

The GC/AED studies on the reactions of sulfur mustard with oxidants

Stanisław Popiel^a, Zygfryd Witkiewicz^{a,b,*}, Aleksander Szewczuk^a

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

^b The Jan Kochanowski Świętokrzyska Academy, Institute of Chemistry, 5, Chęcińska-Street, 25-020 Kielce, Poland

Received 26 July 2004; received in revised form 2 February 2005; accepted 3 February 2005

Available online 3 May 2005

Abstract

A gas chromatograph coupled with an atomic emission detector was used to identify and to determine the products formed on oxidation of sulfur mustard. The oxidation rate and the resulting oxidates were studied in relation to oxidant type and reaction medium parameters. Hydrogen peroxide, sodium hypochlorite, sodium perborate, potassium monopercarbonate, ammonium peroxydisulfate, potassium peroxymonosulfate (oxone), and *tert*-butyl peroxide were used as oxidants. Oxidations were run in aqueous media or in solvents of varying polarities. The oxidation rate was found to be strongly related to oxidant type: potassium peroxymonosulfate (oxone) and sodium hypochlorite were fast-acting oxidants; sodium perborate, hydrogen peroxide, ammonium peroxydisulfate, and sodium monopercarbonate were moderate oxidants; *tert*-butyl peroxide was the slowest-acting oxidant. In non-aqueous solvents, the oxidation rate was strongly related to solvent polarity. The higher the solvent polarity, the faster the oxidation rate. In the acid and neutral media, the mustard oxidation rates were comparable. In the alkaline medium, oxidation was evidently slower. A suitable choice of the initial oxidant-to-mustard concentration ratio allowed to control the type of the resulting mustard oxidates. As the pH of the reaction medium was increased, the reaction of elimination of hydrogen chloride from mustard oxidates becomes more and more intensive.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Gas chromatography; Atomic emission detection; Sulfur mustard; Decontamination; Oxidation products

1. Introduction

In 1993, the UN General Assembly adopted the Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on their Destruction, and in 1997, this Convention came into force [1]. These events as also the fact that some states or subnational groups have been neglecting the international law, made us deem it necessary to continue to develop new methods and materials to be used to destroy the chemical substances that belong to the category of chemical warfare agents (CWA). Improving the decontamination methods and studying the products of decontamination continues to be of great importance because so far neither perfect decontamination procedures nor perfect decontaminants have been developed [2].

A review of the CWA literature reveals three major directions of study. One direction is to develop procedures to destroy CWA on a large scale [3,4]. Such procedures are applicable to the CWA accumulated in the chemical ammunition that still is included into the arsenals of various armies [5,6]. Another direction is to search for new decontamination methods, in view of potential contamination of various objects as a result of military [7–9] or terrorist actions [9–12] using CWA. The third direction comprises basic research intended to analyze the products formed while CWA are being decontaminated [13–15]. This direction stems from the necessary conditions to be met by a good decontaminant. Any CWA should be destroyed rapidly and completely and the resulting products should be non-toxic [2,16].

From the viewpoint of the mechanism of the reactions involved, decontamination of sulfur mustard is a complicated process, which is difficult to carry out. A common belief is that nearly each decontaminant that destroys sulfur mustard

* Corresponding author. Fax: +48 226669041.

E-mail address: witkiew@wp.pl (Z. Witkiewicz).

efficiently can be used to decontaminate nearly any other CWA. One method to decontaminate sulfur mustard is to oxidize it. Numerous conflicting opinions have arisen around the oxidation of sulfur mustard. Oxidants like hydrogen peroxide, nitric acid, potassium permanganate, chromic acid, and hypochlorites oxidize sulfur mustard to the sulfoxide and to the sulfone [17,18]. Some investigators believe that low temperatures and low mustard concentrations are favorable to the formation of the sulfone, rather than the sulfoxide, whereas others are of just the opposite opinion [19]. Discrepant opinions are also uttered about the effect the solvent polarity and initial mustard concentration have on the resulting sulfone-to-sulfoxide ratio. These conflicting opinions may well have been due to the fact that mustard oxidation was studied under dissimilar reaction conditions.

Some sources maintain each of the two major mustard oxidation products to be vesicant, whereas others consider only the sulfone [16,20–22], or only the sulfoxide, to be a vesicant or blister agent [17]. In spite of these conflicting opinions, oxidation of sulfur mustard is generally considered to be a useful decontamination procedure, mainly because, rather than liquids, the oxidates are crystalline solids that have no tendency to percutaneous absorption by the skin. The strong blister action occurs only after these compounds have been injected; yet, the substances are not resorbed through the skin.

The oxidative decontamination of sulfur mustard has been very little looked into because numerous investigators consider this procedure to be relatively inefficient. However, even in this respect, numerous discordances exist: some

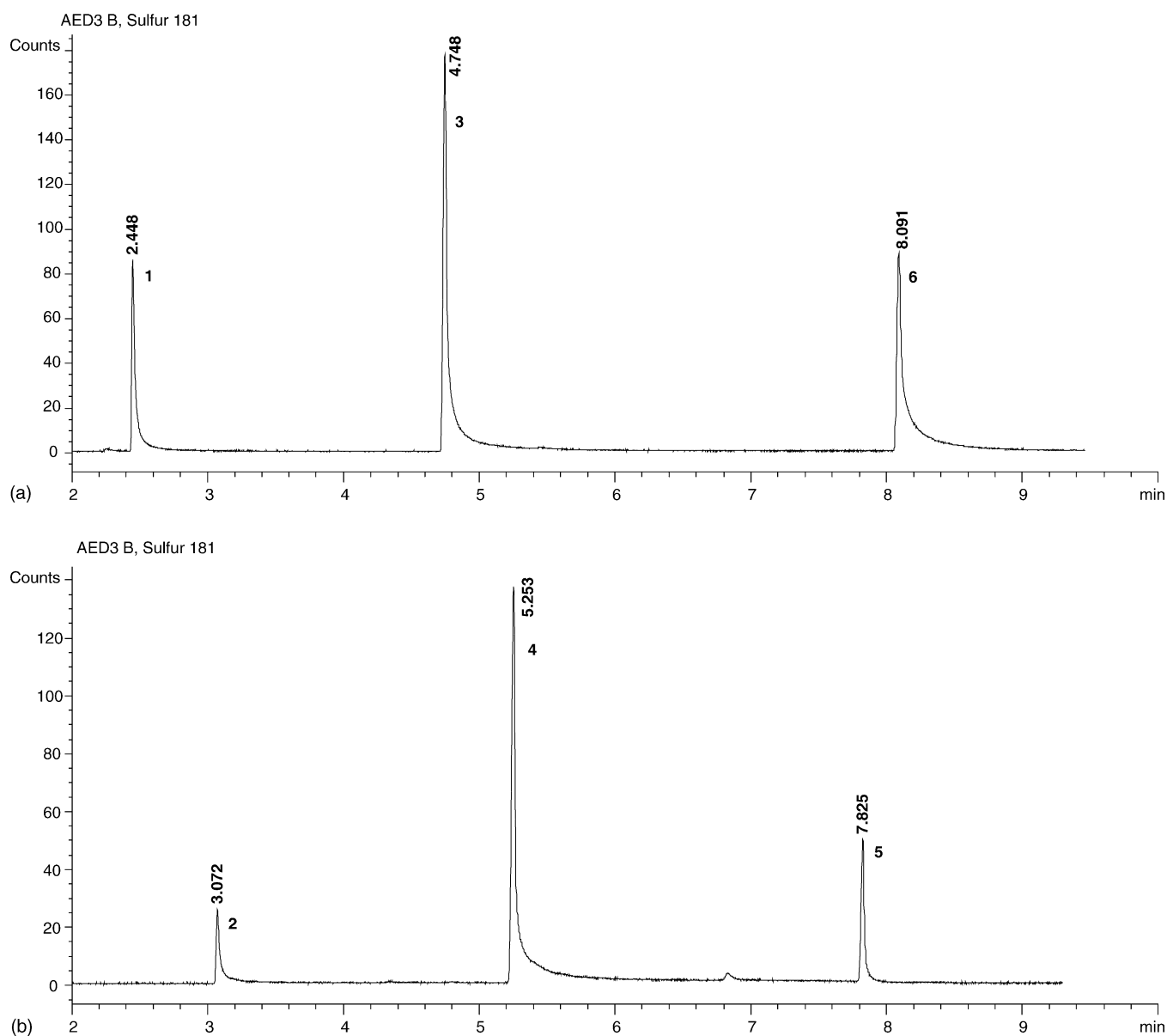


Fig. 1. Chromatograms recorded for the sulfur channel compounds: (a) sulfoxides, (b) sulfones; (1) divinyl sulfoxide, (2) divinyl sulfone, (3) vinyl-2-chloroethyl sulfoxide, (4) vinyl-2-chloroethyl sulfone, (5) mustard sulfone, (6) mustard sulfoxide.

Table 1

Mustard concentrations (relative to initial mustard concentration) in relation to time of mustard reaction with oxidant; [oxidant]/[mustard] initial mole ratio, 5:1; oxidant concentration, 0.027 mmol/mL; reaction temperature, 20 °C

Oxidant	Mustard content in reaction mixture after a period of time (min)						$t_{1/2}$ (min)
	2	20	60	120	600	1200	
Potassium peroxymonosulfate	<0.1	0	0	0	0	0	$\ll 1$
Sodium hypochlorite	84	17	0.5	0	0	0	8
Ammonium peroxydisulfate	94	57	18	3	0	0	24
Sodium perborate	95	59	20	4	0	0	26
Sodium percarbonate	99	87	66	44	2	0	100
Hydrogen peroxide	99	90	73	53	4	0	133
<i>tert</i> -Butyl peroxide	99.9	99	97	94	74	55	1373

The mustard half-value periods in the oxidant solutions are seen to rise in the following ascending order:



low $t_{1/2}$ -value (fast oxidation) \rightarrow high $t_{1/2}$ -value (slow oxidation)

investigators maintain that oxidation is an efficient procedure to decontaminate some CWA, and particularly sulfur mustard [15,17,20,23]. These conflicting opinions as well as the lack of unambiguous evidence to support the one or the other opinion allows to consider further studies on mustard oxidation reactions to be worthwhile. In this study, several oxidants were used to oxidize sulfur mustard and the reaction medium was modeled so as to see the effect of the reaction conditions on the nature and the amounts of the resulting products.

2. Apparatus, reagents and methods

2.1. Apparatus

Each analysis was carried out by the use of a HP 6890 gas chromatograph coupled with an HP G2380A atomic emission detector. A Chemstation HP 35920A program was used to operate the instrument and to process the data recorded.

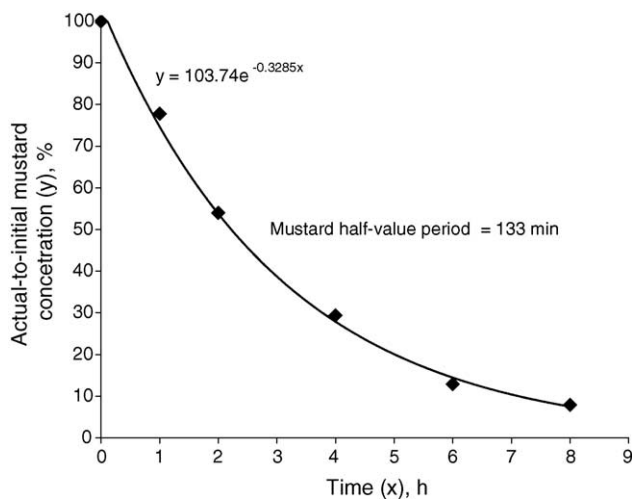


Fig. 2. The fall of mustard concentration in the reaction with H_2O_2 in an aqueous medium at 20 °C; [oxidant]/[mustard] initial mole ratio = 5:1.

