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The reactions of sulfur mustard with the active components of organic decontaminants

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Abstract

Reactions of sulfur mustard with active components of decontaminants ORO and C9 (Polish abbreviations of organic decontaminating solutions) were studied and their products were identified by GC/AED. Quantitative determinations of individual products in the reaction mixtures allowed to evaluate the kinetic parameters of the mustard reactions. The major decontamination product was divinyl sulfide, the product of the elimination reaction. At certain proportions of mustard to the decontaminant's active component, substitution products were also formed.

Keywords: Sulfur mustard; Gas chromatography coupled with atomic emission spectrometry; Sodium alcoholates; Decontaminants; Products of elimination and substitution

1. Introduction

One of the methods used to destroy chemical warfare agents (CWA) involves decontamination. This method uses special substances to remove toxic agents from the contaminated surfaces of equipment and territory. These substances have been divided into two groups. Group one includes chemically inert substances (solvents, sorbents) which do not detoxicate the CWA agent, but only tend to remove it physically from the surface contaminated. Group two substances are much more important. They include chemically active compounds which react with the toxic agents to yield nontoxic or low-toxic products. They are termed the decontaminants. They are intended primarily for use under battle conditions, but can also be applied to destroy toxic agents in compliance with the provisions of the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction [1].

One decontaminants group includes organic decontaminants with alcoholates as active components. These decontaminants include Decontamination Solution 2 (USA DS2) [2] and its Polish equivalents named by symbols: ORO and C9 [3]. The reaction of sulfur mustard with the ORO and the C9 decontaminants in a nonaqueous medium yields substantially an identical final product, viz., divinyl sulfide, which is formed by the reaction of elimination [4,5]. At certain mustard-to-decontaminant weight ratios, substitution products are formed [6]. In the presence of water, at certain concentrations of mustard and water, substitution products are formed in amounts greater than those produced under nonaqueous conditions [4,6]. In an aqueous medium, the higher is the content of water in the medium, the less effective is the decontaminant. This is due to the fact that in alcohol-based solutions of alcoholates with water addition equilibrium between alcoholate and hydroxyl ions develops:

$$ROH + HO^- \rightleftharpoons RO^- + H_2O$$

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If water content in alcohol-based solution of alcoholate does not exceed 1%, this equilibrium is shifted to the right. Increase of water content in the solution leads to hydrolysis of alcoholate and reaction equilibrium is shifted to the left. In course of hydrolysis weaker base is formed, thus effectiveness of the decontaminant is decreased [7].

Some investigators [7,8] believe the formation of either substitution or elimination products to be related to the concentration of alcoholates in the reaction mixture. However, they have not specified the concentration range within which the reactions can be expected to follow the well-defined mechanisms.

This study is intended to identify the products formed in the reactions of sulfur mustard with the ORO and the C9 decontaminants active components at various mustard and active components concentrations.

To identify the products, gas chromatography coupled with atomic emission spectrometry was used. A gas chromatograph equipped with an atomic emission detector (GC/AED) is particularly useful, because it enables not only the components of a sample to be separated and their elemental composition to be determined, but also their approximate empirical formulas to be calculated [9–13].

2. Experimental

2.1. Reagents and equipment

Sulfur mustard (bis(2-chloroethyl) sulfide) was prepared by the Meyer method and distilled at 110 °C/2.4 kPa [7]. Caution: mustard is a potent vesicant and must be handled in a closed system or in a hood with a minimum velocity of 0.5 m/s.

The ORO decontaminant was obtained by dissolution of 2 weight parts of sodium in 25 parts of 2-aminoethanol, 28 parts of ethanol and 45 parts of diethylenetriamine. The C9 decontaminant was obtained by dissolution of 4 weight parts of sodium in 30 parts of 2-aminoethanol and 66 parts of 2-ethoxyethanol.

The ORO active components include sodium aminomonoethanolate and sodium ethanolate. The C9 active components include sodium aminomonoethanolate and sodium 2-ethoxyethanolate. In the ORO, the concentrations of the active components were: 7.2% sodium aminomonoethanolate in monoethanolamine and 5.9% sodium ethanolate in ethanol; in the C9, 14.4% sodium aminomonoethanolate in monoethanolamine, and 19% sodium 2-ethoxyethanolate in 2-ethoxyethanol. The concentrations of the active components correspond to the amounts of the alcohols that would completely react with the amount of sodium used to prepare the decontaminant. Ethanolic 20, 0.5 and 0.05% sodium ethanolate solutions were also used in this study.

Merck's reagent-grade dichloromethane was used. Sodium ethanolate, sodium aminomonoethanolate and sodium 2-ethoxyethanolate were prepared by making ethanol, aminoethanol and 2-ethoxyethanol react with sodium.

A Hewlett-Packard HP 6890 gas chromatograph coupled with an HP G2350A model atomic emission detector was used. An HP-5 capillary column was used, 30 m long and 0.25 mm in internal diameter, provided with a (5:95 w/w) diphenyl-dimethyl-polysiloxane film, 0.25 μm thick.

2.2. Procedure to run the reactions of sulfur mustard with active components of the ORO and C9 decontaminants

To an ORO or C9 active component, 30 mL, in a solution of the generic alcohol (e.g., sodium ethanolate in ethanol) which was placed in a 100 mL thermostated vessel, the whole amount of mustard was added at once using microsyringe and the mixture was stirred magnetically. A similar procedure was used for a mixture of the active components. All investigations on mustard reactions with decontaminants were performed at temperature 20 °C.

The amount of mustard added was 0.1, 0.2, 0.4, 0.7 or 1 mmol/1 mL of the active component solution. To an ethanolic 20, 0.5 or 0.05% sodium ethanolate solution, mustard was added in an amount of 0.2 mmol/1 mL sodium ethanolate solution. In a part of this study involving the 0.5 and 0.05% solutions, reactions were run by using the stoichiometric amount of mustard (1 mol mustard per 2 mol alcoholate).

Samples for analysis were withdrawn in 4, 16, 32, 64, 128, 256, 512 min (8.5 h) and 24, 48 and 168 h reckoned from the moment of addition of mustard to the decontaminant.

2.3. Preparation of samples for chromatographic analysis

Liquid–liquid extraction technique 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 one. 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, shaked 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. The preparation of samples for chromatographic analysis was detaily described elsewhere [4].

2.4. Chromatographic analysis

The dichloromethane extracts containing the products of mustard-decontaminant reactions were analyzed by

GC/AED. The conditions of chromatographic analysis were following: cavity plasma temperature, 270 °C; injector temperature, 260 °C; time of solvent removal from column, 0.9–2.1 min; helium carrier gas flow rate, 2 mL/min. The following reaction gases were used: hydrogen, oxygen or (10:90 v/v) methane–nitrogen. The chromatographic column was maintained 3 min at 40 °C and then heated to 270 °C at a rate of 10 °C/min.

