation using electrolysis and cyclic voltamperometry was investigated in water–methanol solution using different electrodes (platinum, boron doped diamond, graphite and glassy carbon). Obtained results indicate that the DBS electro-oxidation process is irreversible in voltamperometric conditions. It was shown that during DBS electrolytic oxidation on Pt, at the low anode potential (1.8 V), DBS was oxidized to sulphoxide and sulphone. Electrolysis at higher potential (up to 3.0 V) resulted in complete DBS oxidation and formation of various products, including: butyric acid, sulphuric acid, butanesulphinic acid, butanesulphonic acid, identified using gas chromatography (GC–AED) and mass spectrometry (GC–MS) methods.

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1. Introduction

Organic sulphur compounds are compounds of major biological importance. Two amino acids: cysteine and methionine, constituting building blocks for proteins, contain sulphur. They are referred to as sulphur amino acids. Some sulphides are well known as chemical warfare agents (CWA), including: yperite—2,2′-dichlorodiethyl sulphide and sesquiyperite—1,2 bis(2-chloroethylthio)ethane. Huge amounts of organic sulphur compounds are present in natural environment as products of living organisms' metabolism, creating the organic sulphur natural cycle. Only three of them: dimethyl sulphide, dimethyl sulphoxide and dimethyl sulphone, correspond to a major part of the cycle. It is estimated that over 25 million tonnes of those compounds are present in the atmosphere and in the oceans [1]. Studies aimed at determination and liquidation of organic sulphur compounds contained in post-production and municipal wastewaters [2,3], as well as those in CWA [4–6] have been conducted for years. II WW German chemical ammunition sunk in the Baltic Sea constitutes a serious threat for the ecosystem. Approximately 12,000 tonnes of highly toxic CWA, including sulphur mustard and its analogues, have been partially released because of undergoing corrosion of projectiles and containers [7–10].

Various methods of oxidation are most commonly used for destruction of sulphides. Oxidation of, for example, organic sulphides in aqueous solutions, leads to generation of corresponding sulphoxides and sulphones [11]. H_2O_2, ozone and advanced oxidation technique systems (e.g. $UV/H_2O_2/O_3$), variations of the Fenton reaction and oxidation reaction catalyzed by TiO_2 and other catalysts [12,13] are commonly used as oxidizing factors.

Oxidation of organic sulphides was also completed using the method of electrochemical anodic oxidation on various electrodes, most commonly Pt [14,15], and in various aqueous and non-aqueous solvents [16], using various background electrolytes [17–19]. It has been known that aliphatic sulphides undergo irreversible electrochemical oxidation, due to the fast reactions of cation radical, and are transformed mainly into sulphoxides and sulphones as well as some other products [20]. It was found that oxidation of aliphatic sulphides depends on the water content in the applied solvent [21]. At the water content above 1% oxidation products were usually sulphoxides and sulphones formed in corresponding di-electron processes [16–19]. The anodic oxidation of sulphides proceeds in a different way in anhydrous solvent. First of all cation radical is created, which after proton abstraction is

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

converted into sulphonic ion RSCH$_2$S$^+$R, where dimeric dication is suggested as a transient product [20–23]. The main oxidation products were formed in corresponding electrode bi-electron processes. However, mechanisms of anodic oxidation of organic sulphur compounds have not been unanimously clarified.

The aim of the study was to investigate processes taking place during dibutyl sulphide (DBS) oxidation on various electrodes, in voltamperometric conditions and in conditions of electrolytic oxidation on platinum electrodes, with controlled potential.

2. Experimental part

2.1. Electrochemical system

Voltamperometric measurements were done using the electrochemical device Autolab PGSTAT 20 from *ECO CHEMIE B.V.* (the Netherlands), linked to a controlling, data gathering and managing PC. Experiments were realized in a triple-electrode system (Fig. 1), containing the indicator test electrode, platinum-made counter electrode, and external calomel reference electrode, connected with an electrochemical bridge to the test vessel. The following electrodes were used as anodic ones: made of graphite (G), glassy carbon (GC), platinum (Pt) and boron doped diamond (BDD) from *CONDIAS DIACHEM*.

Electrolysis of DBS solutions was carried out using the electrolyzer presented in Fig. 2. The electrolyzer's cathode was a spiral platinum wire positioned centrally inside the anode Pt, in some experiments insulated from the anodic space with a porous ceramic barrier. Anode was also a platinum electrode, in form of a high sur-

face grid. Electrolysis was carried out at 20 °C, and a magnetic stirrer type ES21H was used for solution stirring. A power pack type 5353 from UNITRA powered the system.

2.2. Reagents

The following reagents were used for electrochemical experiments: methanol (analytically pure), acetonitrile (analytically pure) from *POCh* (Gliwice, Poland), lithium perchlorate (analytically pure) from *MERCK*, dibutyl sulphide (analytically pure) from *FLUKA* (Buchs, Switzerland). Redistilled water was obtained from water still made of quartz glass. Basic solutions were prepared of the reagents: (1) 0.1 mol/L LiClO$_4$ in water; (2) 0.1 mol/L LiClO$_4$ in methanol; (3) 0.1 mol/L LiClO$_4$ in acetonitrile; (4) 0.1 mol/L LiClO$_4$ in 50% aqueous-methanol solution.

The following reagents were used in chromatographic experiments: methylene chloride, magnesium (VI) sulphate, hexanol and sodium chloride from *CHEMPUR* (Piekary Śląskie, Poland). All substances were of analytically pure grade. Acetonitrile and ethyl iodide (*CHEMPUR*) were used for derivatization of DBS ozonation products.