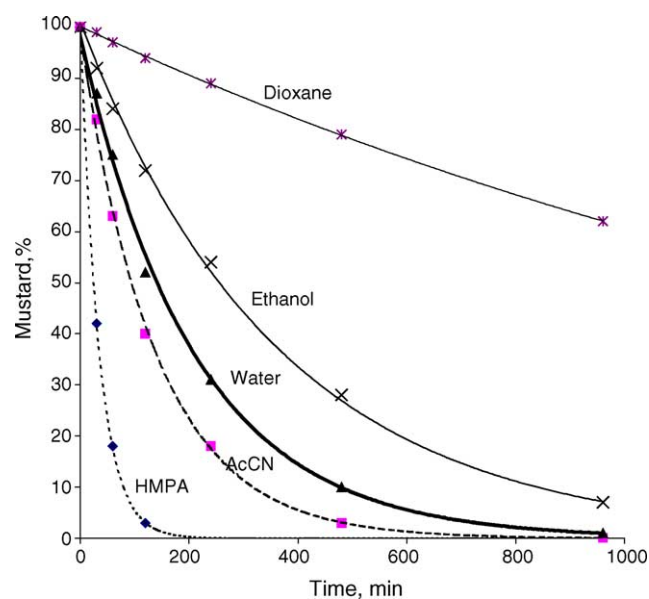


Fig. 3. The effect of solvent's polarity on the rate of oxidation of mustard with hydrogen peroxide.

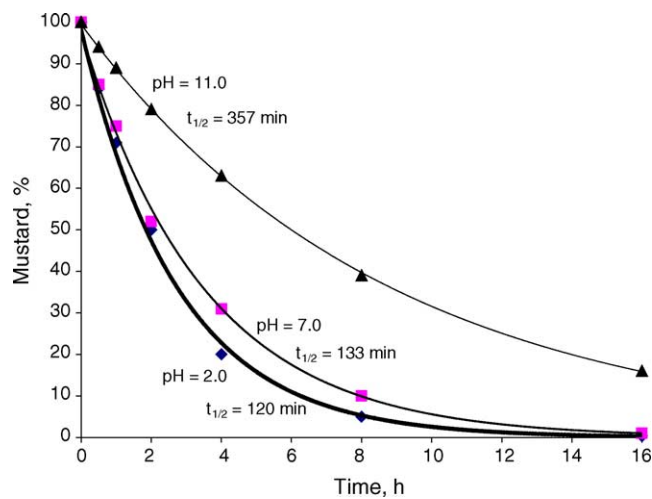


Fig. 4. The mustard oxidation rate in aqueous hydrogen peroxide in relation to pH.

2.2. Reagents and solutions

The oxidants used to oxidize sulfur mustard included reagent-grade potassium monopercarbonate, ammonium peroxydisulfate, sodium perborate, nitric acid, sodium hypochlorite, chromic anhydride, hydrogen peroxide (POCH, Gliwice, Poland), potassium peroxymonosulfate (Oxone) (Riedel-deHaën), and *tert*-butyl peroxide (Merck, Darmstadt).

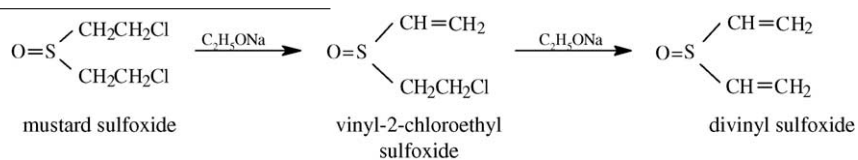
Sulfur mustard was prepared in this laboratory in the 1990s and stored in a sealed glass ampoule; its purity (99.8%) was now checked by GC/MS. *Warning: mustard is a potent vesicant and must be handled in a closed system or in a hood with good ventilation.*

Reagent-grade solvents in which sulfur mustard was oxidized included: hexamethylphosphoric triamide (HMPA) (Merck, Darmstadt), aqueous 15% 1-cyclohexyl-2-pyrrolidinone (Aldrich, Milwaukee), and dioxane, acetonitrile (AcCN), dimethylformamide (DMF), ethanol (POCH, Gliwice). Reagent-grade dichloromethane (POCH, Gliwice) was used to extract mustard oxidation products from reaction mixtures. The dichloromethane solutions prepared by using aqueous samples were dried over anhydrous magnesium sulfate (POCH, Gliwice).

Aqueous hydrogen peroxide solutions, pH 2, 7, and 11, were prepared by mixing aqueous 30% H₂O₂ 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 [24]. Chemicals for the preparation of the Britton–Robinson buffers were obtained from POCH (Gliwice).

2.2.1. Preparation of oxidant solutions

- Aqueous 0.027 and 0.108 mmol/mL sodium perborate, ammonium peroxydisulfate, potassium peroxymonosulfate (Oxone), and sodium monopercarbonate solutions were prepared by weighing a suitable amount of the particular reagent and dissolving it in distilled water.



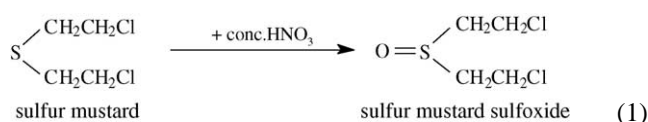
- Aqueous 0.027 and 0.108 mmol/mL hydrogen peroxide, *tert*-butyl peroxide, and sodium hypochlorite solutions were prepared by pipetting the original reagent solution and diluting it with distilled water.
- Solutions of 0.027 mmol/mL hydrogen peroxide in ethanol, dioxane, HMPA, and in aqueous 15% 1-cyclohexyl-2-pyrrolidinone were prepared by pipetting the original hydrogen peroxide reagent solution and diluting it with the corresponding solvent.

2.2.2. Syntheses of standard specimens of substances anticipated to be sulfur mustard oxidates

To identify mustard oxidates, commercial standard specimens of 1,4-thioxane and divinyl sulfone were used. In addition, the following standard specimens were prepared in this laboratory: sulfur mustard sulfoxide, divinyl sulfoxide, vinyl-2-chloroethyl sulfoxide, sulfur mustard sulfone, vinyl-2-chloroethyl sulfone, 2-chloroethyl-2'-hydroxyethyl sulfide (semimustard), 2-chloroethyl-2'-hydroxyethyl sulfone, and vinyl-2-hydroxyethyl sulfone.

The standard specimens synthesized were identified by using the Chemstation HP 35920A program that enabled the empirical formulas to be deduced from the elemental analysis data supplied by GC/AED.

Sulfur mustard sulfoxide [17]:

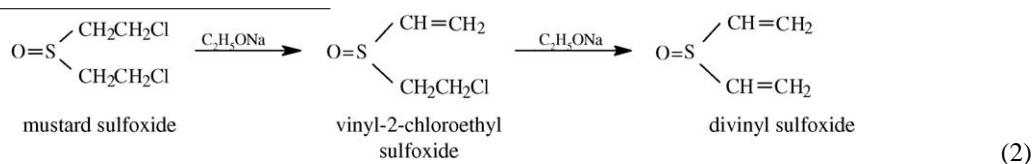


Concentrated HNO₃, 50 mL, was placed in a flat-bottomed flask equipped with a stirrer, a dropping funnel and a reflux cooler, and sulfur mustard, 10 mL, was slowly added dropwise at 20 °C. The reacting mixture was stirred for 1 h, then poured onto ice–water and, after ice had dissolved, the resulting solution was extracted thrice with dichloromethane. The extracts were combined, washed twice with aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, concentrated in a vacuum evaporator, and the resulting solids were crystallized twice from acetone–hexane.

2.2.2.1. Divinyl sulfoxide (authors' original procedure).

Ethanollic sodium ethanolate was added in small portions to 5 mL mustard sulfoxide dissolved in dichloromethane until the chromatograms recorded for the reaction mixture showed only a single peak attributable to divinyl sulfoxide and the remaining peaks (mustard sulfoxide and vinyl 2-chloroethyl sulfoxide) completely disappeared.

The reaction followed the scheme:



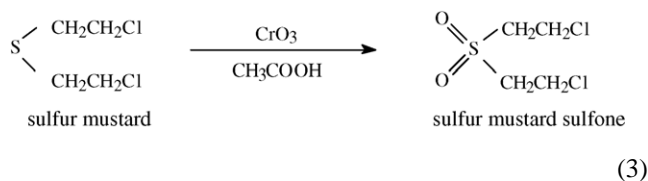
2.2.2.2. Vinyl-2-chloroethyl sulfoxide (authors' original procedure).

Ethanollic sodium ethanolate was added portionwise to 5 mL mustard sulfoxide dissolved in dichloromethane until the chromatograms recorded for the reaction mixture showed only small peaks due to mustard sulfoxide and divinyl sulfoxide, and the peak due to vinyl-2-chloroethyl sulfoxide was the largest.

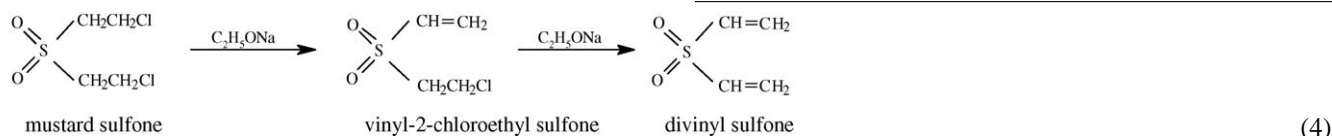
The sulfur compounds chromatogram run for a mixture of the three standard compounds expected to form on oxidation of sulfur mustard is presented in Fig. 1a.

2.2.2.3. *Sulfur mustard sulfone* [17]. To glacial acetic acid, 50 mL, placed in a flat-bottomed flask equipped with a stirrer, dropping funnel and a reflux cooler, 120 g CrO₃ was added; the mixture was stirred with heating to 100 °C, and then 2 mL mustard was added dropwise. After the whole amount of mustard had been added, the reaction mixture was heated at 100 °C for 30 min, then poured onto water–ice, and the resulting solution was extracted thrice with dichloromethane. The extracts were combined, washed twice with aqueous sodium hydrogen carbonate, dried over anhydrous magnesium sulfate, the solvent was evaporated in a vacuum evaporator, and the product was crystallized twice from acetone–hexane.

The reaction followed the scheme:



2.2.2.4. *Divinyl and vinyl-2-chloroethyl sulfones*. Ethanolic sodium ethanolate was added dropwise very slowly to 5 mL mustard dissolved in dichloromethane until the peaks of mustard sulfone, vinyl-2-chloroethyl sulfone, and divinyl sulfone were approximately identical in size. The scheme of the reaction is:

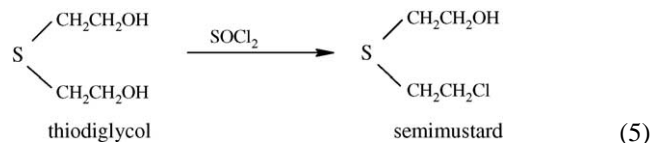


The reactions of mustard sulfone transformation into divinyl sulfone (4) is much faster than the reactions of mustard sulfoxides into divinyl sulfoxide (2). The chromatogram recorded for the standard specimens of the sulfones likely to form on oxidation of sulfur mustard is shown in Fig. 1b.