Atomic emission spectrometer was set up for the detection of following elements: carbon (496 nm), hydrogen (486 nm), chlorine (479 nm), sulfur (181 nm), nitrogen (174 nm) and oxygen (171 nm).

The components of the reaction mixture were identified by comparing their retention times with those of standard specimens and by calculating the empirical formulas from elemental analysis data. Quantitative analyses were carried out by the absolute calibration method.

3. Results and discussion

In each experiment, the initial concentration of mustard was identical, 0.2 mmol/mL active component solution. The ethanolate concentrations, 20, 0.5 and 0.05%, were intentionally different to enhance the effect of concentration of the active component on the course of its reaction with mustard according to a well-defined mechanism.

With the 20% solution, the reaction mixtures were found to contain elimination products (Fig. 1).

Vinyl 2-chloroethyl sulfide (2, t_R = 7.6 min) was formed in as soon as 4 min of the reaction time, and divinyl sulfide (1, t_R = 3.47 min), which is the final product of elimination, was found to appear in 64 min. In 256 min, the reaction mixture was found to contain no mustard (3, t_R = 11.91 min); it contained vinyl-2-chloroethyl sulfide (2) and divinyl sulfide (1).

Fig. 2 shows representative chromatograms of the products of mustard reactions with ethanolic 0.5 and 0.05% solutions of sodium ethanolate. With the 0.5% solution, the reaction mixture was found in 512 min to contain the elimination product (Fig. 2a), viz., vinyl-2-chloroethyl sulfide (1, t_R = 7.32 min), and the substitution product, viz., 2-chloroethyl-2′-ethoxyethyl sulfide (3, t_R = 12.1 min). The unconverted mustard (2, t_R = 11.7 min) was still present in a substantial amount. In 48 h, in addition to the two compounds mentioned above, a novel product, viz., a product of nucleophilic substitution, bis(2-ethoxyethyl) sulfide (4, t_R = 12.89 min), was found to appear.

Representative chromatograms of the products of mustard reactions with the 0.05% solution are shown in Fig. 2b. In 48 h, the reaction mixture was found to contain a substitution product, 2-chloroethyl-2′-ethoxyethyl sulfide (3). In 168 h, the reaction mixture contained 2-chloroethyl-2′-ethoxyethyl sulfide (3), the unconverted mustard (2), and vinyl-2-chlorethyl sulfide (1) in trace amounts.

Variations of the concentration of the nucleophilic agent are thus seen to result in modified mechanisms of the mustard decontamination reaction. High nucleophile concentrations (>2%) are seen to have favored the elimination reaction, the lower concentrations (e.g., ∼0.5%) promoted nucleophilic substitution that commenced to compete with the elimination reaction.

To check the mechanisms followed by the reactions of mustard with sodium ethanolate used in stoichiometric proportions, ethanolic 0.5 and 0.05% sodium ethanolate solutions were used. Results are shown in Fig. 3.

Chromatograms of the mustard reaction products formed with ethanolic 0.5% sodium ethanolate used in stoichiometric proportions are shown in Fig. 3a. In 16 min, the reaction mixture was found to contain the unconverted mustard (3, t_R = 11.4 min) and a substitution product, viz., 2-chloroethyl-2′ethoxyethyl sulfide (4, t_R = 11.8 min). In 32 min, an elimination product appeared, vinyl-2-chloroethyl sulfide (2, t_R = 6.89 min). In 256 min, in addition to the two sulfides mentioned above, the reaction mixture contained divinyl sulfide (1, t_R = 2.69 min). In 48 h, in addition to the compounds mentioned above, the reaction mixture contained also bis(2-ethoxyethyl) sulfide (5, t_R = 12.58 min).

With mustard and sodium ethanolate used in stoichiometric proportions, the reaction proceeding in ethanolic 0.5% sodium ethanolate solution is seen to follow parallel mechanisms of the elimination and of the nucleophilic substitution. With mustard and ethanolic 0.05% sodium ethanolate used in stoichiometric proportions (Fig. 3b), the reaction mixture was found to contain substitution products only.

With mustard used in excess, the substitution products were found to appear in 512 min, whereas with mustard used in stoichiometric proportions, they appeared already in 16 min. Divinyl sulfide (1) appeared (Fig. 3a) only in the stoichiometric mixture, viz., in 256 min in trace amounts and remained unchanged until the 48th hour of the reaction. With the 0.05% solution (in both the stoichiometric mixture and in the mixture with mustard used at 0.2 mmol/mL sodium ethanolate), only substitution products were found to have formed. Similarly as with the 0.5% solution, these products were earlier to form in the stoichiometric solutions.

These facts confirmed our previous findings concerning the reactions of sodium ethanolate with mustard used in a still higher excess over the amount of the active component, viz., 0.4 mmol/mL sodium ethanolate solution [7].

With mustard used in high concentrations with respect to the concentrations of the active components in the ORO decontaminant (0.7 and 1 mmol/mL ORO), nucleophilic substitution products were found to form [4]. This fact is consistent with the results of those studies in which sodium ethanolate (ORO active component) used at various concentrations, was made to react with the equivalent amount of mustard.

At high mustard concentrations added to the decontaminants, the mustard concentration fell initially very