2.3. DBS oxidation

Preliminary voltamperometric measurements were aimed at verification of DBS electrochemical activity in 0.1 mol/L LiClO$_4$ solutions, in selected solvents, using various indicator electrodes (G, GC, Pt, BDD). A technique of cyclic voltamperometry was applied. Registration of current–potential curves was started from various
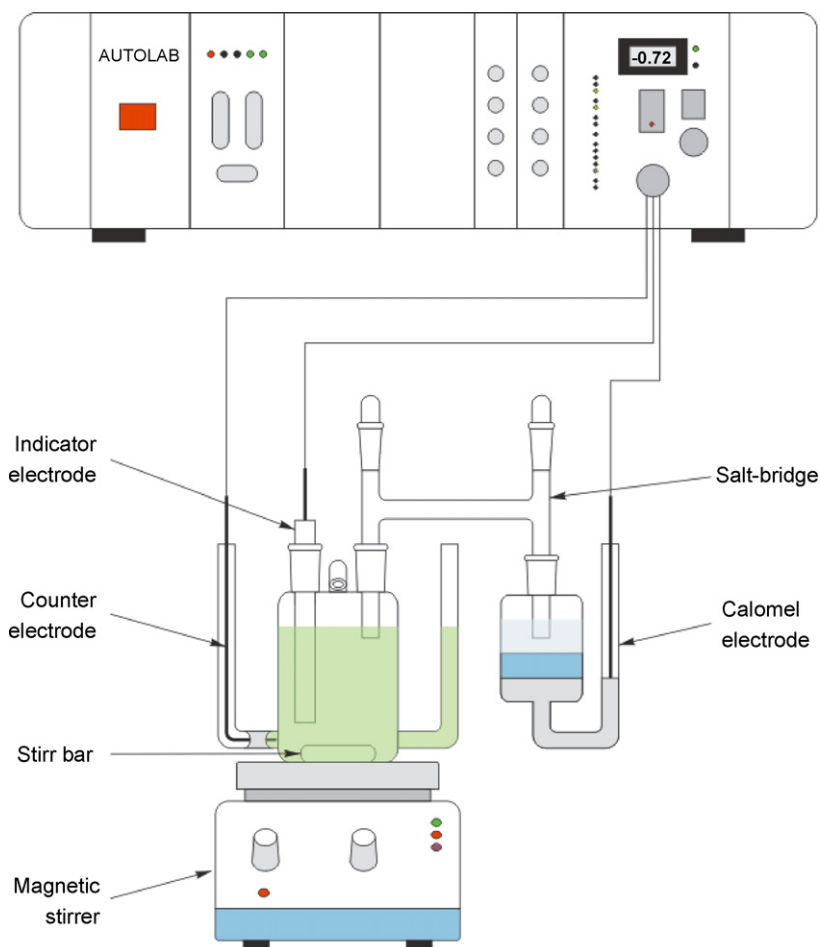

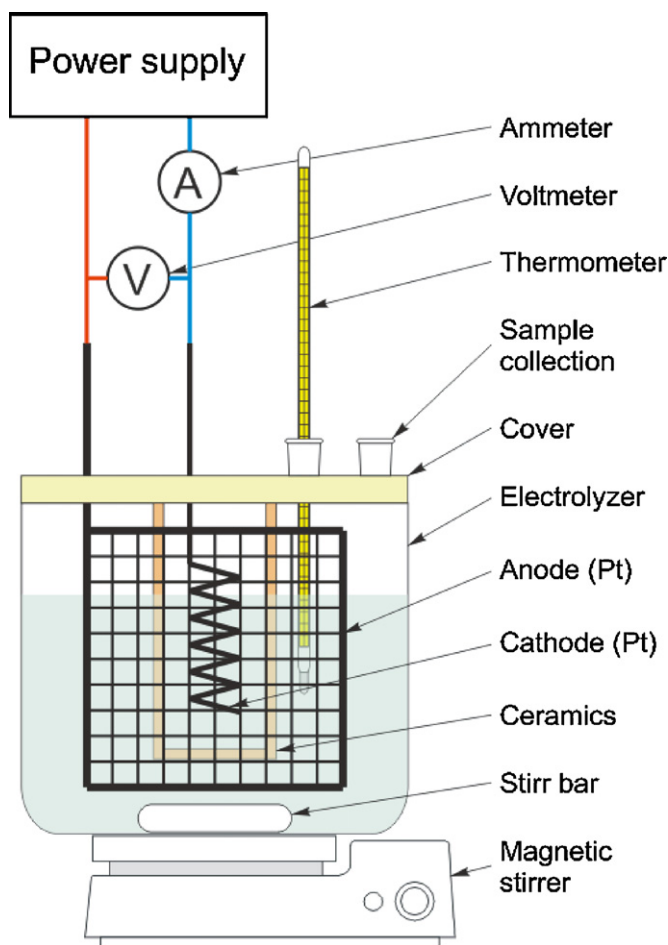Fig. 1. Scheme of the voltamperometric test system.

Fig. 2. Scheme of the system for DBS solution electrolysis.

voltamperometric method and gas chromatography with atomic emission detection (GC–AED) and mass spectrometry (GC–MS).

2.4. Sample preparation

Sample preparation procedure is presented in Fig. 3. Sample preparation for DBS oxidation products analysis using the GC–AED method was performed in two ways. Products soluble in organic phase were separated by liquid–liquid extraction, and compounds soluble in aqueous phase (inorganic and organic acids) were separated by ion-exchange. In order to transform resulting acids into volatile compounds, possible to analyze with gas chromatography, they were derivatized by esterification.

