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Gas Chromatography–Mass Spectrometry Analysis of Products of *O*-Isopropyl Methylphosphonofluoridate Transformation in Aliphatic Alcohols

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A transformation of sarin occurring after its dissolving in methanol, ethanol, *n*-propanol and isopropanol, during preservation of solutions, has been described. For investigation of the compounds originating in the solvents gas chromatograph combined with mass spectrometer were used. Compounds formed as a result of fluor atom replacement by alkoxyl group of alcohol in which sarin was dissolved were identified. In all solutions there is a compound being a pollution of sarin and being the same compound as formed during sarin and isopropanol interaction. A mechanism of formation of this compound has been suggested.

Opisano przemianę sarinu zachodzącą po jego rozpuszczeniu w metanolu, etanolu, *n*-propanolu i izopropanolu w trakcie przechowywania roztworów. Do badania związków powstających w tych roztworach zastosowano chromatograf gazowy sprzężony ze spektrometrem masowym. Zidentyfikowano związki powstające w wyniku zamiany atomu fluoru grupą alkoksylową alkoholu, w którym sarin był rozpuszczony. We wszystkich roztworach występuje związek stanowiący zanieczyszczenie sarinu i będący tym samym związkiem co powstający w wyniku oddziaływania sarinu z izopropanolem. Zaproponowano mechanizm powstawania tego związku.

The analysis of chemical warfare agents, products of their chemical transformation, and compounds for their production is an important problem. The importance of the problem is connected with continually repeating incidents of using chemical weapons on the one hand and with anticipated convention on the prohibition of chemical weapons on the other hand. After signing the treaty, the member countries will have to be inspected. During that control, inspectors of the United Nations may deal with different samples, among them with samples in the form of solutions. The samples may sometimes contain phosphoroorganic pesticides, and the knowledge of transformation of phosphoroorganic compounds can be useful to analyse them and for drawing a conclusion after the analysis. Since investigations of the chemical-warfare-agent transformation are very important, they are conducted in laboratories involved in the analysis of these compounds [1–4].

The rate of transformation of chemical warfare agents in solutions depends on the kind of solvent. The alcoholic solutions of *O*-isopropyl methylphosphonofluoridate (sarin, GB), differently from *e.g.* chloroformic solutions, demonstrate relatively high rate of chemical transformations leading to the decay of primary compound and to formation of some new compounds. This phenomenon limits the time of the suitability of alcoholic solutions which are used *e.g.* for enzymatic analytical reactions in water.

One of the best methods of analysing chemical warfare agents is the chromatographic method, especially gas chromatography, connected with mass spectrometry (GC/MS) [5]. An instrument which can be used on battle-field has been constructed too [6].

The aim of this work is identification of the products of sarin transformation in aliphatic alcohols using GC/MS.

EXPERIMENTAL

Solutions

Sarin was dissolved in chloroform, methanol, ethanol, *n*-propanol and isopropanol (analytical grade, POCh, Gliwice). The concentration of the solutions was 1 mg ml^{-1}. Alcoholic solutions were stored about 30 days at ambient temperature before chromatographic measurement. The chloroformic solution, in which transformation of sarin does not occur, was the standard solution. By using freshly prepared chloroformic solution it was established that one impurity was present in this solution.

Conditions of GC/MS analysis

Mass spectrometer ITD-800 AT (Finnigan MAT) and gas chromatograph AI-93 (Analytical Instruments) were used in our investigations. The two instruments were connected with a transfer line in the form of a fused silica column 1 m×0.25 mm covered with stationary phase SPB1 at temperature 250°C.

The gas chromatograph was equipped with fused silica capillary column 25QC3/BP5/1.0 (SGE), of 25 m×0.32 mm with 1 μm film of stationary phase. Helium was used as the carrier gas. The column temperature was programmed. Initially it was 60°C (3 min) and then it was increased to 260°C at the rate of 10°C min^{-1}. An injector with a moving needle heated to 250°C was used. The volume of chromatographed samples of solutions was 3 μl.