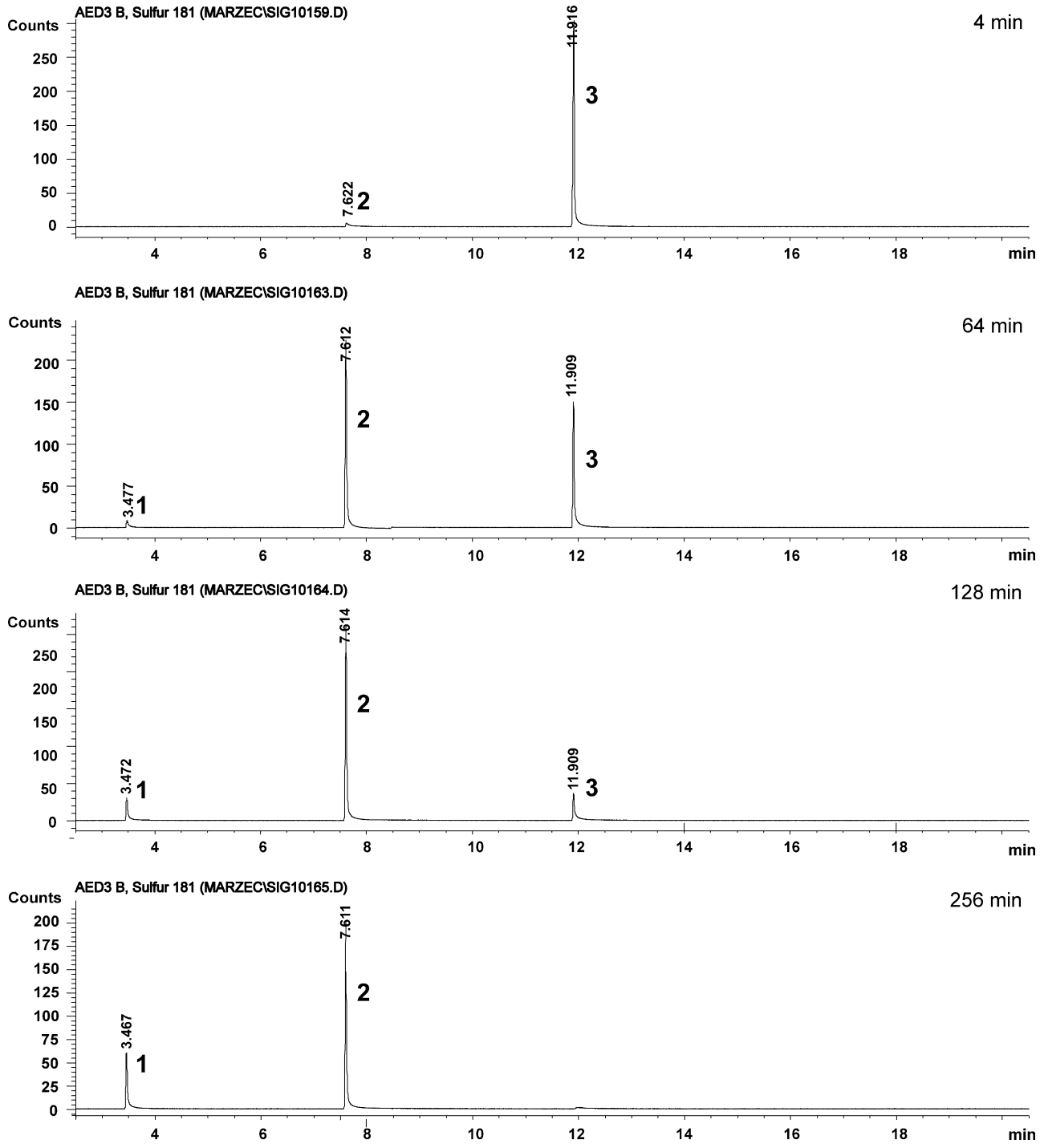


Fig. 1. Chromatograms of sulfur products of the reactions of mustard with ethanolic 20% sodium ethanolate solution at 20 °C: initial mustard concentration, 0.2 mmol/mL. (1) Divinyl sulfide, (2) vinyl-2-chloroethyl sulfide, and (3) mustard.

rapidly; then the reaction was slower and slower, and substitution products started to appear. The resulting substitution products are likely to promote further mustard transformations. The appearing of substitution products is related to the nucleophilic agent concentration. It was not observed to occur when the nucleophile concentration was high enough to make the elimination reaction proceed. Therefore, an experiment with sodium aminomonoethanolate, ORO and C9 second active component, was deemed worthwhile. This active component was used as a 7.2% solution in aminomonoethanol (concentration identical with that in ORO). The initial mustard concentration was 0.7 mmol/mL active component solution. Chromatograms of the products of the reactions of mustard with the sodium

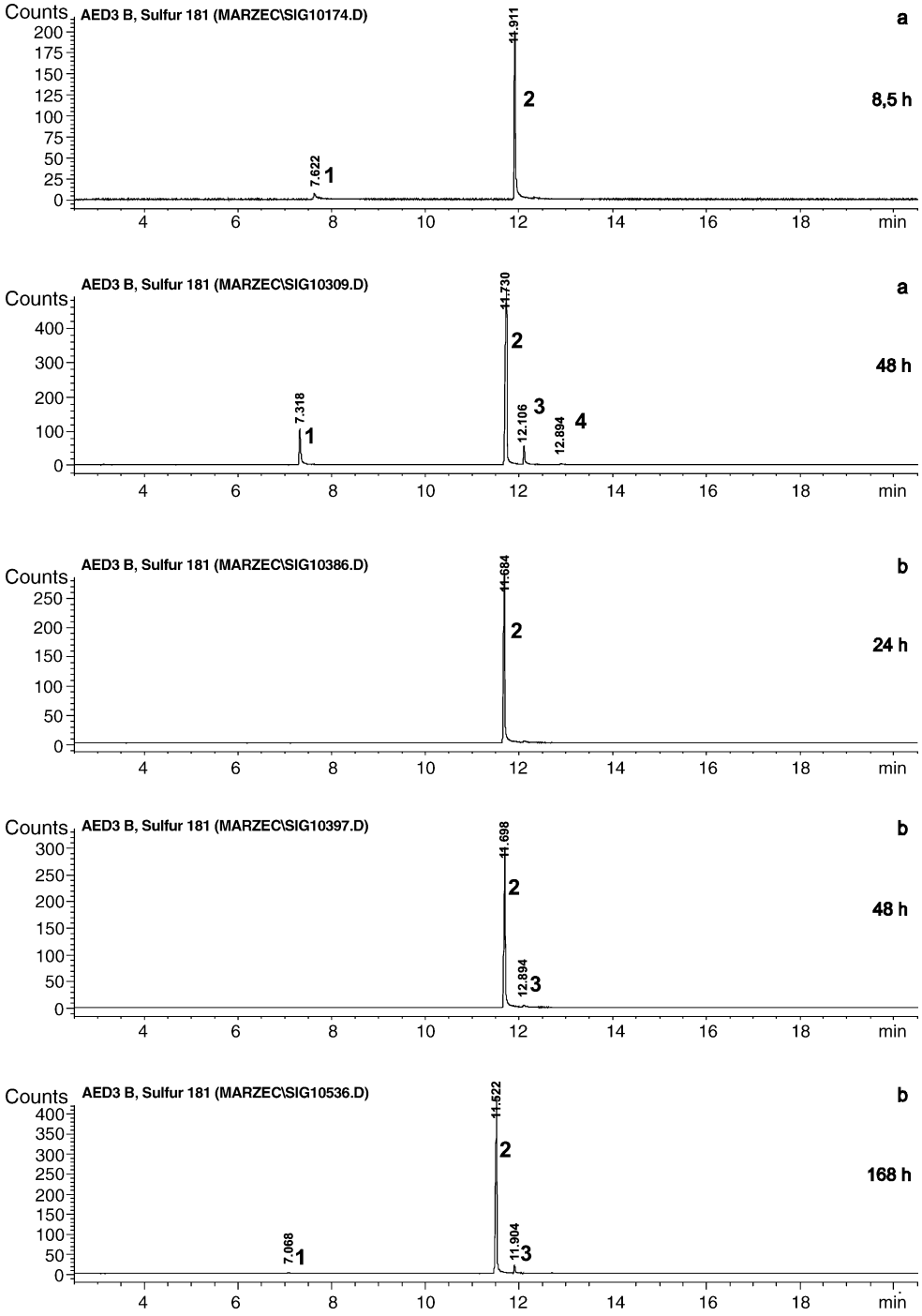


Fig. 2. Chromatograms of sulfur products of the reactions of mustard with ethanolic (a) 0.5% and (b) 0.05% sodium ethanolate solutions at 20 °C; initial mustard concentration, 0.2 mmol/mL. (1) Vinyl-2-chloroethyl sulfide, (2) mustard, (3) 2-chloroethyl-2′-ethoxyethyl sulfide, and (4) bis(2-ethoxyethyl) sulfide.

aminomonoethanolate solution specified above are shown in Fig. 4.