Samples for chromatographic assays were collected with a syringe, 2 mL of DBS solution before and during anodic oxidation at: 5, 15, 30, 60, 90, 120, 150 and 180 min. Collected samples of the solution were extracted and placed in closed tubes, and 2 mL of methylene chloride, 10 μL of chromatographic standard (0.5 mL hexanol in 10 mL acetone) and 100 mg NaCl were added. Then the mixture was shaken for 1 min and dried with anhydrous magnesium sulphate.

In order to transform resulting acids (products of electrochemical DBS oxidation in aqueous-organic environment) into esters, samples were derivatized on an ion-exchange column, according to the procedure described elsewhere [24]. The ion-exchange resin Dowex® 1×2 was used as an ion-exchanger, and acids retained in the column were esterificated with the acetonitrile–ethyl iodide mixture.

2.5. Chromatographic analysis

Identification and quantiative analysis of DBS oxidation products on platinum electrode (anode) was completed on the gas chromatography HP 6890 coupled with the atomic emission detector HP G2350A (GC–AED) from *HEWLETT-PACKARD*. The system was controlled by the Chemstation HP 35920A software which was also used for registration and handling of obtained results.

Gas chromatographic analyses of methyl chloride extracts were performed on a Hewlett-Packard HP 6890 series gas chromatograph equipped with mass selective detector HP 5973, using a HP-5MS capillary column.

Parameters of operation of the gas chromatograph with atomic emission spectrometer were the following: plasma chamber and transfer line temperature: 270 °C; dosing injector temperature: 270 °C, stream splitter: 10:1; time of solvent removal from the detector: from 1 to 3.6 min; helium was the carrier gas and its flow rate was 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 was used for analysis of DBS and its electro-oxidation products, with 5% diphenyl- and 95% dimethylpolysiloxane as a stationary phase. The column length was 30 m, internal diameter 0.32 mm and stationary phase film thick-
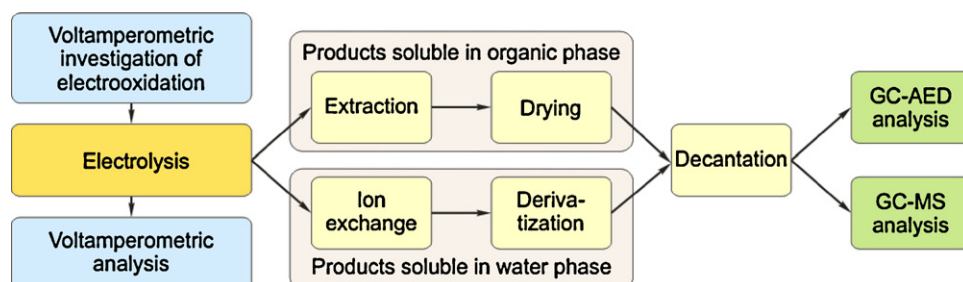
initial values of the indicator electrode potential (0.0, 0.2, 0.4 and 0.6 V). The electrode was polarized as anode to the potential of 2.0 V and then direction of polarization was changed and the measurement cycle was ended when the initial potential of the electrode was achieved. Repetitiveness of the obtained results was controlled registering several measurement cycles. Potential scan rate was 40 mV s^{-1}, and DBS initial concentration in tested solutions was 2.4 mmol/L.

Electrolysis of 60 mL of 2.4×10^{-4} mol/L DBS solution in 0.1 mol/L LiClO$_4$ in 50% aqueous-methanol solution was performed at controlled potential (1.8, 2.0 and 3.0 V), at various times of the electrolysis reaction (up to 180 min), with and without stirring of the oxidized solution, with and without insulation of the anode. To investigate DBS oxidation progress and products, after a specified reaction time, a sample of reaction mixture was collected from the electrolyzer with platinum electrode, and was analyzed using the

Fig. 3. Scheme of experiments in electrochemical DBS oxidation.

ness 0.25 μm. The analysis was performed heating the column from the temperature of 70–270 °C at the rate of 10 °C/min The column was maintained for 5 min at the final temperature. Additionally, separation of chromatographed compounds was performed at a column heated from 40 to 270 °C with rate of 20 °C/min. The column was maintained for 5 min at the initial and final temperatures.

A column TRB-sulphur from *Teknokroma*, Spain (100% dimethylpolysiloxane as a stationary phase) was used for analysis of acids generated during DBS solution electro-oxidation, after their esterification. The column length was 30 m, internal diameter 0.32 mm and stationary film thickness of 4 μm. Analysis of blends obtained as a result of derivatization at programmed temperature: the chromatographic column was heated for 5 min at 45 °C, and then heated up to the temperature of 250 °C, at the rate of 5 °C/min. The column was maintained at the final temperature for 5 min.

2.6. MS determination methodology

The injection volume was 2 μl. The inlet was set to split mode with split ratio 10:1 (split flow 10 mL/min) and temperature maintained at 250 °C. Helium was used as a carrier gas. Temperature parameters of the column were as follows: 60 °C maintained for

3 min, 10 °C/min to 160 °C, 20 °C/min to 250 °C and maintained for 3 min. Column carrier gas constant flow was 1 mL/min. Mass selective detector parameters were as follows: MS source 230 °C, MS quad 150 °C, scan mode with mass range set from 45.0 to 350.0.

All products were identified on the basis of the retention time and mass spectra fragmentation patterns of the examined sample. Some compounds were confirmed by the comparison to mass spectra in database NIST MS Chemstation Library 05.