2.2.2.5. *2-Chloroethyl-2'-hydroxyethyl sulfide* (“semimustard”)[25]. Thionyl chloride (SOCl₂), 4.8 g (0.04 mol), was dissolved in 12 mL chloroform and added dropwise with magnetic stirring to a solution of 9.6 g (0.08 mol) thiodiglycol (TDG, 2,2'-thiodiethanol) in 21 mL chloroform at room temperature. After the last portion of SOCl₂ had been added, stirring was discontinued and the reaction mixture was allowed to stratify into the chloroform-soluble and insoluble phases. The chloroform phase was separated from the water phase, dried over anhydrous MgSO₄ and vaporized in an evaporator to remove the chloroform. To remove small amounts of a mustard by-product, the remaining liquid was extracted four times with 5-mL portions of a (1:1 v/v) cyclohexane–petroleum ether mixture. The residual petroleum ether and cyclohexane were removed in an evaporator. The remaining syrupy liquid was redissolved in 50 mL ethyl ether and rapidly extracted thrice with 5-mL portions of water. This extraction was allowed to remove sulfonium salts, residual TDG, and

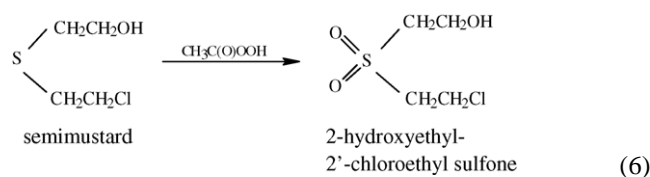
its impurities. The ethereal solution was dried over anhydrous MgSO₄. Since undiluted “semimustard” is known to polymerize and to form sulfonium salts, the preparation was stored as the ethereal solution in a refrigerator and the ether was removed directly before the use of the preparation.

The synthesis run according to the scheme:



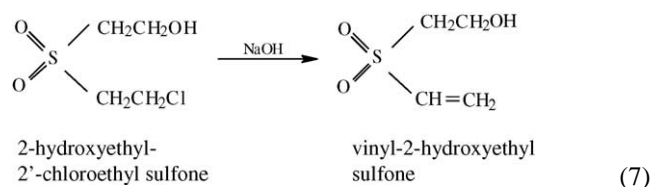
2.2.2.6. *2-Chloroethyl-2'-hydroxyethyl sulfone* (authors' original procedure). Aqueous 30% hydrogen peroxide, 2.2 mL, was added dropwise with magnetic stirring to 11 mL acetic anhydride at a temperature of 80–85 °C. After addition of the last portion, the solution was maintained for 1 h at 90 °C. The resulting peracetic acid solution (~0.022 mol) in acetic acid was cooled to 5 °C and added dropwise to 40 mL “semimustard” solution in ethyl ether at a temperature of 5 °C. The solution contained 1.4 g (0.01 mol) of semimustard. After addition, the reaction mixture was stirred for 60 min and its temperature was progressively increased to room temperature. The resulting solution was freed from the ethyl ether, acetic acid and the excess of peracetic acid in a vacuum evaporator.

The synthesis followed the scheme:



2.2.2.7. *Vinyl-2-hydroxyethyl sulfone* (authors' original procedure). To 2 mL dichloromethane placed in a screw-capped 10-mL test tube, 2-chloroethyl-2'-hydroxyethyl sulfone, 200 μL, was added and then 1.5 mL aqueous 2 M NaOH was added dropwise. The test tube was closed, shaken for 1 min, and set aside to allow phases to stratify. The organic phase was separated and dried over anhydrous MgSO₄.

The synthesis followed the scheme:



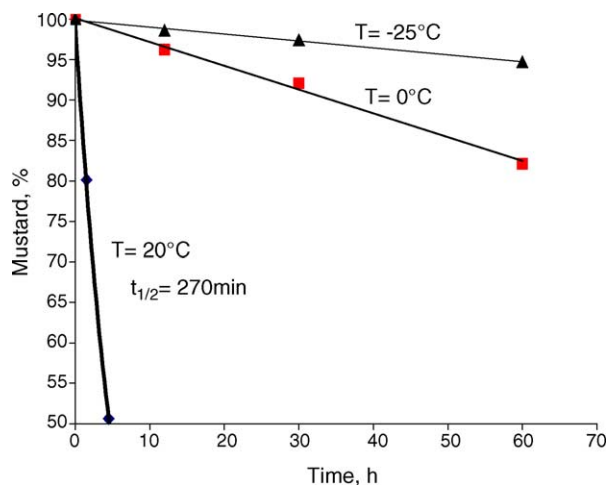


Fig. 5. The mustard oxidation rate in ethanolic hydrogen peroxide solutions in relation to temperature.

2.3. Methods

2.3.1. Reactions of sulfur mustard with oxidants

Sulfur mustard was oxidized in a thermostated vessel with magnetic stirring. Into an oxidant placed in the vessel and stirred for 5 min to allow the temperature to equilibrate, a calculated amount of sulfur mustard was micro-syringed with stirring continued and since then the reaction time was reckoned.

2.3.2. Withdrawal and preparation of samples for analysis

Liquid–liquid extraction was used to prepare samples. This technique allowed the components to be relatively quickly isolated from the reaction mixture. Of the various solvents tried, dichloromethane was found to be the most suitable. It enabled the substances analyzed to be recovered from the reaction mixture in high yields and its boiling point was low enough to enable this solvent to be easily separated from the mixture analyzed when a chromatogram was run.

At specified time intervals, 2 mL of the reaction mixture was pipetted and placed together with 2 mL dichloromethane in a screw-capped test tube, shaken for 15 s and set aside to allow the phases to stratify. The dichloromethane hypophase was transferred into another test tube and dried over anhydrous $MgSO_4$. The dried solution was decanted and analyzed.

Table 2

The mustard oxidation rate expressed in terms of the half-value period established in the solvents in which the reactions were run

Solvent	Dipole moment, D	$t_{1/2}$ (min)
HMPA	5.5	23
Dimethylformamide	3.8	72
Acetonitrile	3.4	88
Water	1.84	133
Ethanol	1.7	270
1,4-Dioxane	0.4	1416

The dipole moments from Lange's Handbook of Chemistry [24].

Table 3
Mustard oxidation products formed with various oxidants

Oxidant	Product types		UC
	Sulfoxides	Sulfones	
$NaBO_3$	++	-	-
H_2O_2	++++	-	-
$KHSO_5$	++	++	+++
$NaOCl$	-	+++	-
$(NH_4)_2S_2O_8$	++++	+	-
<i>t</i> -Butyl peroxide	-	-	++++

(++++) Very large amount; (+++) medium amount; (++) small amount; (+) none; UC: unidentified compounds.

2.3.3. Chromatographic analysis

A HP 6890 gas chromatograph coupled with an HP G2350A atomic emission spectrometer was operated at: cavity plasma temperature, 270 °C; column–detector transfer line temperature, 270 °C; injector temperature, 260 °C; splitter, 20:1; time of solvent removal from column, 0.9–2.2 min; helium carrier gas flow rate, 2 mL/min. The following re-

action gases were used: hydrogen, oxygen, or (10:90,v/v) methane–nitrogen. Chromatograms were run at temperatures increased according to a program. Sulfur mustard and its oxidation products were chromatographed in a HP-5 (30 m × 0.25 mm i.d.) capillary column coated with (5:95, w/w) diphenyl polysiloxane–dimethyl polysiloxane as a stationary phase film, 0.25 μm thick. The column was heated

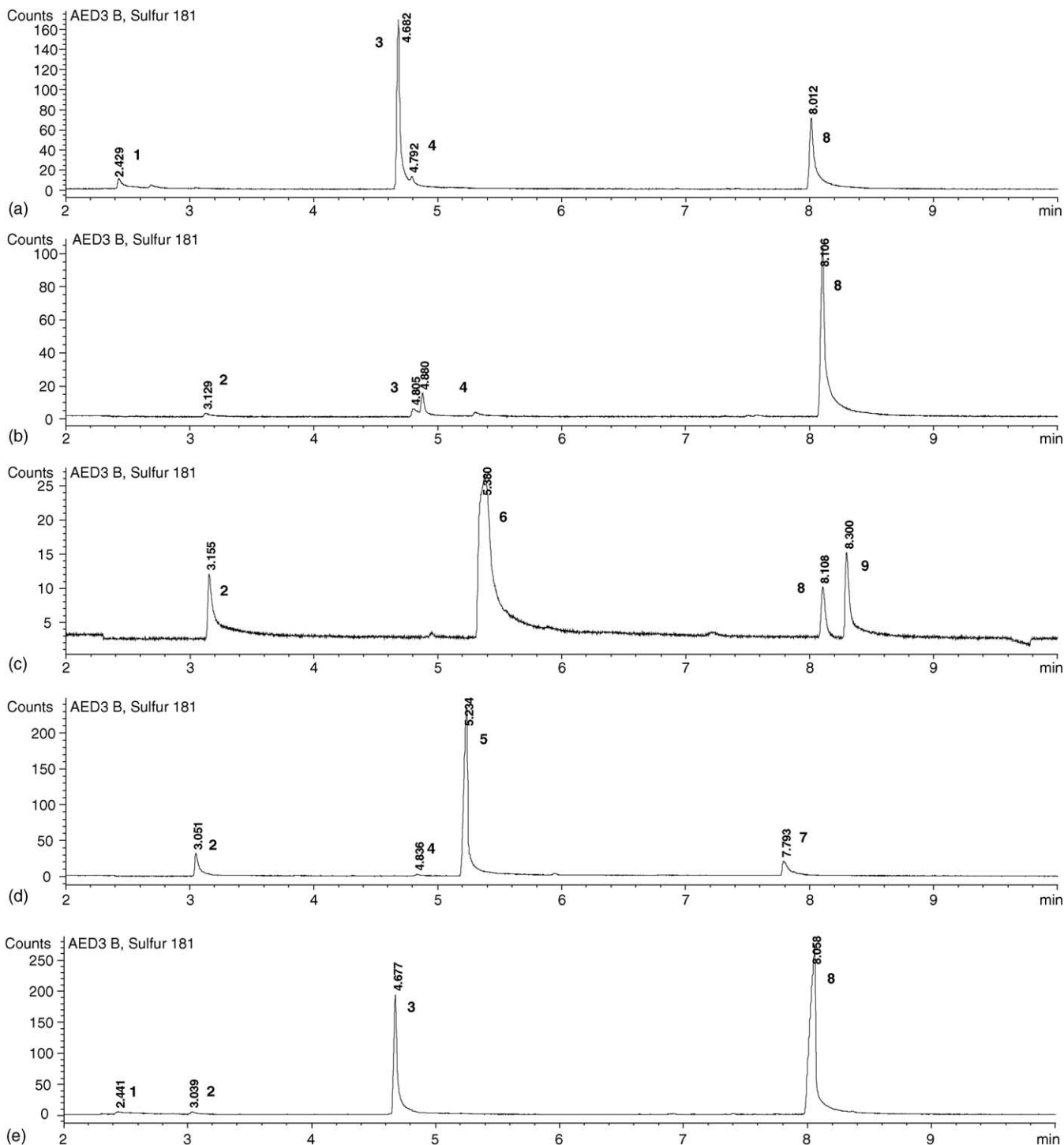


Fig. 6. Chromatograms of sulfur products of the reactions of mustard with the following oxidants: (a) NaBO₃, (b) H₂O₂, (c) KHSO₅, (d) NaOCl, (e) (NH₄)₂S₂O₈, (f) *tert*-butyl peroxide: (1) divinyl sulfoxide, (2) divinyl sulfone, (3) vinyl-2-chloroethyl sulfoxide, (4) unconverted mustard, (5) vinyl-2-chloroethyl sulfone, (6) vinyl-2-hydroxyethyl sulfone, (7) mustard sulfone, (8) mustard sulfoxide, (9) 2-chloroethyl-2'-hydroxyethyl sulfone, (10) unidentified compound.

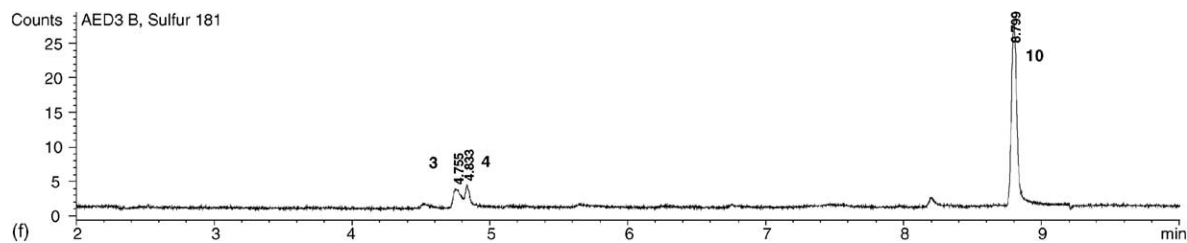


Fig. 6. (Continued).