In 512 min, in the reaction mixture a substitution product was detected which contained no chlorine atom. This product was believed to be bis(2-*O*-aminoethyl)ethyl sulfide (4, t_R = 13.24 min) [4]. In 48 h, the reaction mixture contained no mustard; instead, it contained vinyl-2-chloroethyl sulfide (2, t_R = 7.22 min), divinyl sulfide (1, t_R = 3.0 min), and bis(2-*O*-aminoethyl)ethyl sulfide (4, t_R = 13.24 min). In 168 h, vinyl-2-chloroethyl sulfide was no longer present, but the remaining products continued to occur in the reaction mixture.

The studies carried out allow to conclude that, in a second stage of the reaction, its mechanism, S_N1 or E1, is related to the concentration of the nucleophile. In the solutions of low nucleophile concentrations, the nucleophilic S_N1 substi-

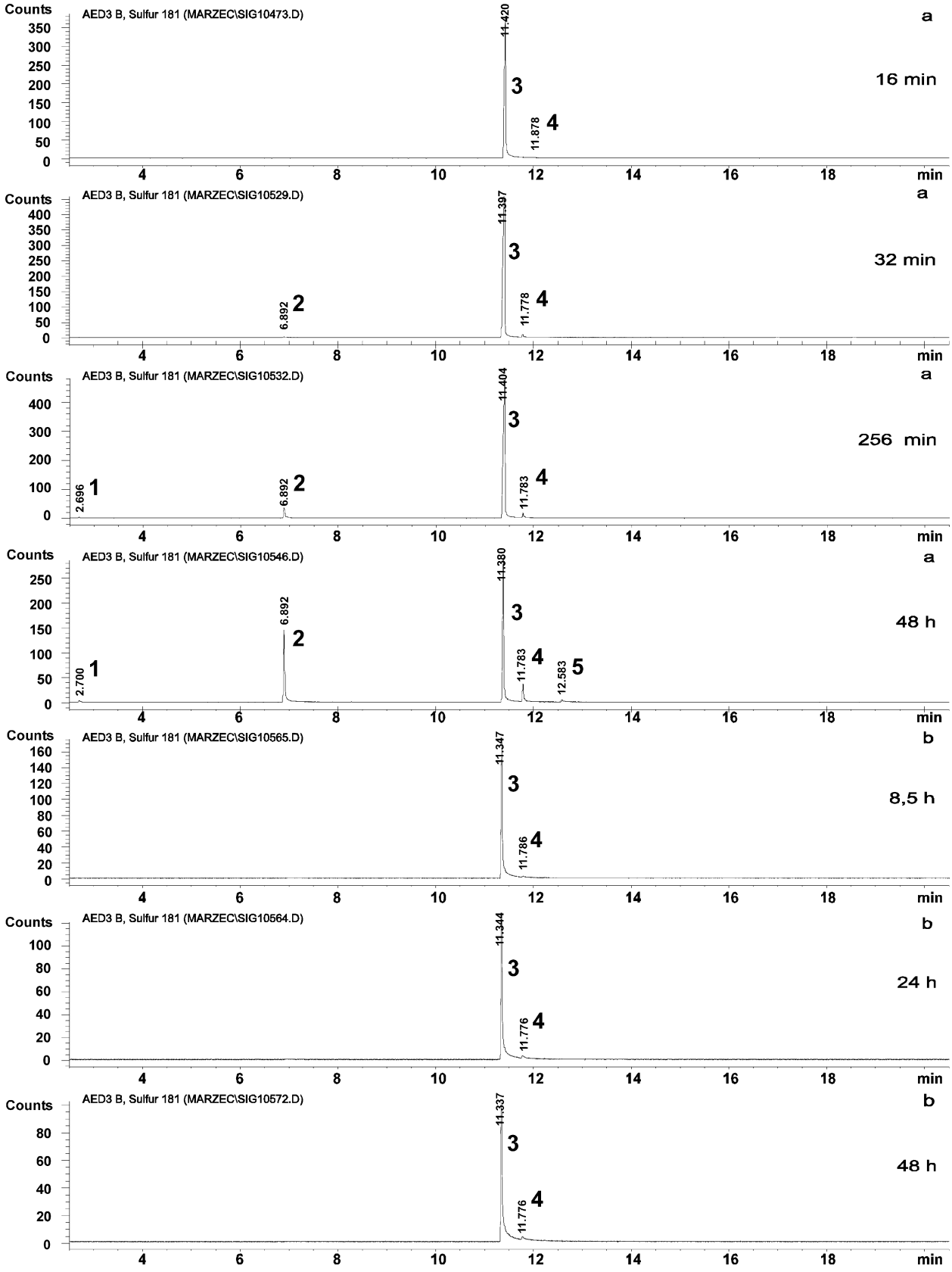


Fig. 3. Chromatograms of sulfur products of the reactions of mustard with ethanolic (a) 0.5% and (b) 0.05% sodium ethanolate solution used in stoichiometric proportions at 20 °C. (1) Divinyl sulfide, (2) vinyl-2-chloroethyl sulfide, (3) mustard, (4) 2-ethoxyethyl-2′-chloroethyl sulfide, and (5) bis(ethoxyethyl) sulfide.