3. Results and discussion

3.1. Voltamperometric studies

Depending on the type of background electrolyte and the applied indicator electrode, the course of anode reaction was different. Peaks of anodic currents associated with DBS electro-oxidation within the tested range of potentials from 1.1 to 2.0 V were registered on voltamperometric curves. Most frequently the oxidation process was a single-stage one.

In acetonitrile solutions, on voltamperometric curves registered on G and on Pt there was only one peak of oxidation of the tested depolarizer. Similar result was obtained for the BDD electrode. In
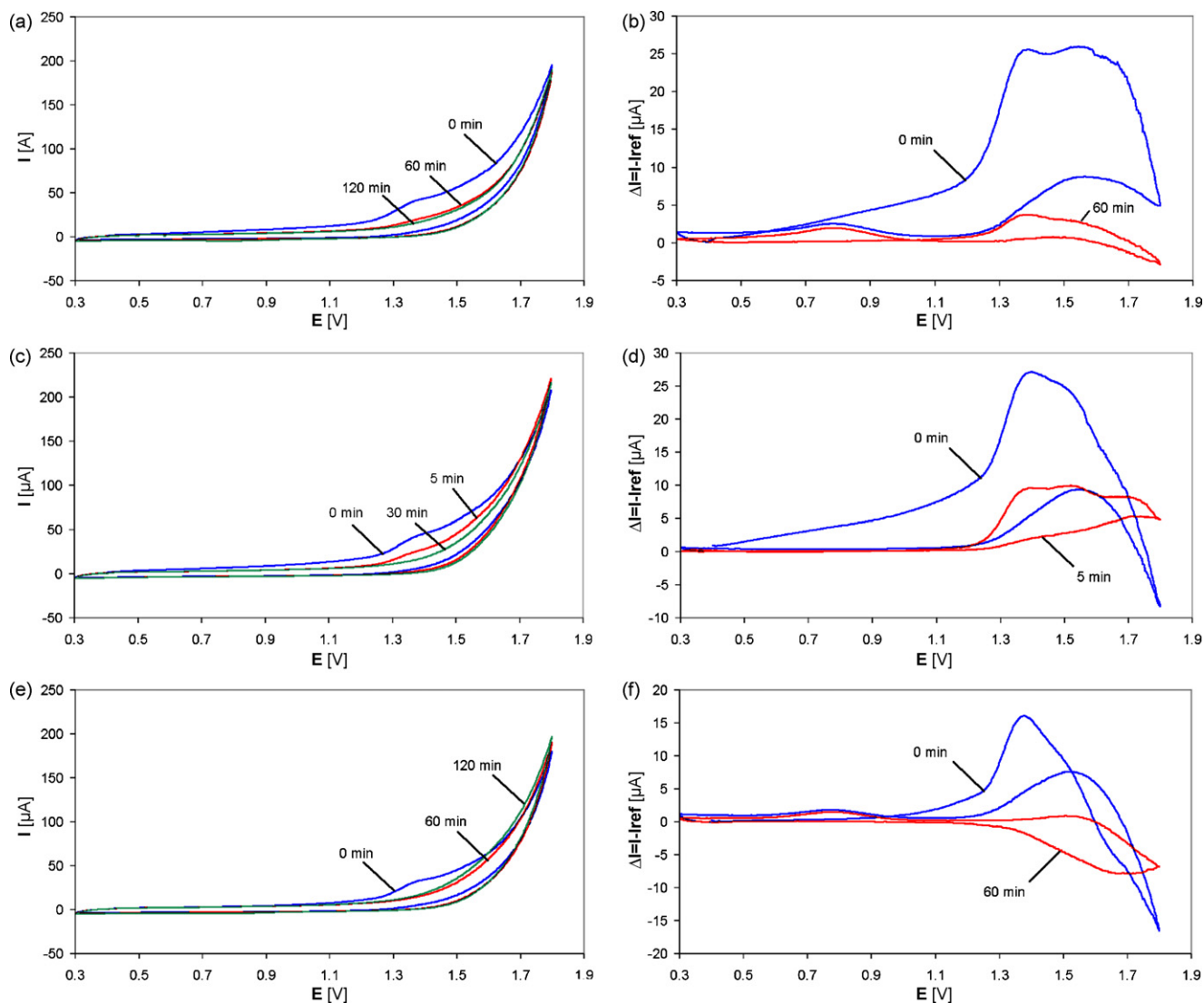

Fig. 4. Voltamperometric curves of DBS oxidation on the BDD electrode, registered at: 0, 60, 120, 180, 300 and 360 min of electrolysis. Background electrolyte: 0.1 M LiClO4 in 50% (v/v) CH₃OH in water. The process of electrolysis was performed at the Pt electrode, potential 3 V: (a and b) non-insulated, without stirring and (c–f) non-insulated, with stirring.

the experiment performed in the acetonitrile solution, using the GC electrode, a double-stage DBS oxidation was observed. Two anodic peaks were formed there, corresponding to double-stage 2-electron reactions of sulphide sulphur atom reactions, first to sulphoxide, and then to sulphone [25]. Two stages of DBS oxidation were observed also for the GC electrode in methanol solution.

DBS oxidation reactions performed at electrodes: G (semi-metal) and Pt (metal) in methanol and acetonitrile solutions were fast, giving a single current peak in voltamperometric measurements. Resistance of the system with the electrode/solution phase boundary was low, at the level of 2–6 kΩ. Catalytic effect of graphite and Pt on DBS oxidation was observed there. The system with phase boundary of the BDD electrode (semiconductor)/methanol was characterized by a slightly higher resistance of 9 kΩ. Also in that case a single current peak was observed. The situation was completely different for the GC/methanol, and GC/acetonitrile system. Lack of catalytic effect of glassy carbon allowed more slowly and selective DBS oxidation and generation of two current peaks. The system with phase boundary GC/methanol had the highest resistance of 136 kΩ.