Using the mass spectrometer, ions of 40-300 amu were detected. Electron impact or chemical ionization with the use of methan was applied. Electrons energy was 70 eV and ions source temperature was 210°C. The ionization time in the range of 10 μs to 25 ms was optimized by a microcomputer according to the analyte concentration in the ions source.

A signal from MS was transformed, using an IBM AT microcomputer, to the form of reconstructed ion chromatogram or to the form of mass spectrum.

The identification of the analysed samples components was conducted by comparison of the obtained spectrum with the mass spectra stored in the computer memory or by comparison with the spectra published in literature.

RESULTS AND DISCUSSION

A typical chromatogram of sarin dissolved in chloroform is shown in Fig 1. In the chromatogram, we can also see a small peak (C2) of the compound which is always present in sarin and is its impurity. The height of the peak was constant over the time of solution preservation.

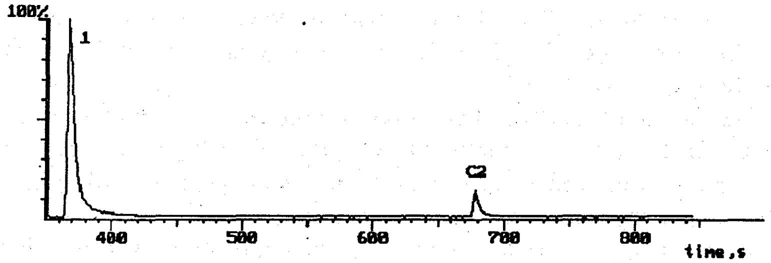


Figure 1. Chromatogram of sarin dissolved in chloroform, 1 – sarin, C2 – sarin impurity; conditions are given in the text

Figure 2 presents a chromatogram of methanolic solution of sarin obtained after about 30 days of the solution preservation. It can be seen that in the solution there is no more sarin but only two other compounds. One of them (M2) is probably the same impurity which is present in chloroform and the other one is a result of sarin interaction with solvent (methanol).

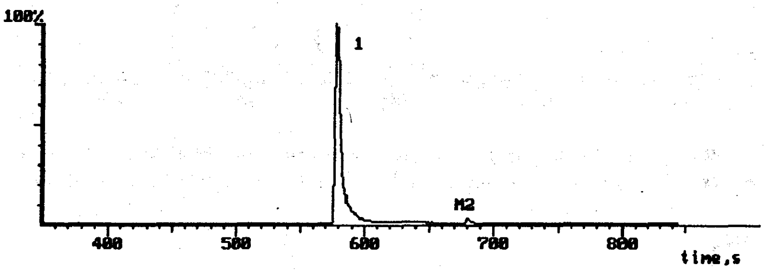


Figure 2. Chromatogram of components of sarin solution in methanol: 1 – product of sarin interaction with methanol, M2 – sarin impurity; conditions are given in the text

In Figure 3 a chromatogram of sarin solution in ethanol is shown. There are three peaks over there. One of them is the peak of sarin and out of the two others the smaller one (E3) probably corresponds to the same compound that produced peaks C2 and

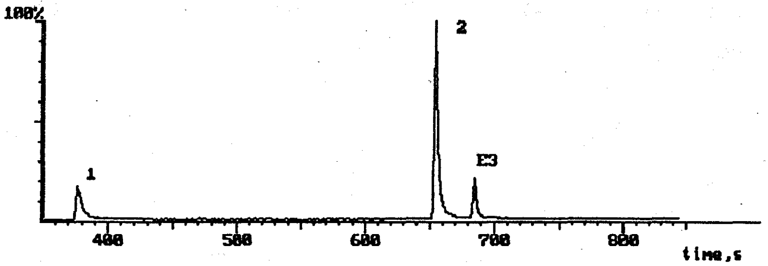


Figure 3. Chromatogram of components of sarin solution in ethanol: 1 – sarin, 2 – product of sarin interaction with ethanol, E3 – sarin impurity; conditions are given in the text