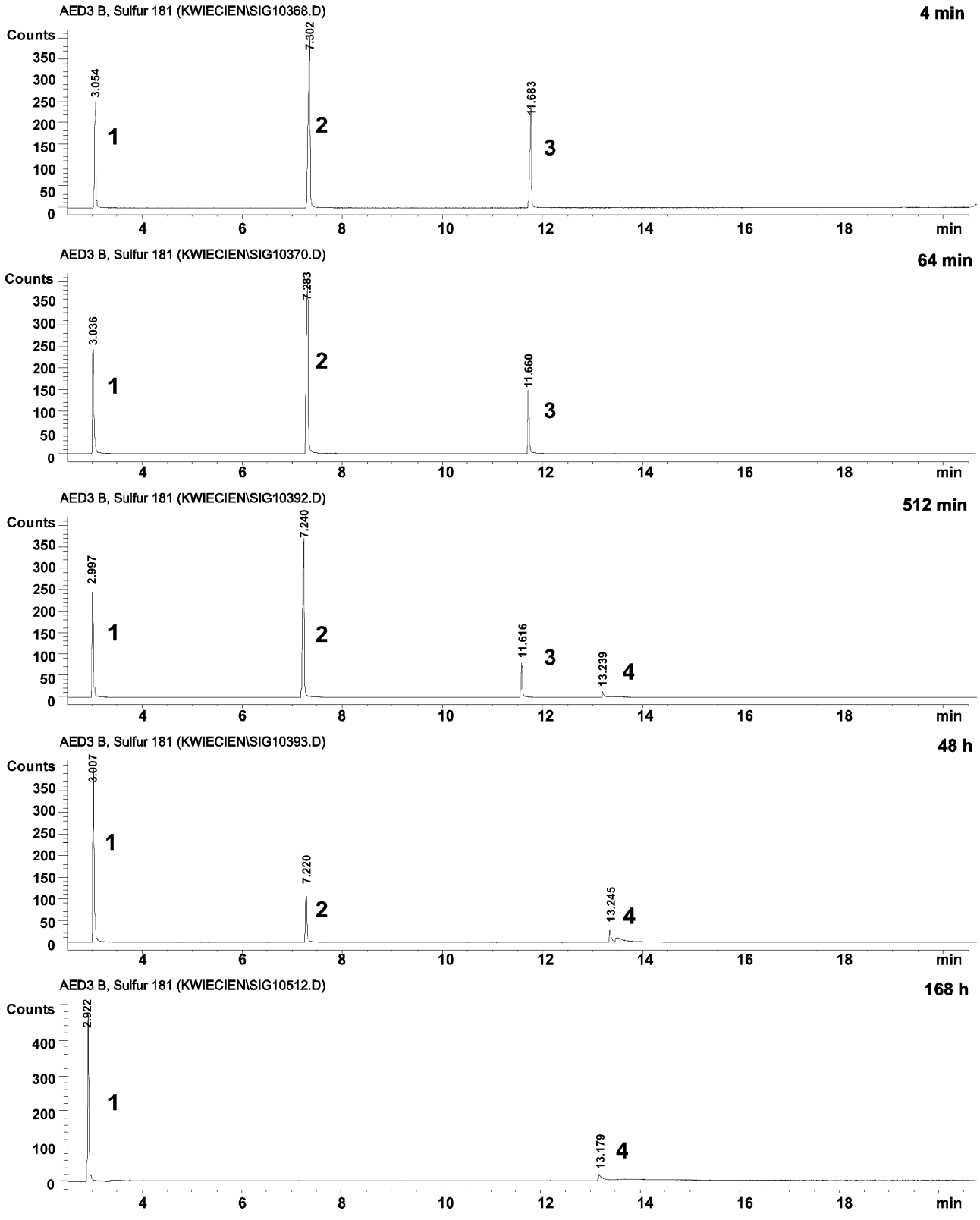


Fig. 4. Chromatograms of mustard reaction products formed with 0.7% sodium aminomonoethanolate in monoethanolamine at 20 °C. Initial mustard concentration, 0.7 mmol/mL active component solution. (1) Divinyl sulfide, (2) vinyl-2-chloroethyl sulfide, (3) mustard, and (4) bis(2-*O*-aminoethyl)ethyl sulfide.

tution is the favored reaction. In practice, this situation occurs only when the amount of the decontaminant is very low with respect to that of mustard.

The experiments described so far involved interactions of mustard with the individual active components of the ORO and C9 decontaminants. To see how mixtures of these components affect the nature of the resulting products in relation to component concentration, the following mixtures were prepared: (**I**) sodium aminomonoethanolate–sodium ethanolate and (**II**) sodium aminomonoethanolate–sodium 2-ethoxyethanolate; the ratios of the components were 0:100; 20:80; 40:60; 50:50; 60:40; 80:20; 100:0. A solution of 7.2% sodium aminomonoethanolate in monoethanolamine and a solution of 5.9% sodium ethanolate in ethanol were used to prepare type **I** mixtures; and a solution of 14.4% sodium aminomonoethanolate in monoethanolamine and a solution of 19% sodium ethoxyethanolate in 2-ethoxyethanol were used to prepare type **II** mixtures. The concentration of mustard was 0.2 mmol/mL for type **I** or **II** mixture. In the study of the effect of alcoholate concentration, the proportions of the weight concentrations of sodium aminomonoethanolate to sodium 2-ethoxyethanolate were: 3.03; 1.44; 0.76; 0.51; 0.19 and the proportions of sodium aminomonoethanolate to sodium ethanolate were: 4.88; 1.83; 1.22; 0.81; 0.31.

Representative chromatograms of the mustard reaction products formed with mixture **II** in 4 min are presented in Fig. 5.

The products included were divinyl sulfide (1, t_R = 3.45 min) and vinyl-2-chloroethyl sulfide (2, t_R = 7.62 min). As the proportion of sodium aminomonoethanolate was reduced, the rate of fall of the mustard (3, t_R = 11.91 min) concentration in the reaction mixture decreased. The results of investigation allowed to suppose that the percentual composition of the active components in the C9 decontaminant is likely to be ca. 10% sodium aminomonoethanolate and ca. 90% sodium 2-ethoxyethanolate.

It is important to establish the actual content of the active components in the decontaminants, because the procedure used to prepare the ORO and the C9 decontaminants is to react sodium with the two alcohols and not with each alcohol individually. In such mixtures, the ratio of the concentrations of the resulting alcoholates remains unknown.

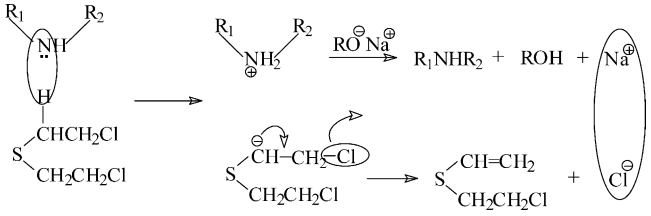
Fig. 5 shows the products formed in 4 min, viz., divinyl sulfide (1) and vinyl-2-chloroethyl sulfide (2), to be the products of elimination. After longer reaction times the products remained identical. With the 50:50, 40:60 and 20:80 sodium aminomonoethanolate–sodium ethanolate (type **I**) mixtures, vinyl-2-chloroethyl sulfide was detected in 8, 16 and 32 min. With sodium ethanolate (sodium aminomonoethanolate absent), in addition to the products of elimination, a small amount of the nucleophilic substitution product was found to occur in 64 min of the reaction.

Similarly as with the C9 decontaminant active components, with the ORO active components the rate of fall of mustard concentration was found to diminish as the amount of sodium aminomonoethanolate was decreased. Comparison of the contents of the reaction products formed by mustard with a mixture of active components of the ORO decontaminant with those formed in the reaction of mustard with the ORO, allowed to conclude that the percentage of the active components in the ORO decontaminant is as follows: 60% sodium aminomonoethanolate and 40% sodium ethanolate.