Based on analysis of results obtained in preliminary voltamperometric studies of DBS anodic oxidation, 50% aqueous-methanol solution of 0.1 mol/L LiClO$_4$ was chosen as a background electrolyte for further studies of the depolarizer electro-oxidation in conditions of electrolysis with controlled potential. The BDD electrode was chosen as the indicator electrode for voltamperometric measurements of electro-oxidation results.

Obtained results indicate that the DBS electro-oxidation process in voltamperometric conditions is irreversible.

Results of voltamperometric tests of DBS electro-oxidized in aqueous-methanol solution on lithium perchlorate are presented for the system with non-insulated anode, in Fig. 4. Left-hand pictures (a, c, e) present voltamperometric curves, and right-hand pictures (b, d, f) present differences between them in form of current differences for subsequent curves and the reference curve. In each case the reference curve was the voltamperometric curve corresponding to complete DBS oxidation (maximum electrolysis time). That approach to data analysis is possible only in case of repeatable experimental results. Fig. 4a and b presents a system with non-insulated anode and without stirring, and Fig. 4c–f with stirring. In all presented voltamperometric curves characteristic, broadened peaks at the 1.4 V potential are visible, except for reference curves. Current difference curves (on the right-hand side) present stages of the process much more clearly. Two current peaks are visible at potentials equal 1.4 and 1.54 V. It may be assumed that the first one corresponds to the reaction of DBS oxidation to DBSO, and the other one corresponds to DBSO$_2$ generation. Potential difference between the observed peaks is 0.14 V. It indicates that it is possible to separate the processes electrochemically, which means it is possible to carry the oxidation out selectively. The second stage of oxidation requires higher activation energy, which is consistent with studies on chemical DBS oxidation, in which a 6.6-fold difference in value (k_1/k_2) of DBS decomposition rate constants (k_1) and sulphone formation (k_2) was observed.

3.2. GC–AED studies

Analysis of DBS solution electro-oxidation products was performed using the GC–AED method. Result data for systems with a non-insulated anode, without and with stirring, at times: 0, 60 and 120 min of electrolysis were collected. After 60 min of electrolysis, in the system without stirring, a small quantity of DBS was observed (R.T. = 11.06 min), and in the system with stirring—the compound was absent. After completion of electrolysis, in experimental conditions, the following oxidation products were detected in the solution: dibutyl disulphide (R.T. = 12.74 min) and dibutyl
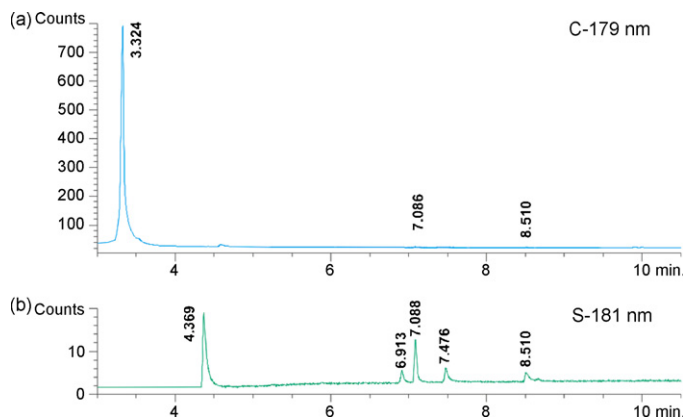

Fig. 5. Chromatograms GC–AED of products obtained as a result of derivatization of compounds present in the aqueous phase of electrochemical DBS oxidation. Detection for the emission line C-179 (a) and S-181 nm (b). Product identification: 3.324—butyric acid ethyl ester, 4.369—ethyl sulphate, 7.476—butanosulphonic acid ethyl ester, 8.510—butanosulphinic acid ethyl ester, 6.913—unidentified compound, and 7.088—4-(4-hydroxy-butylsulphanyl)-butyraldehyde.

sulphone (R.T. = 13.67 min). After 120 min of electrolysis, in the system without stirring, trace quantities of DBS and oxidation products were detected. In the system with stirring, only two oxidation products were detected in trace quantities.

It was clearly shown that under set conditions electrolysis led to decline both DBS, as well as dibuthyl sulphoxide and sulphone, drawing suggestion, that arising transitional products should undergo subsequent degradation, e.g. to acids. Disappearance of products soluble in organic phase suggested necessity of looking for other oxidation products soluble in aqueous phase. For that purpose a derivatization of chemical compounds contained in the aqueous phase using esterification method was conducted.

3.3. Derivatization of DBS electrolysis products

Aqueous acid solutions obtained from DBS electrolysis were derivatized. Results of chromatographic analysis of obtained compounds are presented in Fig. 5. Among DBS oxidation products low quantities of butanesulphonic and butanesulphinic acid were detected. Moreover, generation of relatively high quantities of sulphuric and butyric acid was found. Presence of those latter compounds among products means a complete degradation of DBS molecule in the electro-oxidation process, according to the reaction diagram presented in Fig. 6 during an aggressive electro-oxidation reaction—with higher anode potential.

With mild DBS oxidation conditions (Fig. 8), the reaction takes place mainly via the pathway A, leading to sulphoxide and dibutyl sulphone.