M2 in Figs. 1 and 2 respectively. The chromatogram certificates that sarin transformation in ethanol occurs more slowly than in methanol. The same conclusion is right in the case of solutions in *n*-propanol and isopropanol. The chromatogram of sarin solution in *n*-propanol is similar to the one obtained for a solution of that compound in ethanol. In the chromatogram there is a peak of sarin and two peaks corresponding to two other compounds. The retention time of the smaller peak is the same as the retention times of peaks C2, M2 and E3 that are present in chloroform, methanol and ethanol solution, respectively.

The chromatogram of sarin that was preserved for about 30 days in isopropanol contains two peaks only – the smaller one of sarin and the bigger one of the compound with the retention time 685 s. The latter compound is present in all other solutions. It can be concluded that this compound, always present in sarin, is the same compound as that one which was formed as a result of sarin reaction with isopropanol.

In Fig. 4 the chromatogram of mixture of sarin solutions in the used alcohols is presented.

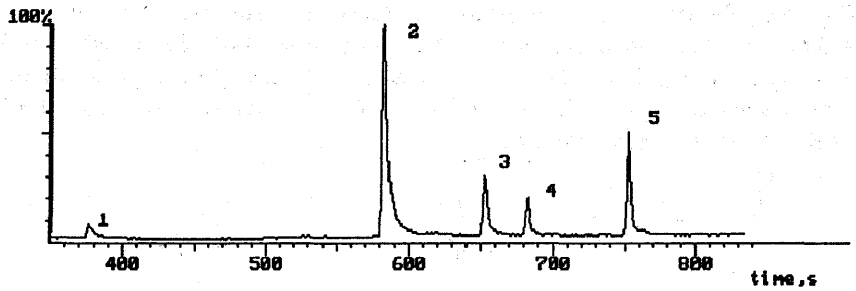


Figure 4. Chromatogram of components mixture of sarin solutions in alcohols, 1 – sarin; products of sarin interactions with: 2 – methanol, 3 – ethanol, 4 – isopropanol, 5 – *n*-propanol

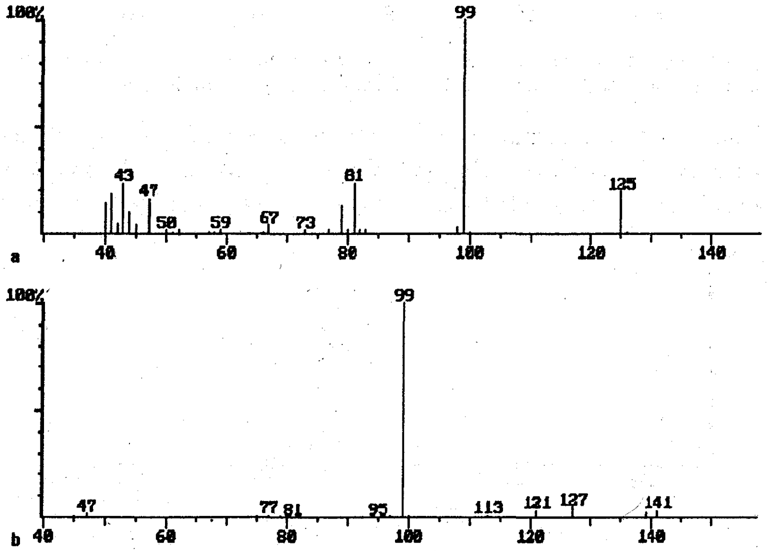


Figure 5. Sarin mass spectra (peak 1 from Fig. 1): a) electron impact, b) chemical ionization