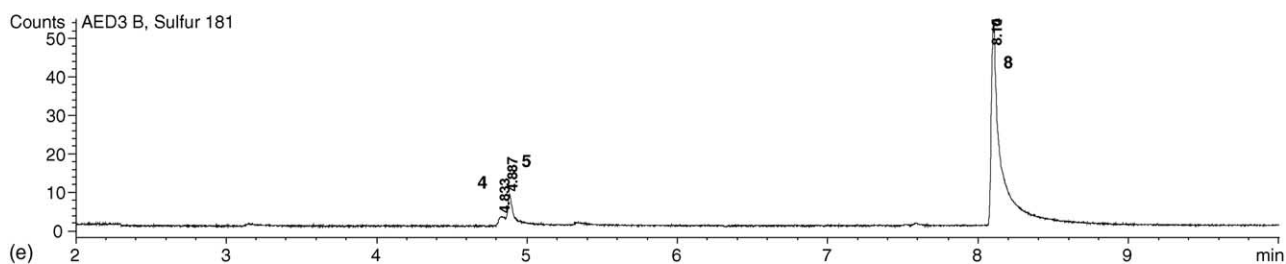
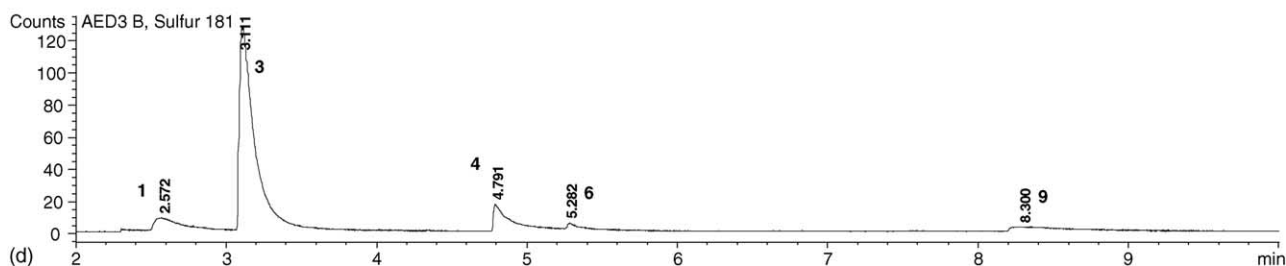
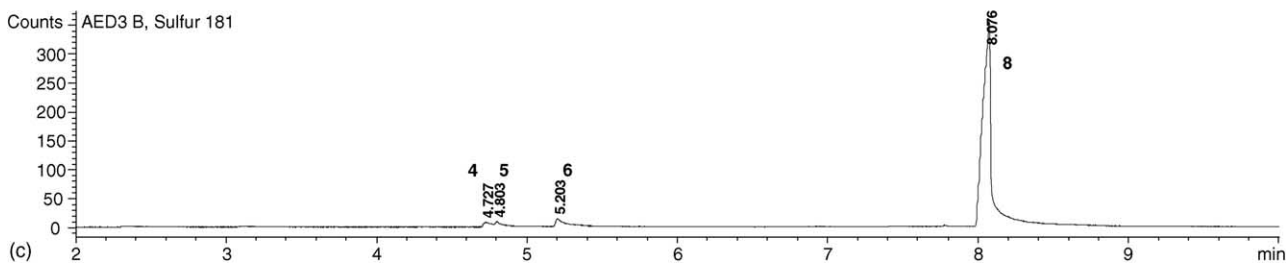
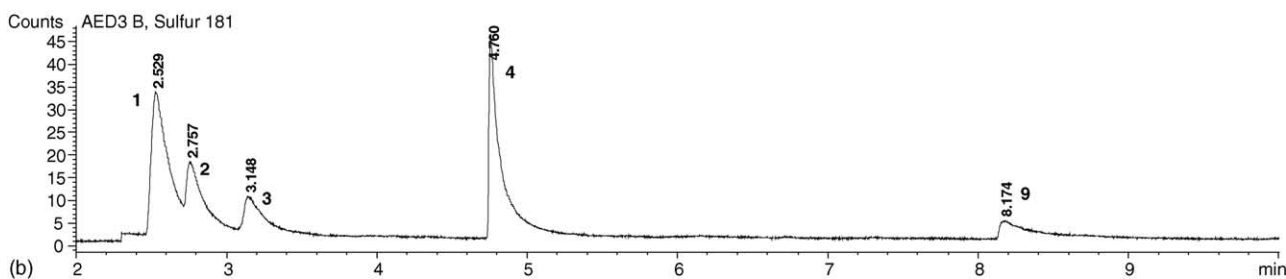
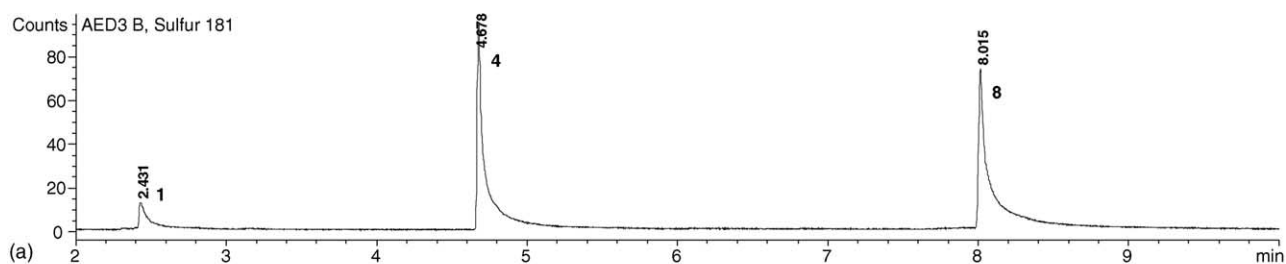


Fig. 7. Chromatograms of sulfur products of the reactions of mustard with NaBO_3 : (a) 5:1, (b) 20:1; $(\text{NH}_4)_2\text{S}_2\text{O}_8$, (c) 5:1, (d) 20:1; or H_2O_2 , (e) 5:1, (f) 20:1. (1) Divinyl sulfoxide, (2) unidentified compound, (3) divinyl sulfone, (4) vinyl-2-chloroethyl sulfoxide, (5) unconverted mustard, (6) vinyl-2-chloroethyl sulfone, (7) unidentified compound, (8) mustard sulfoxide, (9) unidentified compound.

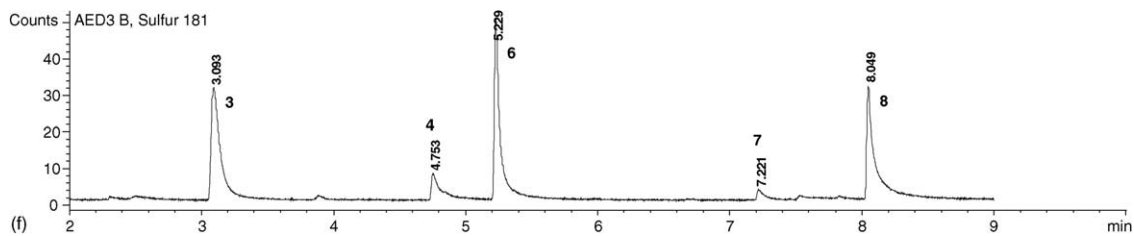


Fig. 7. (Continued).

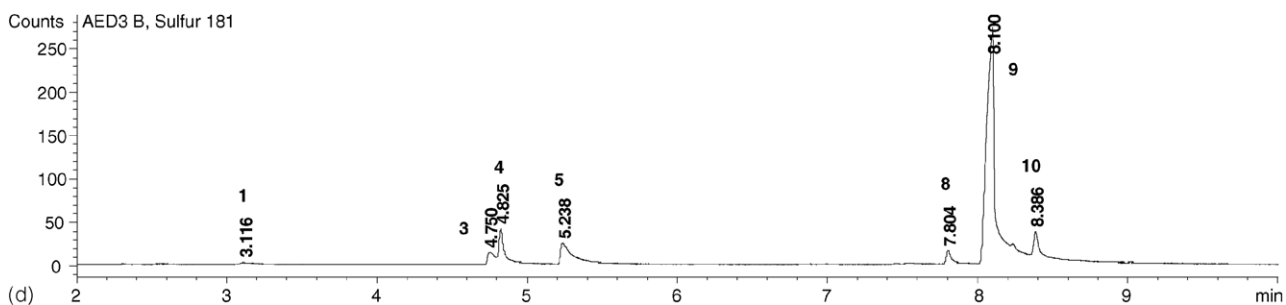
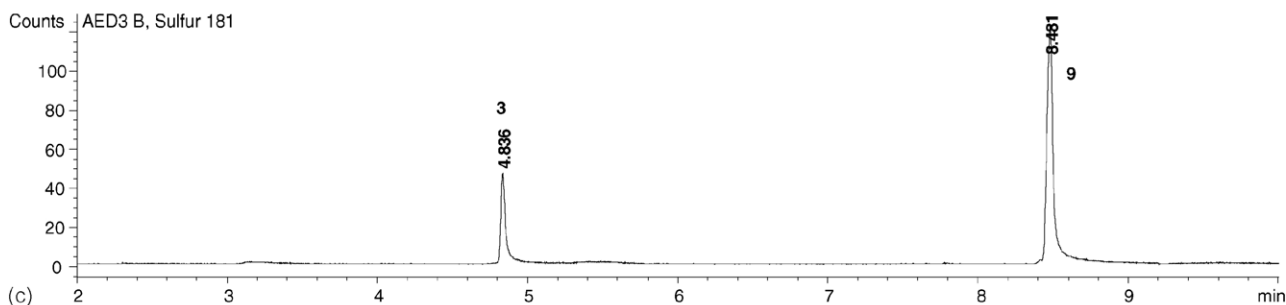
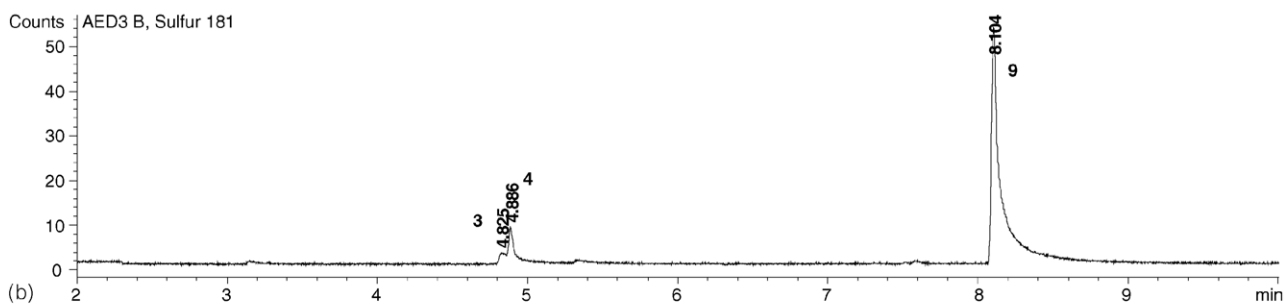
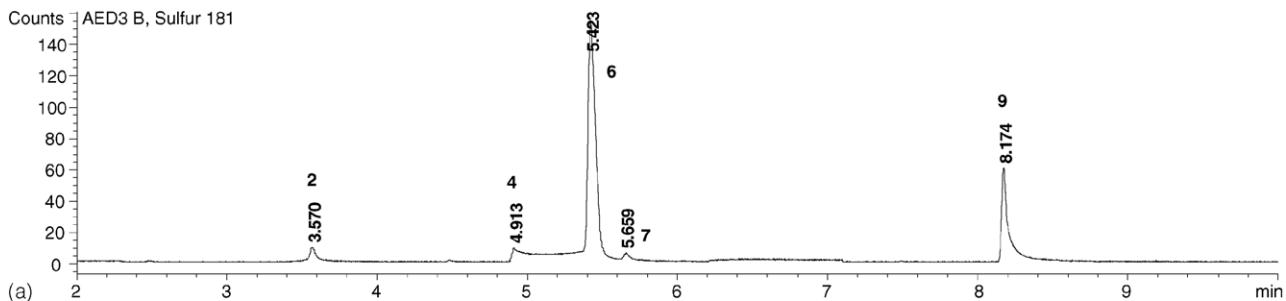


Fig. 8. Chromatograms of sulfur products of the reactions of mustard with H_2O_2 in solvents of various polarities: (a) HMPA, (b) water, (c) aqueous 15% 1-cyclohexyl-2-pyrrolidinone, (d) ethanol: (1) divinyl sulfone, (2) unidentified compound, (3) vinyl-2-chloroethyl sulfoxide, (4) unconverted mustard, (5) vinyl-2-chloroethyl sulfone, (6) vinyl-2-hydroxyethyl sulfone, (7) unidentified compound, (8) mustard sulfone, (9) mustard sulfoxide, (10) 2-chloroethyl-2'-hydroxyethyl sulfone.

from a temperature of 80 to 270 °C at a rate of 10 °C/min. The final temperature of the column was maintained for 5 min (chromatography conditions I). Some chromatograms were recorded at temperatures raised from 82 to 110 °C at a rate of 1 °C/min; the final temperature was maintained for 10 min (chromatography conditions II).