Using *ACD Labs* free software some properties including molar volume and surface tension of DBS and its oxidation products: sulphoxide and sulphone were calculated. We noticed reduction of molar volume of sulphoxide (170.0 cm^3) in relation to sulphide (174.5 cm^3), which is a favourable factor for the first oxidation stage. Simultaneously, there is a significant increase in sulphoxide surface tension, by 35% (DBS—27.8 dyne/cm, DBSO—37.6 dyne/cm). At the second stage of oxidation, sulphone molar volume (181.6 cm^3) increased and its surface tension (32.4 dyne/cm) was reduced by 14% compared to sulphoxide. Direction of the a.m. compounds properties change influence the reaction rate at both stages of DBS oxidation.

Other reaction pathways (B, C, D and E) lead to a set of by-products. More aggressive oxidation (Fig. 5) leads to generation of the acids: butyric, sulphuric, and butanosulphonic.
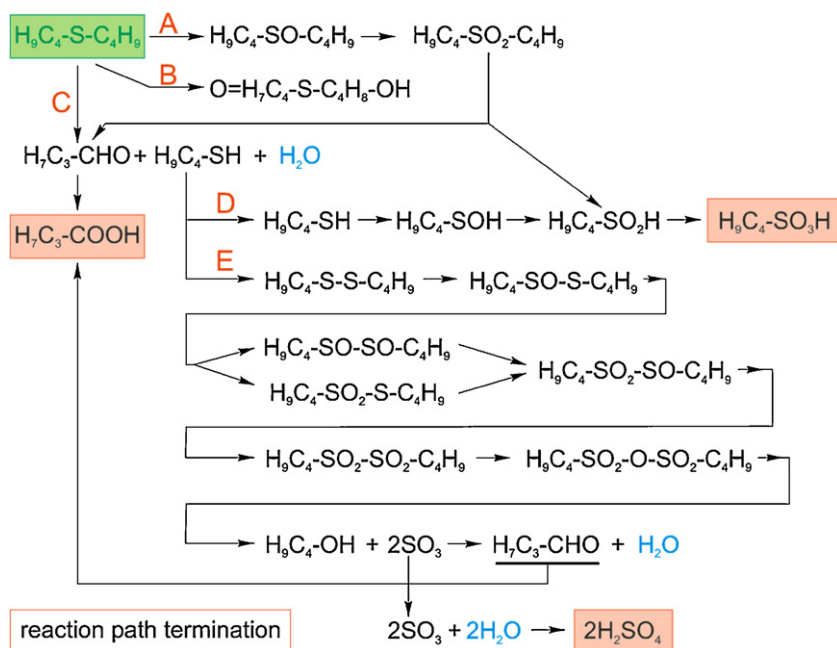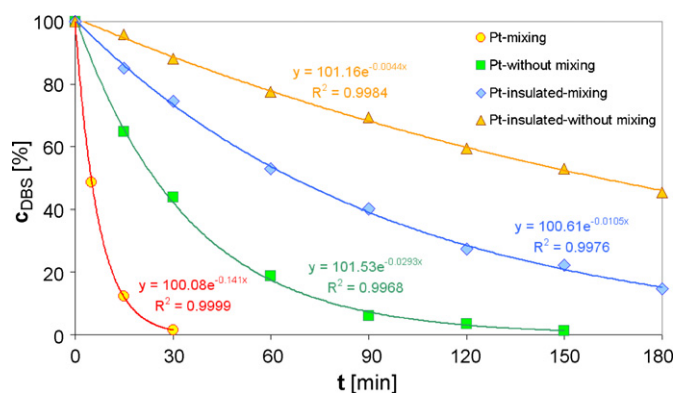
Fig. 6. DBS electrochemical oxidation diagram.

Fig. 7. Kinetics of the DBS electro-oxidation reaction on the Pt electrode.

Table 1
DBS electrolytic oxidation rate constants in various conditions in 0.1 mol/L $LiClO_4/H_2O–CH_3OH$ electrolyte.

System	Electrode	$k\,(s^{-1})$	k_s/k_{s4}
S1	Pt – non-insulated – stirred	0.1410	32
S2	Pt – non-insulated – without stirring	0.0293	6.7
S3	Pt – insulated – stirred	0.0105	2.4
S4	Pt – insulated – without stirring	0.0044	1[a]

[a] Reference system.