The results of the present study were also used to evaluate the half-life of mustard at 20 °C in the reaction with the active components studied. With sodium ethanolate (5.9%) as reactant, the half-value period was 193 min. With sodium aminomonoethanolate (7.2%), the half-value period was 3.5 min and with sodium aminomonoethanolate (14.4%) this period was shorter than 0.5 min. In the first case, the total time of decontamination of mustard to react with sodium aminomonoethanolate was about 8 min; in the second case the time was about 4 min. With the 19% sodium 2-ethoxyethanolate in 2-ethoxyethanol, the half-value period of mustard was 12 min.

Table 1 lists the concentrations of mustard and of the products formed by mustard with the ORO and the C9 decontaminant active components in relation to reaction time. Analysis of the data of Table 1 allows to conclude that sodium aminomonoethanolate, which is the component of both ORO and C9, is the major active component reacting with mustard. Compared with that, the remaining alcoholates are only slightly reactive (especially that sodium aminomonoethanolate is both an alcoholate and an amine). The results of the reactions of mustard with the types **I** and **II** mixtures allow to deduce that the percentages of sodium aminomonoethanolate in the ORO and in the C9 are about 4.3% and only about 1.4%, respectively.

With no diethylenetriamine (DETA) present in the ORO decontaminant, the mixture termed the "ORO without DETA" has been shown [4] to react with mustard more slowly than did the DETA-containing ORO decontaminant. If DETA is assumed to catalyze the reactions of mustard with the alcoholates, then the MEA (which is present in ORO) is the weaker catalyst than DETA. Thus, it is DETA that acts as an efficient catalyst in the ORO decontaminant. If the role of DETA and the concentrations of sodium aminomonoethanolate are taken into account, it becomes obvious why ORO is more effective than C9 as the decontaminant of mustard, even if more sodium is used to prepare the latter. The probable mechanism of the reaction of active components with mustard along with DETA is following:



The changes of ingredients concentration in mixture during the reaction of sulfur mustard with solution 20% sodium ethanolate in ethanol are presented in Fig. 6. The products of elimination are formed in the reaction.

The change of sulfur mustard concentration and the products of reaction with a mixture 14.4% sodium aminomonoethanolate in ethanol and 19.9% sodium 2-ethoxyethanolate in 2-ethoxyethanol in proportion 20:80 is presented in Fig. 7. Such a composition of alcoholates mixture is similar to the composition of C9 decontaminant.

Similarly as in the reactions of the ORO and the C9 decontaminants with mustard, the reactions of the active components of these decontaminants with mustard are first-order with respect to mustard but the kinetic of the reactions of formation of vinyl-2-chloroethyl sulfide and its conversion into divinyl sulfide is more complicated, probably of fractional-order.

The log (mustard concentrations) in relation to time of mustard reactions with ethanolic 20, 0.5 or 0.05% sodium ethanolate solution and with the 80:20 mixture of 7.2% sodium aminomonoethanolate in aminoethanol and ethanolic 5.9% sodium ethanolate solution are presented in Fig. 8 (in which this mixture is designated as M:E (80:20)). The 80:20 composition is close to that of the ORO decontaminant.

Comparison of the variations of mustard concentration in the reactions with this mixture, with ethanolic 20%

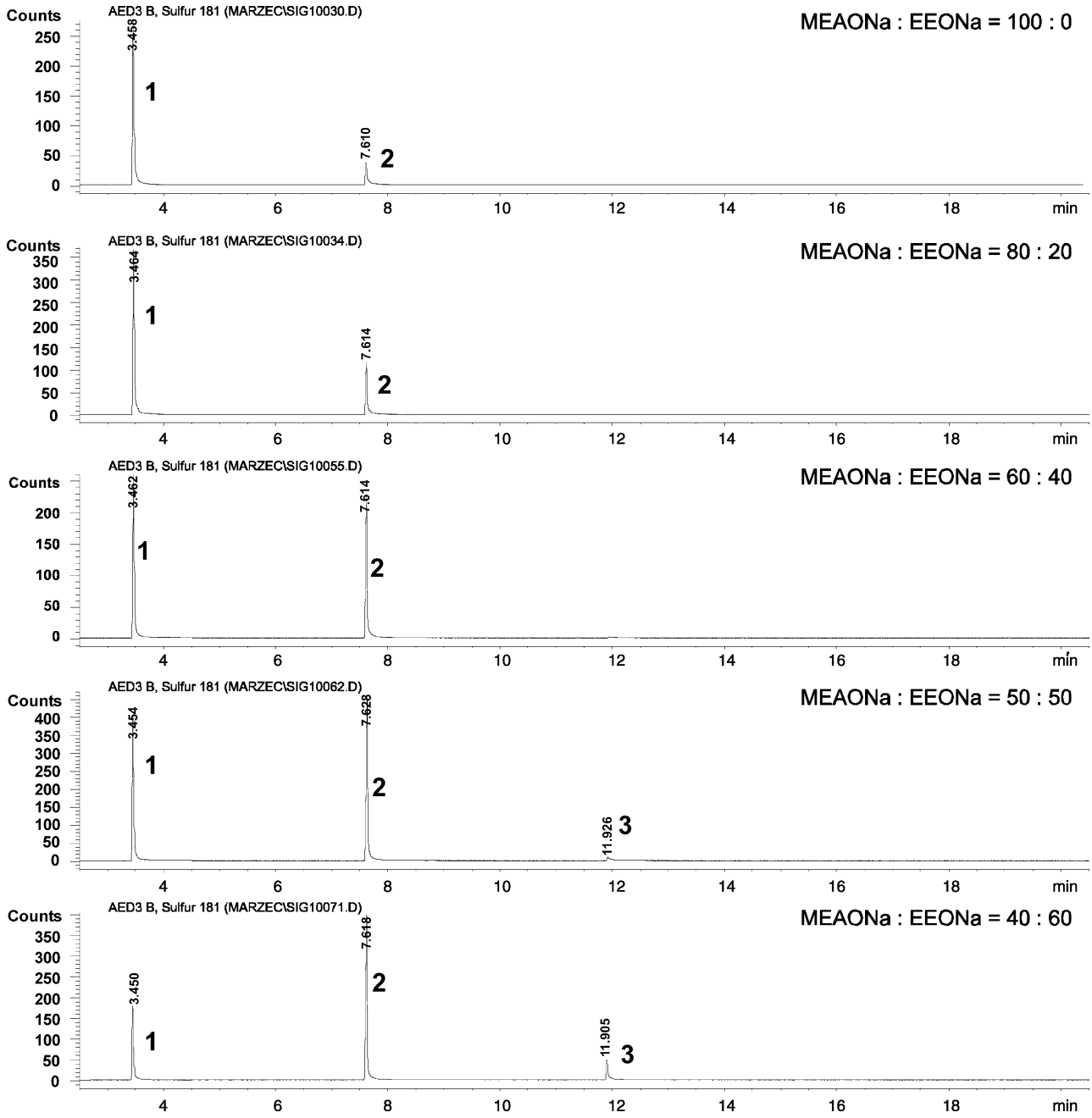


Fig. 5. Chromatograms of mustard reaction products formed with a mixture of sodium aminomonoethanolate (MEAONa) and sodium 2-ethoxyethanolate (EEONa) in 4 min at 20 °C. Initial mustard concentration, 0.2 mmol/mL. (1) Divinyl sulfide, (2) vinyl-2-chloroethyl sulfide, and (3) mustard.