For purposes of identification, the retention times and the elemental analyses of mustard oxidates were compared with those of standard specimens. Quantitative analyses were carried out by the absolute calibration method.

2.3.4. Determination of reaction rates

Mustard's half-value period ($t_{1/2}$), i.e. the time required for the concentration of mustard to decrease to one-half its original value in the oxidizing solution, was used to determine the mustard oxidation rate. Quantitative chromatographic analyses allowed to evaluate the percentual content of mustard in the reaction mixture and to calculate the fraction of the initial mustard content. As a result, curves were drawn of mustard concentrations in the reaction mixture as a function of time. An illustrative plot used to determine the mustard half-value period is presented graphically in Fig. 2.

3. Results and discussion

3.1. Mustard oxidation rate in relation to oxidant type

Mustard oxidation reactions with various oxidants are summarized in Table 1. In each case, the initial concentration ratio of the oxidant-to-mustard was 5:1 by moles. Preliminary experiments showed that, when the oxidant concentration exceeded five times the mustard concentration, the oxidation proceeded to completion and the solution continued to retain its oxidizing capability even after mustard had been entirely degraded. In the present studies, the initial mustard concentration was 0.0054 mmol/mL, which corresponds to the maximum solubility of mustard in water at 20 °C.

3.2. The effect of solvent polarity on mustard oxidation rate

Hydrogen peroxide was used to study the effect of solvent's polarity on mustard oxidation rate. In each experimental reaction mixture, the initial concentration of hydrogen

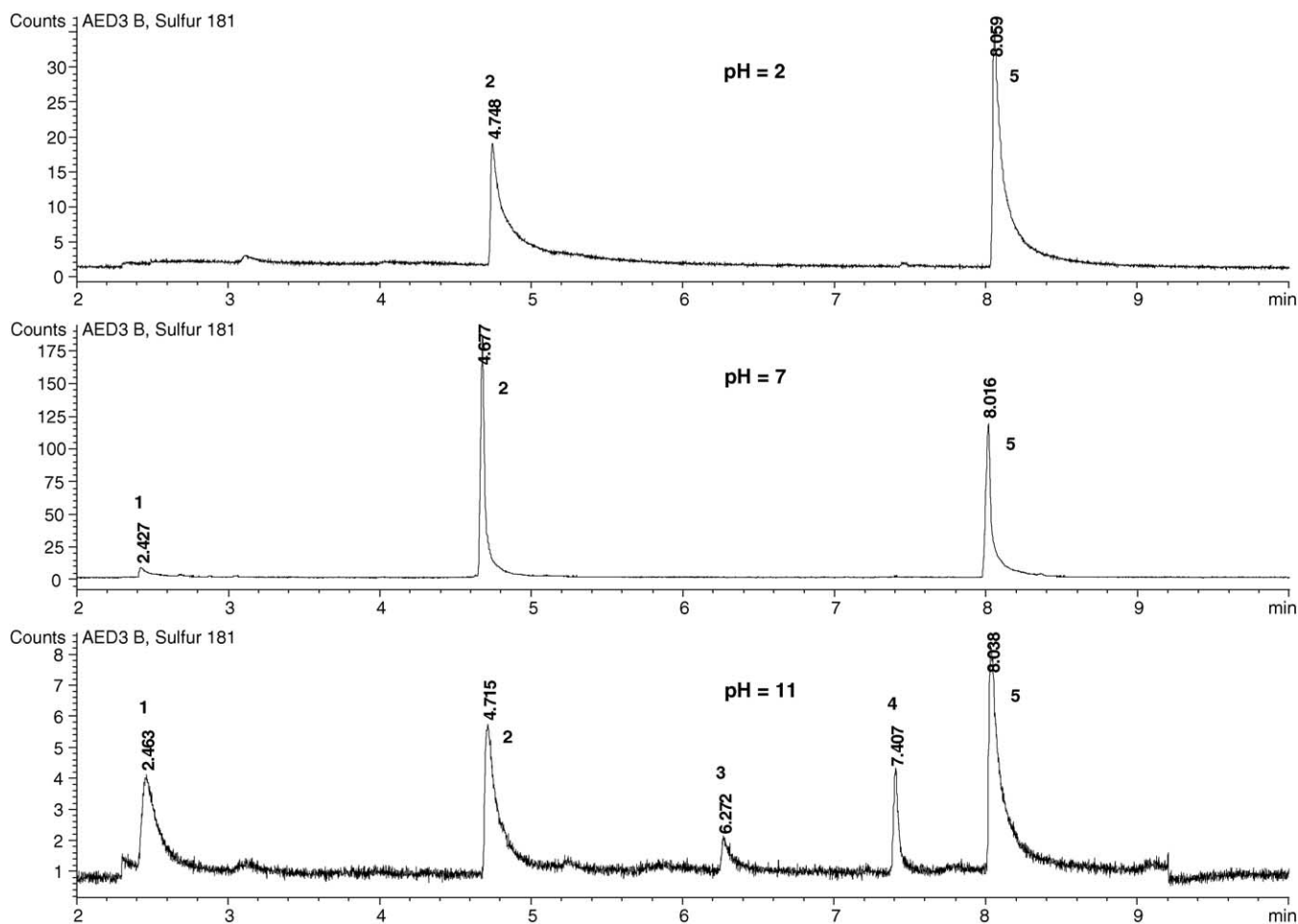


Fig. 9. The chromatograms of the sulfur channel compounds illustrating the transformations of mustard on oxidation with hydrogen peroxide in aqueous solutions of various pH. (1) Divinyl sulfoxide, (2) vinyl-2-chloroethyl sulfoxide, (3) unidentified compound, (4) unidentified compound, (5) mustard sulfoxide.

peroxide was 0.027 mmol/mL and the mole concentration ratio of the oxidant-to-mustard was 5:1. An increase in solvent's polarity, expressed in terms of the dipole moment of the solvent in which the reaction was run, was found to result in accelerated oxidation of sulfur mustard (Fig. 3).

To show more clearly, the mustard oxidation rate in relation to solvent polarity, dipole moments of the solvents used and the mustard half-value periods are summarized in Table 2.

3.3. The effect of pH on the rate of oxidation of mustard with hydrogen peroxide

Aqueous hydrogen peroxide solutions, pH 2, 7, and 11, were used to study the rate of oxidation of mustard at initial H_2O_2 concentration and $[\text{H}_2\text{O}_2]/[\text{mustard}]$ mole ratio of 0.027 mmol/mL and 5:1, respectively. Curves showing how mustard concentration decreased as a function of reaction time are presented in Fig. 4 at incremented pH values. Over

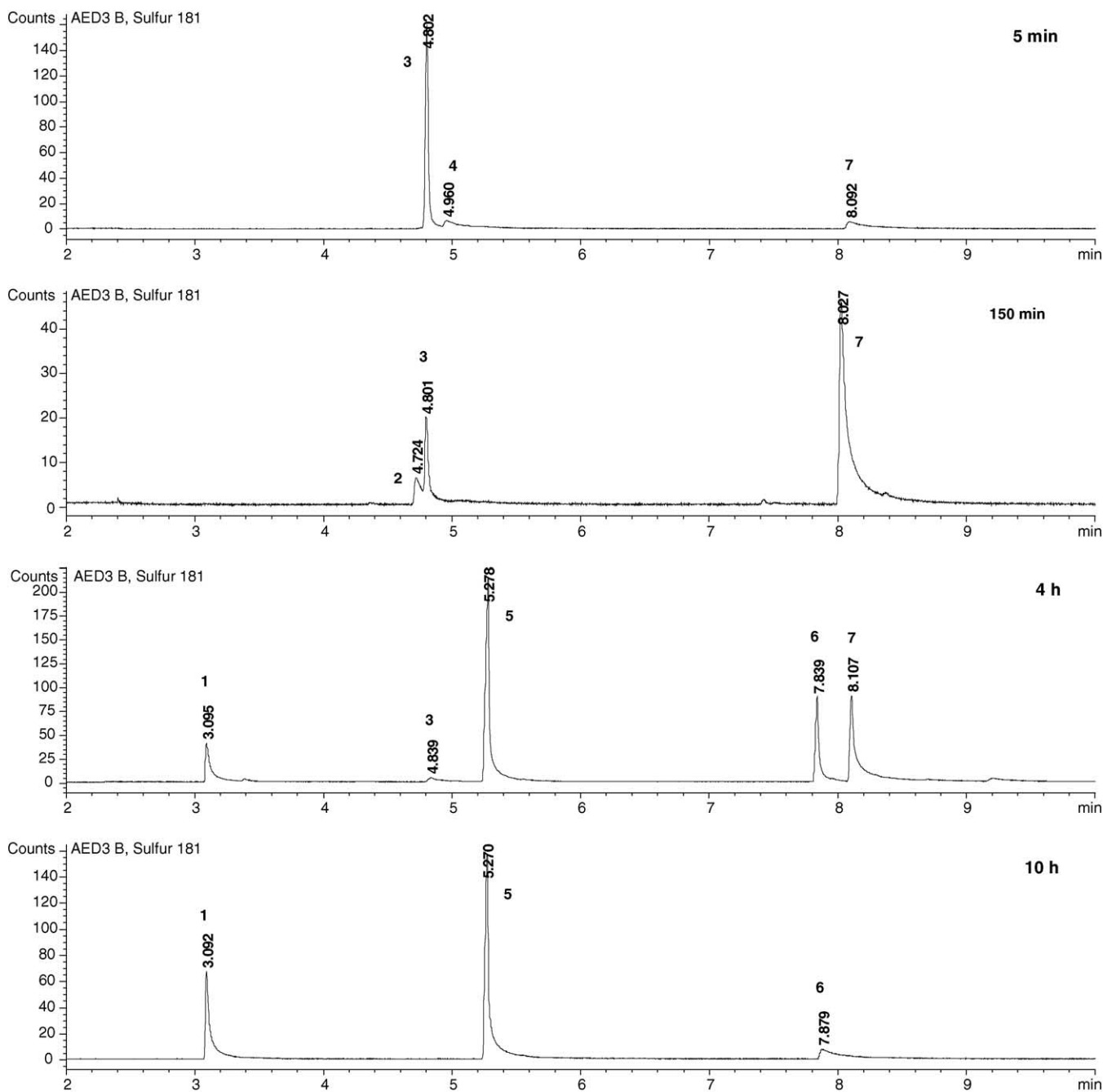


Fig. 10. The chromatograms of the sulfur channel compounds formed on oxidation of mustard with sodium monopercarbonate in relation to reaction time: (1) divinyl sulfone, (2) vinyl-2-chloroethyl sulfoxide, (3) unconverted mustard, (4) unidentified compound, (5) vinyl-2-chloroethyl sulfone, (6) mustard sulfone, (7) mustard sulfoxide.

pH 2–7, the mustard oxidation rates are seen to remain almost unaffected and, over pH 7–11, to decrease by a factor of nearly 3.