3.4. Kinetics of DBS oxidation

Fig. 7 presents DBS electro-oxidation on the Pt electrode kinetic curves for various systems (insulated and non-insulated electrode, with and without stirring). The DBS oxidation reaction is the slowest in the system of insulated electrode, without stirring. The
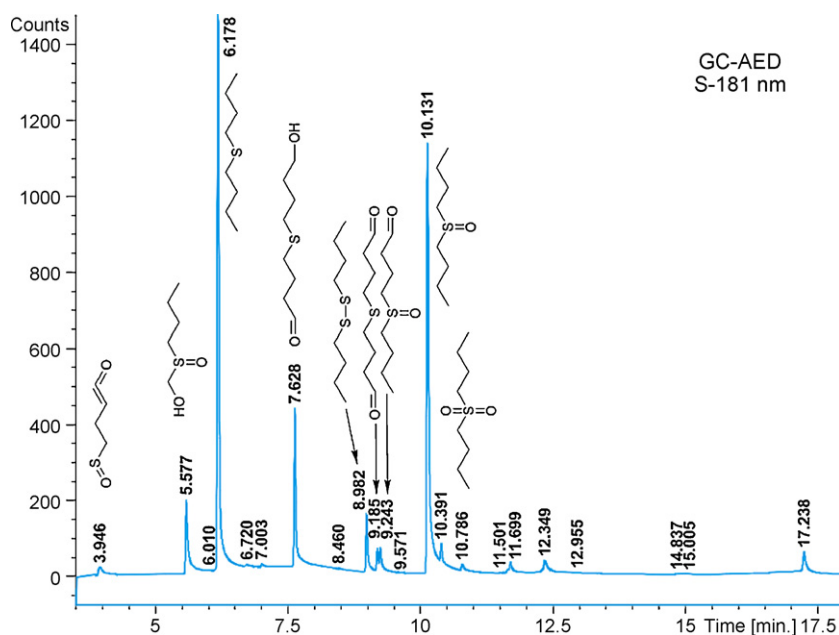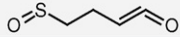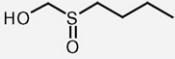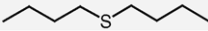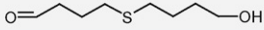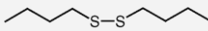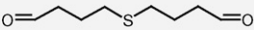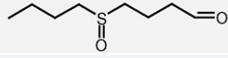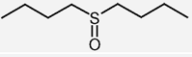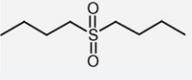

Fig. 8. GC–AED chromatogram for the emission line S-181 nm obtained as a result of analysis of solutions resulting from electrochemical DBS oxidation. Voltage applied during the electrolysis 2 V, time 120 min, working electrode Pt.

Table 2
Mass spectra of DBS electro-oxidation products.

Compound	R.T. (min)	M.W.	Main ions mass spectrum, m/z (relative intensity)
oxo(4-oxobut-3-en-1-yl)sulphonium	3.097	117.100	75.1 (100), 45.1 (46), 87.1 (43), 71.1 (12), 55.1 (11), *117.1 (1)*
(Butane-1-sulphinyl)-methanol	7.581	136.214	57.1 (100), 80.0 (43.4), 105.1 (22), 120 (5), *136 (4)*
Di-n-butyl sulphide	8.436	146.295	61.1 (100), *146 (76)*, 56.1 (93), 90.1 (33), 103.1 (24), 117.1 (12)
4-(4-Hydroxy-butylsulphanyl)-butyraldehyde	10.291	176.278	87.1 (100), 45.1 (64), 55.1 (25), 71.1 (9), 144.1 (4), *176 (4)*
Disulphide, dibutyl	11.829	178.360	57.1 (100), *178.1 (95)*, 122 (61), 87.1 (10)
4-(4-Oxo-butylsulphanyl)-butyraldehyde	12.077	174.262	87.1 (100), 45.1 (72), 55.1 (22), 71.1 (21), 117.1 (2), 132.1 (1), *174.1 (2)*
4-(Butane-1-sulphinyl)-butyraldehyde	12.144	176.278	87.1 (100), 45.1 (74), 55.1 (20), 71.1 (18), 117.1 (2), 132.1 (1), 163 (1), 109 (1), *174.1 (2)*
Di-n-butylsulphoxide	13.096	162.294	89.1 (100), 57.1 (63), 106.1 (45), 145.1 (45), *162.1 (7)*
Di-n-butylsulphone	13.751	178.294	57.1 (100), 123.1 (53), 89.1 (21), 146.1 (9), 106.1 (7)

reaction is 2.4-fold faster after stirring introduction, and 6.7-fold faster after removal of the ceramic insulation; and as much as 32-fold acceleration the system of non-insulated electrode and stirred solution (Fig. 4c–f and Table 1). Change of the reaction rate constants in subsequent systems is presented in the column (k_s/k_{s4}) in Table 1.

3.5. Identification of DBS oxidation products

In order to obtain products of DBS electrochemical oxidation at various stages, an additional experiment was performed, using voltage of 2 V for 120 min. Then, the voltage was increased to 3 V and electro-oxidation time was extended by next 90 min. Solutions obtained that way were analyzed using GC–AED and GC–MS, and majority of them were identified. Some of them are transitional products and were not included in the reaction diagram (Fig. 6).

Fig. 8 presents results of analysis and identification of the reaction products using the GC–AED method. Dibutyl sulphoxide is a predominating reaction product.

A big peak of DBS, corresponding to the retention time of 6.178 min is well visible. The predominating oxidation product is easily formed dibutyl sulphoxide (R.T. = 10.131 min). The final DBS oxidation product—dibutyl sulphone (R.T. = 10.786 min) was observed only in small quantities. Among identified compounds there is a large variety of various oxidation semi-products. Those are compounds formed upon oxygen attack on terminal carbon atoms, a process leading to formation of corresponding alcohols and aldehydes.

Listing of the identified DBS oxidation products, their retention times and molar weights, and mass spectra are presented in Table 2.

4. Conclusions

Oxidation of DBS on platinum electrode led to complete degradation of initial compound as well as dibuthyl sulphoxide and sulphone as emerging transitional products. Applying different conditions of anode oxidation on Pt electrode (with and without mixing of solution, with separating electrodes sintered glass and without) led in all cases to decay of DBS which followed the first order kinetics. In the case when solution was mixed and no sintered glass separator was used, the fastest decline of DBS was observed. And in contrary, when anode was separated from cathode with sintered glass and turned off mixing of solution the slowest decline of DBS was registered. In the first case reaction proceeded 32 times faster compare to the second one.