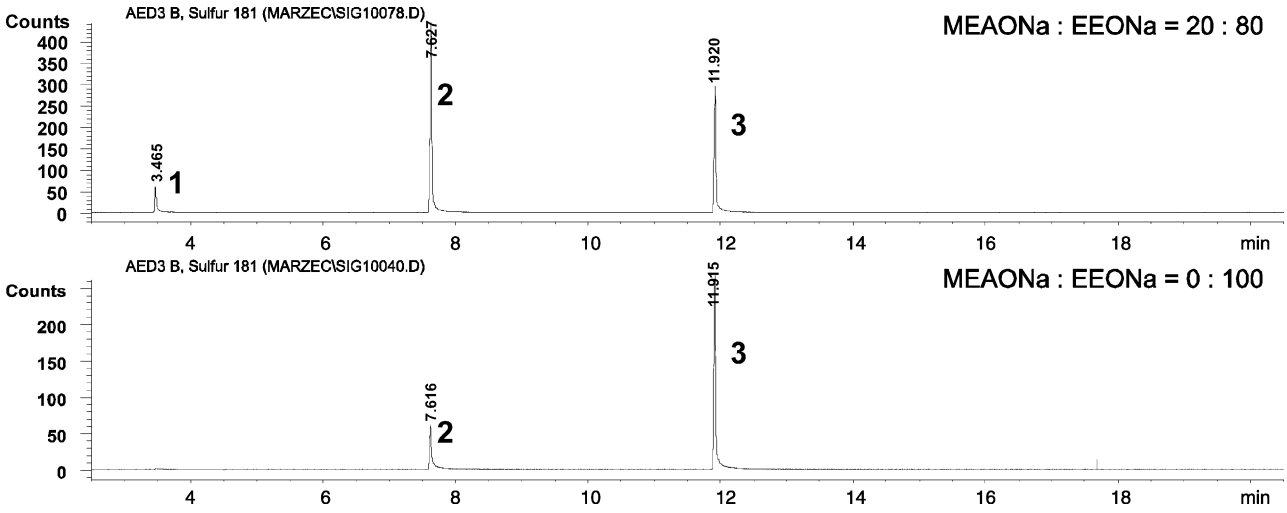


Fig. 5. (*Continued*).

sodium ethanolate and with ethanolic 0.5 and 0.05% sodium ethanolate solutions at 20 °C allows to conclude that their concentration has a considerable effect on the rate of the mustard reactions with the active components. This concentration governs the mechanism to be followed by the mustard decontamination reactions. At active component concentrations higher than 2%, elimination is the major mechanism and, once the concentration is diminished, the reaction rate decreases. At the concentration of 0.05% of sodium ethanolate in ethanol, nucleophilic substitution is the favored reaction. However, it is the elimination mechanism that is crucial for the decontamination process, because the decrement

Table 1
Percentages of mustard and of mustard reaction products formed with alcoholates in relation to reaction time

Reaction time (min)	Mustard and products of mustard reactions	Active component			
		$NH_2C_2H_4ONa$ (7.2%)	C_2H_5ONa (5.6%)	$NH_2C_2H_4ONa$ (14.4%)	$C_2H_5OC_2H_4ONa$ (19.0%)
		ORO		C9	
4	HD	8.1	99.8	0.0	79.0
	VCES	58.9	0.2	14.0	21.0
	DVS	33.0	0.0	86.0	0.0
8	HD	0.0	99.6	0.0	62.7
	VCES	47.1	0.4	0.0	37.3
	DVS	52.9	0.0	100.0	0.0
16	HD	0.0	99.4		40.0
	VCES	16.5	0.6		57.2
	DVS	83.5	0.0		2.8
32	HD	0.0	95.0		16.0
	VCES	0.0	5.0		75.0
	DVS	100.0	0.0		9.0
64	HD		72.5		0.0
	VCES		27.3		75.3
	DVS		0.0		24.7
	MEDM		0.2		0.0
128	HD		53.5		0.0
	VCES		46.0		56.4
	DVS		0.2		43.6
	MEDM		0.3		0.0
256	HD		38.3		0.0
	VCES		59.8		31.0
	DVS		1.5		69.0
	MEDM		0.4		0.0

HD: sulfur mustard, VCES: vinyl-2-chloroethyl sulfide, DVS: divinyl sulfide and MEDM: monoethoxy derivative of mustard.

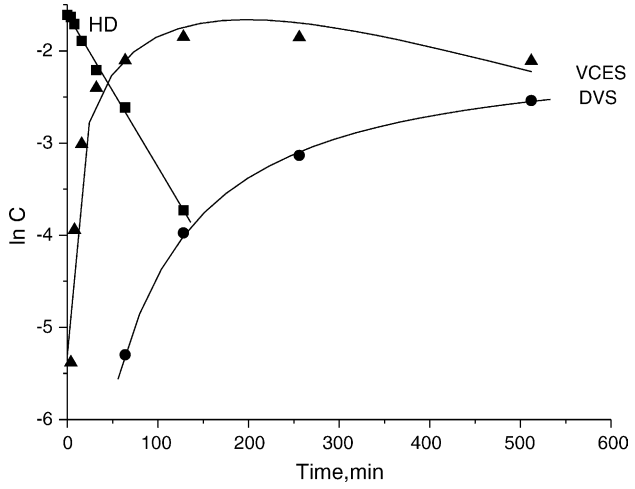


Fig. 6. The concentrations of mustard reaction products formed with ethanolic 20% sodium ethanolate solution in relation to time. Initial mustard concentrations, 0.2 mmol/mL; temperature, 20 °C. HD: unconverted mustard, VCES: vinyl-2-chloroethyl sulfide, DVS: divinyl sulfide.