3.4. The effect of temperature on mustard oxidation rate

Mustard was oxidized with ethanolic hydrogen peroxide solution at temperatures of -25 , 0 , and $+20$ °C. The initial H_2O_2 concentration in ethanol was 0.027 mmol/mL. At each temperature, the initial $[\text{H}_2\text{O}_2]/[\text{mustard}]$ mole ratio was 5:1. Curves showing how mustard concentration decreased on oxidation at the specified temperatures are presented in Fig. 5.

At -25 and 0 °C, the oxidation rates were too slow to determine the half-value periods. At -25 °C, a non-freezing solution was required. Therefore, an alcoholic solution of H_2O_2 had to be used. In this solution, the mustard disappearance rate was rather low (cf. Point 3.2) and it would take too long to monitor its course until the half-value was attained and crossed.

3.5. The nature of mustard oxidation products in relation to oxidant nature

Reaction mixtures were analyzed for mustard oxidation products after the oxidation had been terminated (and mustard concentration fell below 1% of the initial value). Aqueous oxidant solutions were used. In each oxidation experiment, the initial oxidant-to-mustard concentration ratio was identical, 5:1 by moles. The initial concentration of the oxidant was in each experimental reaction system identical at 0.027 mmol/mL. Oxidation was carried out at 20 °C. Chromatograms of the reaction mixture components are presented in Fig. 6; the resulting groups of oxidation products are listed in Table 3.

With hydrogen peroxide, ammonium persulfate, sodium monopercarbonate, and sodium perborate used as oxidants, sulfoxides were the major oxidates formed under the experimental conditions. With sodium hypochlorite as oxidant used under identical conditions, mustard was oxidized to sulfonium compounds (to yield mainly vinyl-2-chloroethyl

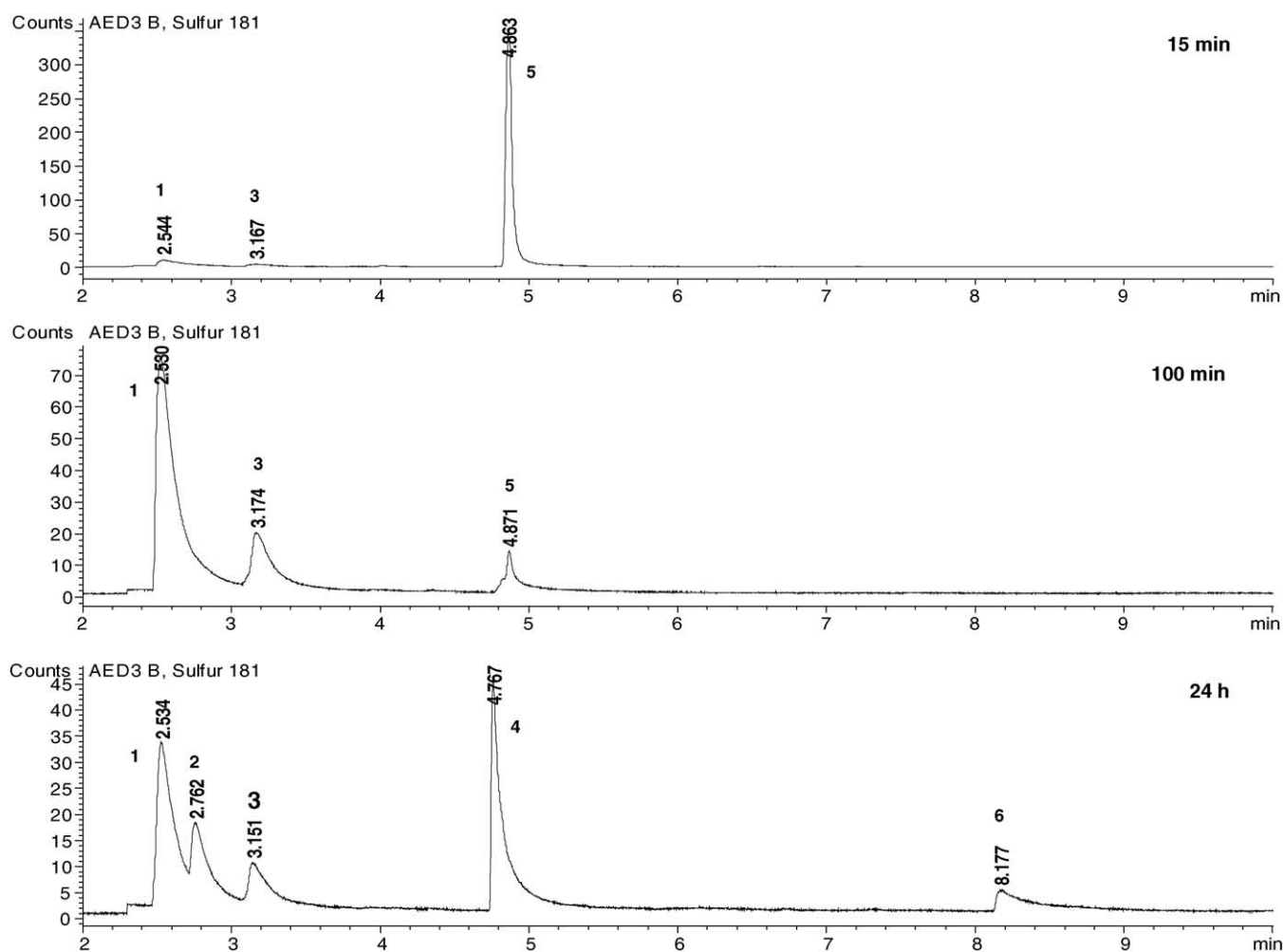


Fig. 11. The chromatograms of the sulfur channel products formed on oxidation of mustard with sodium perborate in relation to reaction time: (1) divinyl sulfoxide, (2) unidentified compound, (3) divinyl sulfone, (4) vinyl-2-chloroethyl sulfoxide, (5) unconverted mustard, (6) mustard sulfoxide.

sulfone and slight amounts of mustard sulfone and divinyl sulfone). Potassium peroxymonosulfate oxidized mustard mainly to vinyl 2-hydroxyethyl sulfone and to chloroethyl-2'-hydroxyethyl sulfone.

Analysis of the data presented in Table 3 and in Fig. 6 allows to conclude that, even if there is hardly any relation between the oxidant type and the nature of the resulting mustard oxidates, potassium peroxymonosulfate deserves special mention because it afforded products different from those obtained with the other oxidants.

The data listed in Table 1 can help us explain these results. They show the time to reach the half-value period of mustard oxidized with potassium peroxymonosulfate to be much shorter than the half-value period of mustard hydrolysis. Hydrolysis of mustard is well known to accompany the oxidation of mustard and to proceed as an independent process. In this situation, hydrolysis affords a considerable number of semimustard molecules, which are

almost immediately oxidized to yield semimustard sulfone (2-chloroethyl-2'-hydroxyethyl sulfone), which in a subsequent reaction is converted into the major product, viz., vinyl-2-hydroxyethyl sulfone. The remaining oxidants oxidize mustard slowly enough (cf. Table 1) to convert only a part of the mustard into thiodiglycol, and this fact allows products of oxidation of unhydrolyzed mustard to be detected. It should also be taken into account that hydrolysis of 2-hydroxyethyl-2'-chloroethyl sulfide is faster than is the hydrolysis of mustard and, therefore, no thiodiglycol oxidation products were found to occur under the present experimental conditions.

3.6. The type of mustard oxidates in relation to oxidant-to-mustard concentration ratio

NaBO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and H_2O_2 were used as oxidants in the mole ratio of 5:1 or 20:1 with respect to mustard (Fig. 7).

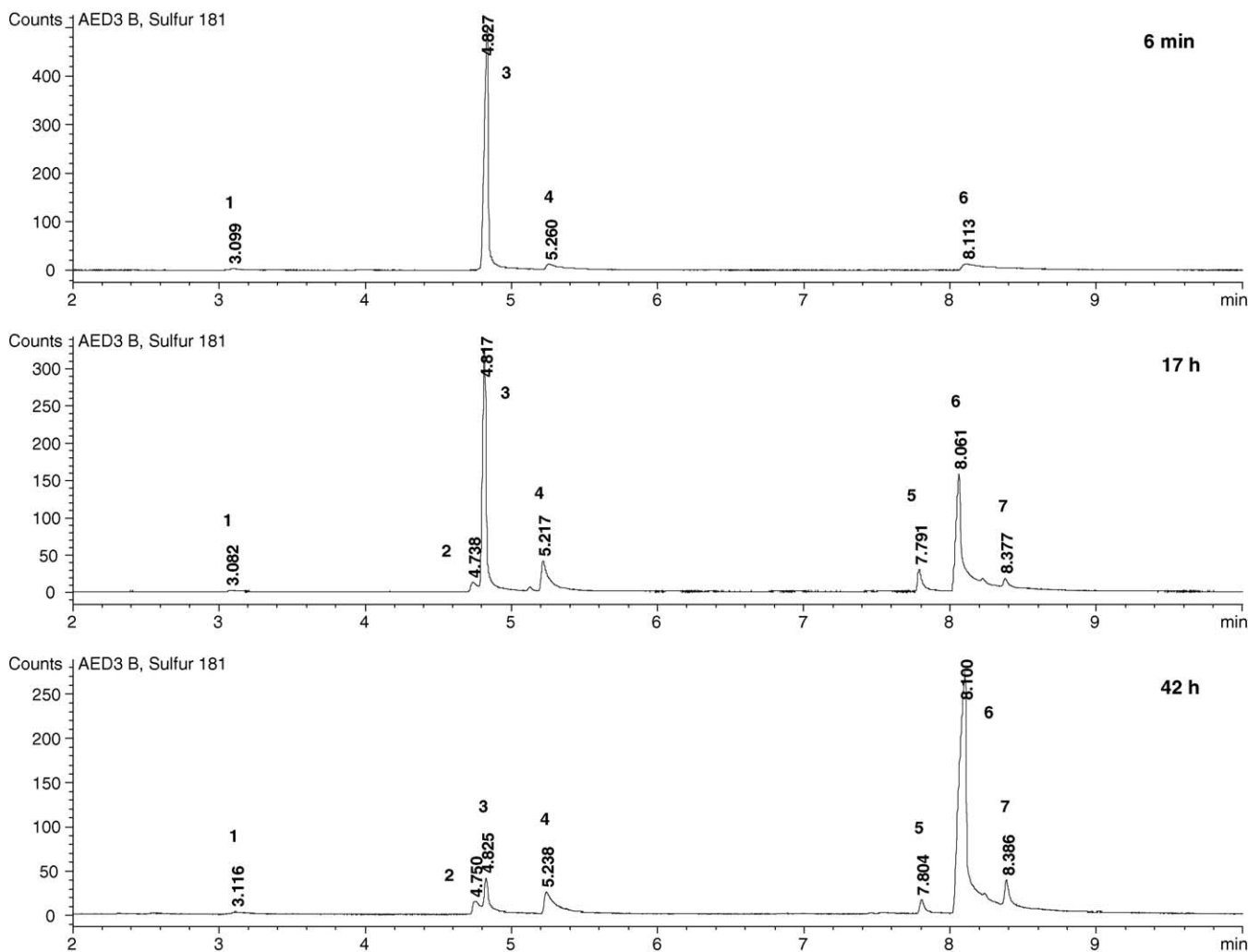


Fig. 12. The chromatograms of the sulfur channel compounds showing the effect of oxidation time on the nature of mustard oxidates formed with hydrogen peroxide in an ethanolic solution: (1) divinyl sulfone, (2) vinyl-2-chloroethyl sulfoxide, (3) unconverted mustard, (4) vinyl-2-chloroethyl sulfone, (5) mustard sulfone, (6) mustard sulfoxide, (7) 2-chloroethyl-2'-hydroxyethyl sulfone.