In the process of electrochemical DBS oxidation on glassy carbon anode two subsequent reactions were detected. In this case two anode current peaks were registered corresponding to 2-electron oxidation of sulphur atom in sulphide molecule in the first stage, leading to sulphoxide and in the second stage to sulphone. Using other electrodes (graphite, platinum, and boron doped diamond) resulted in a single current peak showing one stage oxidation process of DBS.

Electrochemical DBS oxidation on platinum electrode, with anode potential of 1.8 V leads mainly to dibutyl sulphoxide and sulphone. DBS electrolysis at higher potentials is more rapid and more effective, leading to fast decline of DBS and also main transi-

tional products as dibuthyl sulphoxide and sulphone and moreover degradation of other various compounds and formation of small amounts of buthylosulphonic and buthylosulphinic acids and larger amounts of butyric and sulphuric acids. Applying chromatographic analysis (GC–AED) and mass spectrometry (GC–MS) made possible identification of nine products of DBS oxidation.

Acknowledgement

References

[1] I. Barnes, J. Hjorth, N. Mihalapoulos, Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere, Chem. Rev. 106 (2006) 940–975.
[2] E. Smet, H. Van Langenhove, Abatement of volatile organic sulfur compounds in odorous emissions from the bio-industry, Biodegradation 9 (1998) 273–284.
[3] Y. Sheng, F. Chen, X. Wang, G. Sheng, J. Fu, Odorous volatile organic sulfides in wastewater treatment plants in Guangzhou, China, Water Environ. Res. 80 (2008) 324–330.
[4] R. Stankiewicz, T. Nalepa, Z. Witkiewicz, S. Popiel, Determination of sulfur mustard hydrolysis products by potentiometric titration, Anal. Chem. (in English), Warszawa 50 (2005) 55–70.
[5] S.S. Talmage, A.P. Watson, V. Hauschild, N.B. Munro, J. King, Chemical warfare agent degradation and decontamination, Curr. Org. Chem. 11 (2007) 285–298.
[6] 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.
[7] H. Sanderson, P. Fauser, M. Thomsen, P.B. Sørensen, Screening level fish community risk assessment of chemical warfare agents in the Baltic Sea, J. Hazard. Mater. 154 (2008) 846–857.
[8] H. Sanderson, P. Fauser, M. Thomsen, P.B. Sørensen, Human health risk screening due to consumption of fish contaminated with chemical warfare agents in the Baltic Sea, J. Hazard. Mater. 162 (2009) 416–422.
[9] A. Szarejko, J. Namieśnik, The Baltic Sea as a dumping site of chemical munitions and chemical warfare agents, Chem. Ecol. 25 (2009) 13–26.
[10] M. Mazurek, Z. Witkiewicz, S. Popiel, M. Śliwakowski, J. Chromatogr. A 919 (2001) 133.
[11] F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori, Selective oxidation of sulfides to sulfoxides and sulfones using 30% aqueous hydrogen peroxide and silica-vanadia catalyst, J. Mol. Catal. A 286 (2008) 124–127.
[12] K. Jeyakumar, D.K. Chand, Selective oxidation of sulfides to sulfoxides and sulfones at room temperature using H_2O_2 and a Mo(VI) salt as catalyst, Tetrahedron Lett. 47 (2006) 4573–4576.
[13] K. Bahrami, Selective oxidation of sulfides to sulfoxides and sulfones using hydrogen peroxide (H_2O_2) in the presence of zirconium tetrachloride, Tetrahedron Lett. 47 (2006) 2009–2012.
[14] F. Fichter, P. Sjostedt, Chem. Ber. 43 (1910) 3422.
[15] F. Fichter, F. Braun, Chem. Ber. 47 (1914) 1526.
[16] P.T. Cottrell, C.K. Mann, Electrochemical oxidation of aliphatic sulfides under nonaqueous conditions, J. Electrochem. Soc. 116 (1969) 1499–1503.
[17] J.A. Pursley, U.S. Patent 3,200,054 (1965); C.A. 63, 4023 (1965).
[18] E. Works, G. Heter, E. Singel, S. Afr. Patent 6,806,392 (1969); C.A. 72, 3030 (1970).
[19] M.M. Nicholson, Diffusion currents at cylindrical electrodes. A study of organic sulfides, J. Am. Chem. Soc. 76 (1954) 2539–2545.
[20] M.N. Elinson, J. Simonet, Electrochemical oxidation of aliphatic sulfides under very weakly nucleophilic conditions—the transient formation of a dicationic dimer, J. Electroanal. Chem. 336 (1992) 363–367.
[21] H. Lund, O. Hammerich (Eds.), Organic Electrochemistry, fourth ed., Marcel Dekker, New York, 2001.
[22] M. Goebl, M. Bonifacic, K.D. Asmus, Substituent effects on the stability of three-electron-bonded radicals and radical ions from organic sulfur compounds, J. Am. Chem. Soc. 106 (1984) 5984–5988.
[23] M.D. Ryan, D.D. Swanson, R.S. Glass, G.S. Wilson, Studies of the EE mechanism. Evidence for reversible dimer formation in electrochemical oxidation of a cyclic dithioether, J. Phys. Chem. 85 (1981) 1069–1075.
[24] P. Verner, F. Pehal, Ion-exchange extractive alkylation of organic acids, J. Chromatogr. B: 382 (1986) 237–241.
[25] A. Aced, E. Anklam, K. Asmus, K. Pohl, L.K. Steffen, G.S. Wilson, Anodic oxidation of 1,n-halo(alkylthio)alkanes and 1,n-chloro(alkylsulfinyl)alkanes, Phosphorus Sulfur Silicon Relat. Elem. 48 (1990) 53–62.