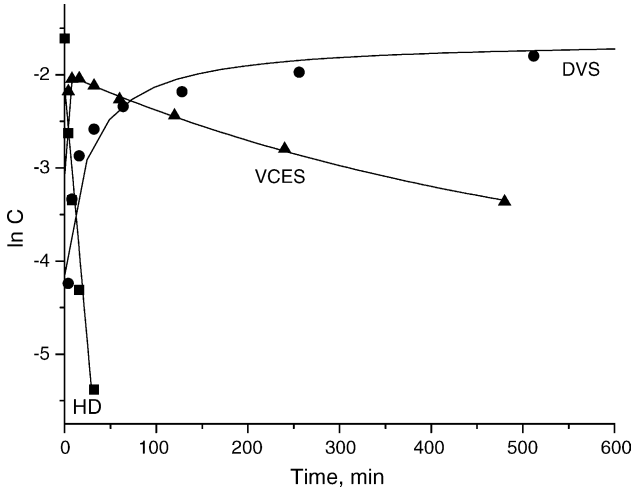
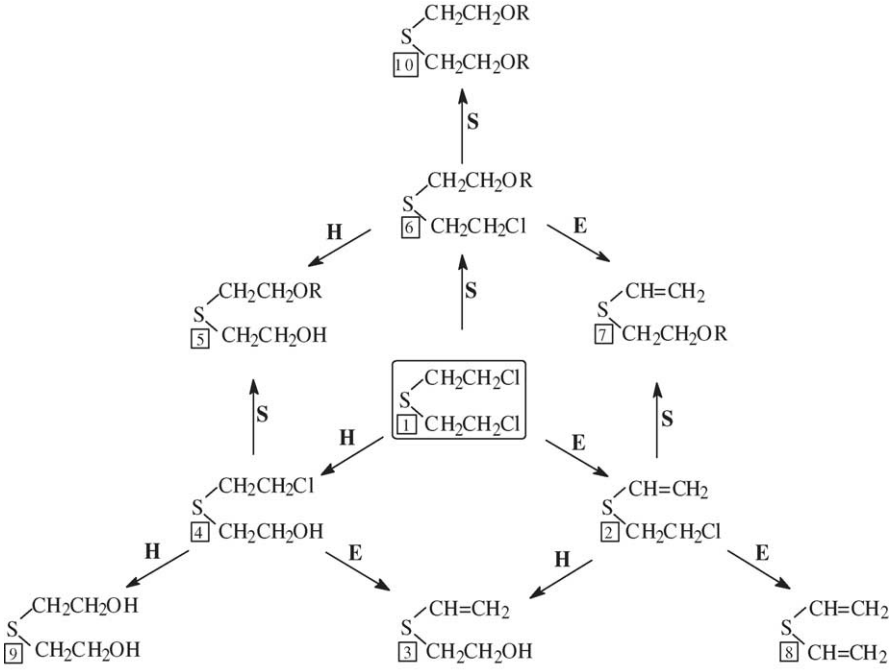


Fig. 7. The concentrations of mustard reaction products formed with the mixture of the C9 active components (14.4% sodium aminomonoethanolate in aminoethanol and 19% sodium 2-ethoxyethanolate in 2-ethoxyethanol in the ratio 20:80) in relation to time. Initial mustard concentration, 0.2 mmol/mL mixture of active components; temperature, 20 °C (for symbols see Fig. 6).

of mustard following its reaction with the active components is the fastest of all. Substitution is seen to be the reaction of minor importance for decontamination processes. However, it cannot be neglected because at high mustard concentrations after the active components have been considerably depleted, substitution comes to be the major decontamination process.

Sulfur mustard transformations in the reactions with active components of organic decontaminants in the presence of water is shown on the scheme:



Abbreviations and acronyms explanation:

E – Elimination; **H** – Hydrolysis; **S** – Substitution.
R = CH_3CH_2-O-CH_2CH_2– or CH_3CH_2– or H_2N-CH_2CH_2–

(1) sulfur mustard, (2) vinyl-2-chloroethyl sulfide, (3) vinyl-2-hydroxyethyl sulfide, (4) 2-chloroethyl-2′-hydroxyethyl sulfide, (5) 2-hydroxyethyl-2′-alkyloxyethyl sulfide, (6) 2-chloroethyl-2′-alkyloxyethyl sulfide, (7) vinyl-2-alkyloxyethyl sulfide, (8) divinyl sulfide, (9) thiodiglycol and (10) bis(2-alkyloxyethyl) sulfide.

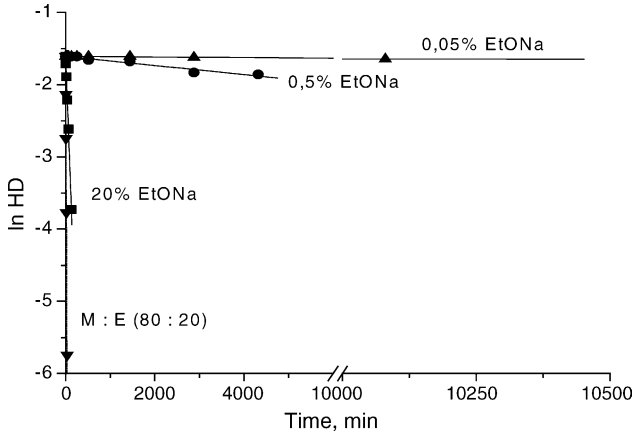


Fig. 8. Sulfur mustard concentration variations in the reactions with ethanolic 20, 0.5 and 0.05% sodium ethanolate solutions and with an (80:20 w/w) mixture of ORO decontaminant's active components (7.2% sodium 2-aminomonoethanolate in 2-aminoethanol: 5.9% sodium ethanolate in ethanol). Initial mustard concentration, 0.2 mmol/mL mixture of active components; temperature, 20 °C.

4. Conclusions

- The reactions of mustard with decontaminants ORO and C9 active components provide mostly an identical final product, viz., divinyl sulfide, which is formed in the reaction of elimination.
- The reaction of mustard with the ORO and the C9 decontaminants is a first-order reaction. The formation of vinyl-2-chloroethyl sulfide and its transformation into divinyl sulfide is more complicated, probably fractional-order reactions.
- The type of the mechanism followed by mustard reactions with the alcoholates is determined by the concentration ratio of mustard to alcoholate. At low alcoholate concentrations, the S_N1 nucleophilic substitution reaction is favored. In typical battle field situations, when the concentration of the decontaminant is much higher than that of mustard, decontamination follows the E1 elimination mechanism.
- High concentrations of the nucleophilic agent (>2%) are favorable to the elimination reaction; at lower concentrations with respect to a fixed mustard concentration, nucleophilic substitution reaction becomes competitive to the elimination reaction.
- The elimination mechanism is decisive for the rate of the mustard decontamination process, as borne out by the fastest decrement of mustard concentration accompanying this mechanism.
- The most active component in either of the decontaminants, viz., sodium aminomonoethanolate, is present at concentrations of 4.3 and 1.4% in the ORO and the C9 decontaminant (based on the total weight of the decontaminant), respectively.

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