When used in the 20:1 and 5:1 ratios, these oxidants oxidized mustard primarily to sulfonic compounds and to mustard sulfoxide, respectively. This fact shows that the oxidant-to-mustard concentration ratio allows to control the type of the resulting mustard oxidates.

3.7. The type of mustard oxidates in relation to solvent polarity

The effect of solvent polarity on mustard oxidation rate has been described under Point 3.2. The effect of solvent

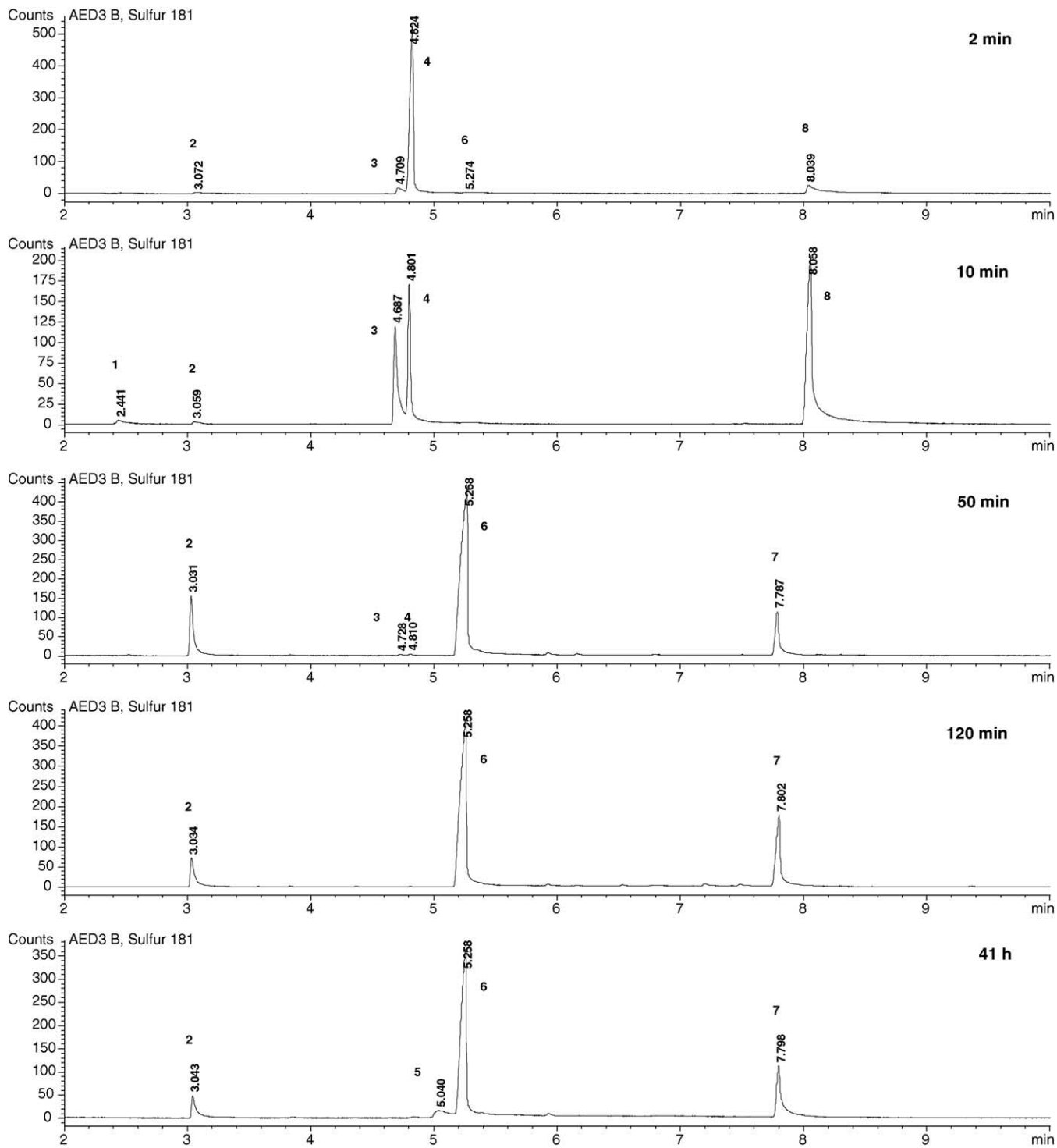


Fig. 13. The chromatograms of the sulfur channel compounds showing the effect of oxidation time on the nature of mustard oxidates formed with sodium hypochlorite: (1) divinyl sulfoxide, (2) divinyl sulfone, (3) vinyl-2-chloroethyl sulfoxide, (4) unconverted mustard, (5) unidentified compound, (6) vinyl-2-chloroethyl sulfone, (7) mustard sulfone, (8) mustard sulfoxide.

type was studied in the oxidation of mustard with hydrogen peroxide ($[\text{H}_2\text{O}_2]/[\text{mustard}] = 5:1$ by moles), carried out in several solvents. The initial concentration of hydrogen peroxide was 0.027 mmol/mL, and the initial concentration of mustard was 0.0054 mmol/mL.

The chromatograms (Fig. 8) show the oxidation of mustard with hydrogen peroxide run in water and ethanol as solvents to yield mainly mustard sulfoxide; and, with HMPA, mainly vinyl-2-hydroxyethyl sulfone; on the other hand, the oxidation run in the solution of 1-cyclohexyl-2-pyrrolidinone afforded mainly 2-chloroethyl-2'-hydroxyethyl sulfone.

3.8. The type of mustard oxidates in relation to pH of the oxidant solution

Fig. 9 shows the chromatograms recorded for the sulfur compounds from the sulfur channel produced on oxidation of mustard with aqueous hydrogen peroxide solutions of various pH-values. The initial concentrations of hydrogen peroxide and mustard were 0.027 and 0.0054 mmol/mL, respectively. Oxidation was continued until the content of mustard in the solution fell beneath 1% of the original concentration.

The chromatograms (Fig. 9) show the products formed in the neutral and acidic solutions to be quite similar; they include mainly mustard sulfoxide and vinyl-2-chloroethyl sulfoxide. In the acidic solution, mustard sulfoxide was transformed into vinyl-2-chloroethyl sulfoxide much more reluctantly than in the neutral solution. In the alkaline solutions, oxidation of mustard afforded more products, viz., three sulfoxides (2,2'-dichlorodiethyl, vinyl-2-chloroethyl, and divinyl) and two more compounds that could not be identified.

3.9. The type of mustard oxidates in relation to oxidation time and oxidant concentration

Four oxidants were selected for the study, viz., sodium monopercarbonate, sodium perborate, hydrogen peroxide, and sodium hypochlorite. In each case, water was used as solvent, and the experimental temperature was 20 °C.

Fig. 10 allows to conclude that oxidation of sulfur mustard with sodium monopercarbonate led in the first place mainly to the sulfones. Throughout the entire time of the reaction, divinyl sulfone and vinyl-2-chloroethyl sulfone were building up. At the final stage of the reaction, mustard sulfone and mustard sulfoxide appeared. This sulfoxide is likely to have been formed as a result of oxidation of successive amounts of mustard when the oxidant concentration was already depleted. Whereas mustard sulfone is likely to have formed because, at this stage of the oxidation, equilibrium was established in the solution and not all the molecules of the ever-forming sulfone could be transformed into vinyl-2-chloroethyl sulfone and then into divinyl sulfone.

Sodium perborate (Fig. 11), from the very beginning of the reaction, oxidized mustard to yield mainly divinyl sulfoxide and divinyl sulfone. After some period of time, vinyl-2-

chloroethyl sulfoxide began to build up and its amount continued to increase throughout the entire reaction time. Mustard sulfoxide, too, was found to appear, but its transformation into the vinyl and divinyl derivatives was incomplete.

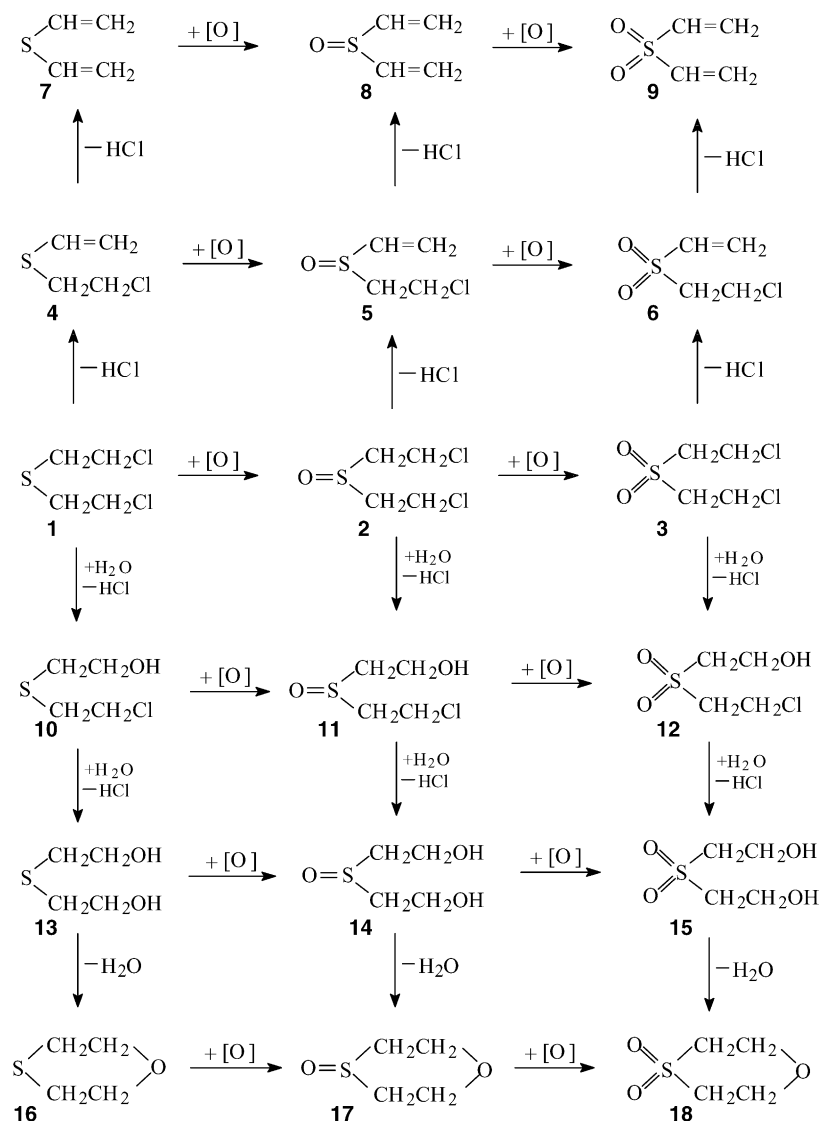
The chromatograms of Fig. 12 show mustard sulfoxide to be the major product formed on oxidation of mustard with hydrogen peroxide in an ethanolic solution at a relatively low initial concentration ratio ($[\text{H}_2\text{O}_2]/[\text{mustard}] = 5:1$ by moles). Sulfone compounds were formed, too, as minor by-products.

As evident from the chromatograms of Fig. 13, sodium hypochlorite oxidized mustard first to the sulfoxides and later, after the whole mustard had been oxidized, the reaction mixture contained mainly three sulfones. Such a composition of the reaction mixture was found to occur in 50 min of the reaction time.