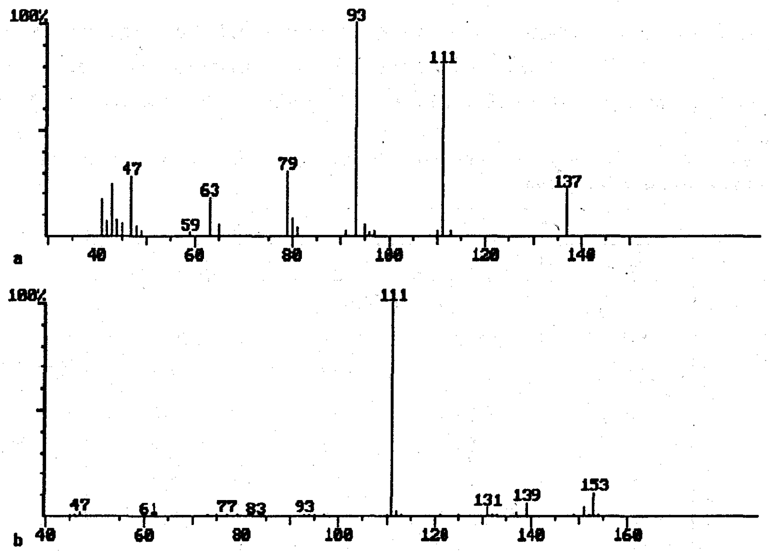


Figure 6. Mass spectra of interaction product of sarin and methanol (peak 1 from Fig. 2): a) electron impact, b) chemical ionization

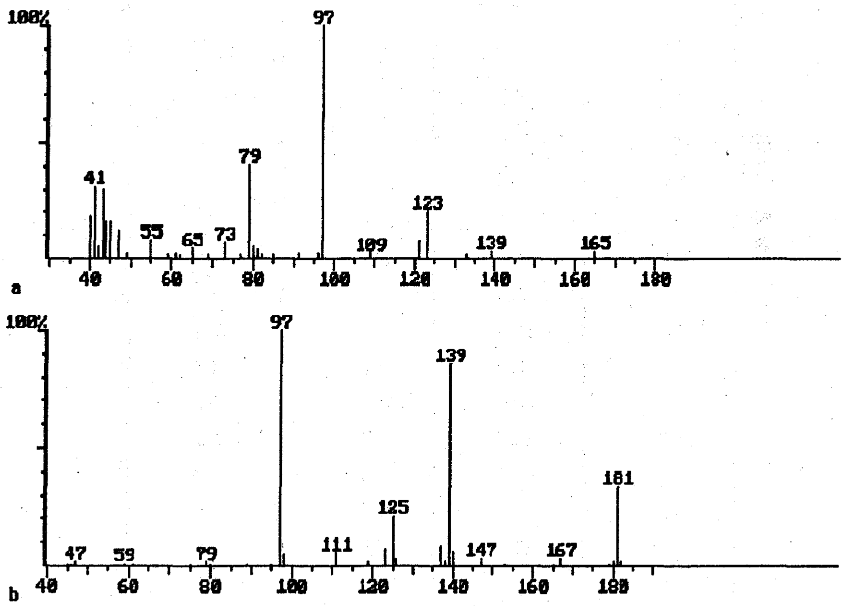


Figure 7. Mass spectra of interaction product of sarin and *n*-propanol: a) electron impact, b) chemical ionization

The precise identification of the sarin transformation products originated in alcohols was possible using mass spectrometry. The mass spectra of sarin are shown in Fig. 5 and examples of mass spectra of the sarin main transformation products in methanol and *n*-propanol are shown in Figs. 6 and 7. The mass spectrum of the sarin transformation product in isopropanol corresponds to the mass spectrum of the component which is present in all solutions and is an impurity of sarin.

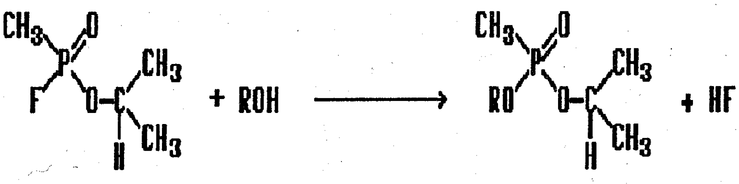
In Table 1 the data characterizing the mass spectra of the components present in sarin solutions are collected. The solutions were prepared in different solvents and the mass spectra were obtained after about 30 days of solutions preservation.