4. Summing up and conclusions

A general scheme (Schemes 1 and 2: part I, part II) was developed to depict the mustard transformations occurring in aqueous oxidant solutions. The organosulfur compounds grouped in columns represent sulfides, sulfoxides and sulfones in due succession. In aqueous oxidant solutions, sulfur mustard can undergo hydrolysis (downward arrows in the scheme), oxidation (horizontal arrows), and elimination of hydrogen chloride (upward arrows). Mustard hydrolysis products undergo oxidation, too. Mustard oxidates can in turn undergo elimination of hydrogen chloride, which, however, does not rule out further oxidation reactions as a possibility.

The solutions of strong oxidants were found to be extremely reactive toward mustard. They resulted in a nearly immediate oxidation of this sulfide to the sulfone. The oxidation afforded compounds in which the hydrogen atoms bound to α -carbon atoms became fairly mobile and were rapidly eliminated together with the chlorine atoms. As a result, the 2-chloroethyl groups were converted to yield vinyl groups. These are fast consecutive reactions, which occur from the very beginning of mustard oxidation reactions to yield divinyl sulfone. As the reaction time is protracted, hydrogen chloride concentration rises and, as a result, its elimination reaction slows down. Since the reaction of mustard oxidation continues to proceed with a fairly high yield, the amount of vinyl-2-chloroethyl sulfone continues to rise and finally an equilibrium condition becomes established between the three sulfones (divinyl, vinyl-2-chloroethyl and 2,2'-dichlorodiethyl). After a period of time, when the concentration of the oxidant is much lower, the sulfoxides start to appear in the reaction mixture, viz., divinyl, vinyl-2-chloroethyl and 2,2'-dichlorodiethyl. Chemically, the sulfoxides are much more stable than are the sulfones and that is why the reaction mixtures contain mainly 2,2'-dichlorodiethyl sulfoxide because from the molecules of this compound hydrogen chloride is eliminated much less rapidly than it is from the sulfone molecules.



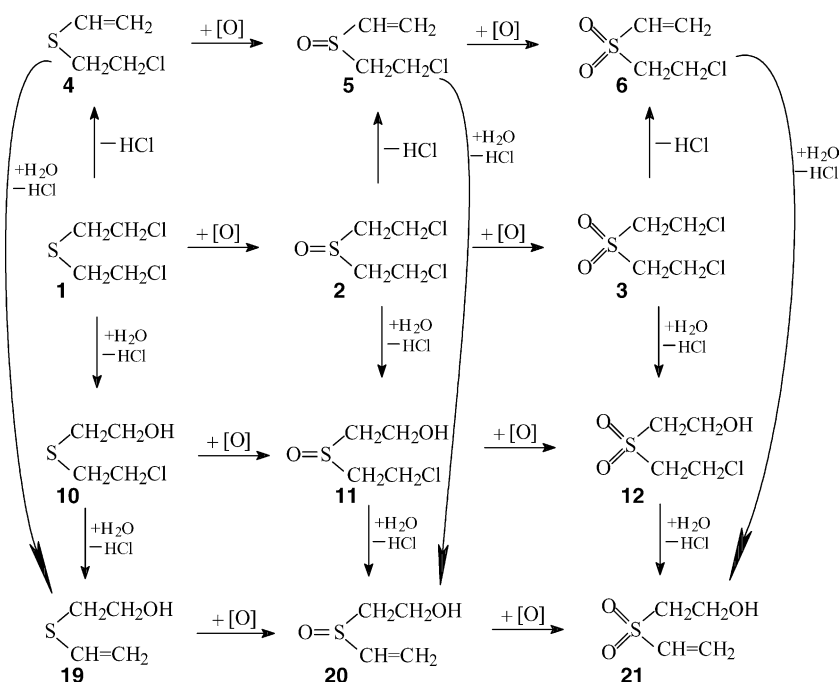
Scheme 1. Sulfur mustard transformations in aqueous oxidant solutions (part I). The names of the compounds from this scheme are given in the part II of this scheme.

The final product of mustard oxidation shown in the scheme is divinyl sulfone. This compound is likely to enter into further oxidation reactions (to yield gaseous products), but these processes go already beyond the scope of the present study.

A gas chromatograph coupled with an atomic emission detector enabled the sulfur mustard transformations caused by oxidants to be studied qualitatively and quantitatively. The following conclusions could thus be deduced:

- The rate of oxidation is strongly related to oxidant type. The fast-acting oxidants include potassium peroxydisulfate (Oxone) and sodium hypochlorite. The oxidants like sodium perborate, hydrogen peroxide, ammonium peroxydisulfate, and sodium monopercarbonate are moderate oxidants; *tert*-butyl peroxide is the slowest oxidant.

- Mustard oxidation rate is strongly controlled by the polarity of the solvent used as a reaction medium. The higher the solvent polarity, the faster the oxidation rate.
- In the acid and neutral media, mustard oxidation rates are comparable; in the alkaline medium, oxidation is evidently slower.
- A suitable choice of the initial oxidant-to-mustard concentration ratio allows to control the type of the resulting mustard oxidates.
- As the pH of the reaction medium is increased, the reaction of elimination of hydrogen chloride from mustard oxidates becomes more and more intensive.
- As a result of the hydrogen chloride elimination reaction, the β -chloroethyl sulfones are converted into vinyl derivatives much faster than β -chloroethyl sulfoxides. This finding contradicts the reported statement: “in a basic medium



Scheme 2. Sulfur mustard transformations in aqueous oxidant solutions (part II). (1) Sulfur mustard, (2) mustard sulfoxide, (3) mustard sulfone, (4) vinyl-2-chloroethyl sulfide, (5) vinyl-2-chloroethyl sulfoxide, (6) vinyl-2-chloroethyl sulfone, (7) divinyl sulfide, (8) divinyl sulfoxide, (9) divinyl sulfone, (10) 2-chloroethyl-2'-hydroxyethyl sulfide, (11) 2-chloroethyl-2'-hydroxyethyl sulfoxide, (12) 2-chloroethyl-2'-hydroxyethyl sulfone, (13) thiodiglycol (TDG), (14) TDG sulfoxide, (15) TDG sulfone, (16) 1,4-thioxane, (17) 1,4-thioxane sulfoxide, (18) 1,4-thioxane sulfone, (19) vinyl-2-hydroxyethyl sulfide, (20) vinyl-2-hydroxyethyl sulfoxide, (21) vinyl-2-hydroxyethyl sulfone.

the reaction of elimination run faster for sulfoxides than for sulfones” [17].

- The qualitative composition of the mustard oxidation products was found to be hardly related to the oxidant type. On the other hand, this composition is strongly related to the physicochemical parameters of the oxidation reaction.

References

- [1] Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction. The Technical Secretariat of the Organization for Prohibition of Chemical Weapons (OPCW), The Hague, 1997.
- [2] S. Franke, P. Franz, G. Grümmer, W. Warnke, Lehrbuch der Militärchemie, vol. 2, Militärverlag der DDR, Berlin, 1977.
- [3] G.S. Pearson, R.S. Magee, Critical evaluation of proven chemical weapon destruction technologies (IUPAC Technical Report), Pure Appl. Chem. 74 (2002) 187–316.
- [4] Y.-C. Yang, Chemical reactions for neutralising chemical warfare agents, Chem. Ind. 9 (1995) 334–337.
- [5] A. Johnson-Winegar. The U.S. Chemical Demilitarization Program, Statement before the Senate Armed Services Committee, Subcommittee on Emerging Threats and Capabilities, U.S. Senate, 12 July 2001.
- [6] Government of the Russian Federation, Resolution No. 510 of 5 July 2001. On Making Amendments and Additions to the Resolution by the Government of the Russian Federation of March 21, 1996 (No. 305) on Approving the Federal Special Program “Chemical Weapons Stockpiles Destruction in the Russian Federation”. Available at <http://www.armscontrol.org>.
- [7] Report of the Mission Dispatched by the Secretary-General to Investigate Allegations of the Use of Chemical Weapons in the Conflict Between the Islamic Republic of Iran and Iraq. 25 April 1988. S/19823 and S/19823/Addendum 1; 20 July 1988. S/20060 and S/20060/Addendum 1; 25 July 1988. S/20063 and S/20063/Addendum 1; 19 August 1988. S/20134. United Nations, New York, 1988.
- [8] S. Khateri, M. Ghanei, S. Keshavarz, M. Soroush, D. Haines, Incidence of lung, eye, and skin lesions as late complications in 34,000 Iranians with wartime exposure to mustard agent, J. Occup. Environ. Med. 45 (2003) 1136–1143.
- [9] V. Murray, F. Goodfellow, Leading article. Mass casualty chemical incidents—towards guidance for public health management, Public Health 116 (2002) 2–14.
- [10] T. Okumura, K. Suzuki, A. Fuduka, A. Kohama, N. Takasu, S. Ishimatsu, S. Hinohara, The Tokyo sarin attack: disaster management Part 1: Community emergency response, Part 2: Hospital response, Part 3: National and international responses., Acad. Emerg. Med. 5 (1998) 613–628.
- [11] H. Wheeler, Chemical terrorism: the Japanese experience and lessons learnt, Chem. Incid. Rep. 14 (1999) 10–12.
- [12] E. Croddy, C. Perez-Armendariz, J. Hart, Chemical and Biological Warfare, Springer-Verlag, New York, 2002.
- [13] R.M. Black, B. Muir, Derivatisation reactions in the chromatographic analysis of chemical warfare agents and their degradation products, J. Chromatogr. A 1000 (2003) 253–281.
- [14] E.W.J. Hooijschuur, Ch.W. Kientz, U.A.Th. Brinkman, Analytical separation techniques for the determination of chemical warfare agents, J. Chromatogr. A 982 (2002) 177–200.
- [15] Y.-C. Yang, J.A. Baker, J.A. Ward, Decontamination of chemical warfare agents, Chem. Rev. 92 (1992) 1729–1743.
- [16] N.B. Munro, S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King, V. Hauschild, The sources, fate, and toxicity of chemical

- warfare agent degradation products, *Environ. Health Perspect.* 107 (1999) 933–974.
- [17] S. Franke, *Lehrbuch der Militärchemie*, vol. 1, Militärverlag der DDR, Berlin, 1977.
- [18] K.E. Jackson, β , β' -Dichloroethyl sulfide (mustard gas), *Chem. Rev.* 15 (1934) 425–462.
- [19] G.W. Wagner, Y.-C. Yang, Proceedings of the 1998 ERDEC Science Conference on Chemical and Biological Defense Research; U.S. Army Edgewood Chemical Biological Center, 1999.
- [20] K. Lohs, S.J. Lundin, T. Stock, The destruction of chemical weapons and chemical warfare agents, Stockholm International Peace Research Institute, Sweden, Stockholm, 1990.
- [21] S. Buda, E. Szczucki, *Chemia procesów odkażania (The Chemistry of Decontamination Processes—in Polish)*, WAT, Warsaw, 1981.
- [22] Y.-C. Yang, L.L. Szafraniec, W.T. Beaudry, F.A. Davis, A comparison of the oxidative reactivities of mustard (2,2'-dichlorodiethyl sulfide) and bivalent sulfides, *J. Org. Chem.* 55 (1990) 3664–3666.
- [23] E. Raber, R. McGuire, Oxidative decontamination of chemical and biological warfare agents using L-Gel, *J. Hazard. Mater.* B93 (2002) 339–352.
- [24] J.A. Dean (Ed.), *Lange's Handbook of Chemistry*, 14th ed., McGraw Hill Inc., New York, 1992.
- [25] W.M. Grant, V.E. Kinsey, Synthetic preparation of 2-chloro-2'-hydroxydiethyl sulfide, reaction with cysteine and valine, and measurement of reaction rate in aqueous media, *J. Am. Chem. Soc.* 68 (1946) 2075–2076.