Table 1. Mass spectra of substances corresponding to the maximum chromatographic peak after 30 days of sarin solution preservation

EI		CI	
mass	% max peak	mass	% max peak
Chloroform			
99	100.0	99	100.0
125	19.6	127	4.8
81	14.6	141	3.5
43	12.7	121	3.3
41	12.2	139	2.8
47	12.0	47	1.6
79	9.1	100	1.3
42	4.5	125	1.1
40	4.1		
44	3.0		
67	3.0		
82	2.6		
83	2.4		
Methanol			
93	100.0	111	100.0
111	80.6	153	9.4
79	31.0	139	7.8
47	28.3	131	4.5
43	24.6	151	3.2
137	22.2	47	2.5
63	18.3	112	2.3
41	17.3	137	1.8
40	11.9	93	1.5
80	9.2	75	1.5
44	8.0	95	1.5
42	7.3	77	1.4
94	6.6	46	1.3
Ethanol			
97	100.0	125	100.0
79	89.1	97	28.4
123	36.6	167	27.2
43	35.6	153	8.9

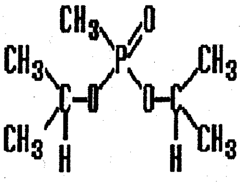
41	26.7	126	6.7
125	22.6	111	5.7
80	22.1	123	4.7
45	21.6	151	2.7
47	17.1	165	2.7
65	12.9	79	2.6
151	11.7	47	2.0
81	9.7	98	2.0
44	8.1	124	1.8
n-Propanol			
97	100.0	97	100.0
79	41.3	139	86.3
41	31.3	181	34.3
43	30.1	125	21.8
123	21.1	137	8.7
40	18.8	123	7.4
44	16.7	140	6.4
45	16.6	111	6.1
47	12.4	98	4.7
121	8.4	167	3.8
55	7.9	147	3.5
73	7.1	126	3.2
80	6.1	79	2.2
Isopropanol			
97	100.0	97	100.0
123	47.3	139	24.5
43	40.2	125	19.8
45	36.1	181	17.2
79	35.1	111	6.0
41	34.4	137	5.6
47	13.4	123	4.8
40	11.1	147	3.6
80	11.1	47	1.8
42	8.1	119	1.8
44	8.1	98	1.8
59	6.9	138	1.6
139	4.7	79	1.5

Basing on the mass spectra which are shown in the Figures and are described in Table 1 we can write the following reaction occurring in alcoholic solutions:

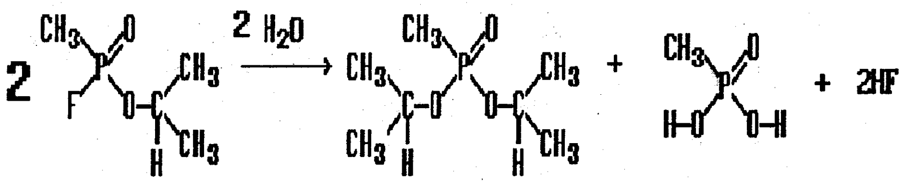


R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7

In all the solutions the presence of the impurity described by the formula:



was established. This compound is produced, in some amount, during the synthesis of sarin and during its preservation. The producing of the compound during sarin preservation can be caused by interaction of sarin molecules in presence of water according to the scheme:



Some investigations are undertaken to confirm or exclude the occurrence of this reaction.

Conclusions

Sarin dissolved in aliphatic alcohols interacts with them in such a way that in sarin molecule the fluor atom is replaced by the alcoxyl group.

The transformation of sarin into its derivative is quickest in methanol and not so quick in other alcohols.

In pure sarin and in sarin dissolved in isopropanol the same compound is present. The proposed mechanism of formation of the compound without isopropanol should be confirmed.

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