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Investigation of Stability and Composition of the Conversion Products of Russian Poisonous Substance VX in Aqueous Media

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Abstract—The data on properties and existence forms of Russian poisonous substance VX (RVX) in environmental objects are presented. Hydrolysis of RVX with excessive amount of water in acidic medium as well as autocatalytic hydrolysis with equimolar amount of water were investigated. It was shown that in the first case destruction of RVX proceeded slower with more diverse composition of the products.

Keywords*:* Russian poisonous substance VX (RVX), hydrolysis, gas chromatography–mass spectrometry, methylphosphonic acid, isobutyl methylphosphonic acid

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Substances of VX group (V-gases) are considered as the most danger chemical warfare agents of nerve-convulsing effect [1]. V-gases are low volatile liquids with high value of boiling point therefore their stability is essentially higher than stability of more volatile organophosphorus poisonous compounds such as sarin or soman. Moreover V-gases are much more toxic than the other warfare agents of nerve-convulsing effect. Thus, substance XV is approximately twice more toxic than sarin at inhalation, 10 folder more toxic at oral administration and 170 folder more toxic at topical use [2]. As a rule getting of small drops of V-gases on skin leads to lethal outcome.

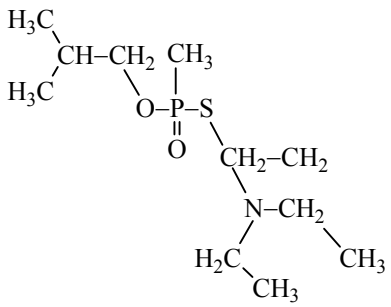
Under conventional designation XV the group of methylphosphonic acid *O,S*-diesters $ROPO(CH_3)S\cdot(CH_2)_2N(R1)_2$ is conceived. *O*-Isobutyl-*S*-(2-diethylaminoethyl)methylthiophosphonate (R = *i*-Bu, R^1 = Et) produced since 1972 exclusively in former USSR, outside the USSR got name Russian VX (RVX, Cas #159939-87-4) has chemical formula $C_{11}H_{26}SNPO_2$, molecular mass 276.37 a.u. and the structure presented on the figure.

One of the most important tasks of ecological chemistry is investigation of behavior of highly toxic compounds in the environment. Under behavior of such compounds we imply their stability, mechanisms of possible conversions, composition of the products of the conversions and their toxicity. Among the well-known toxicants the compounds from VX-group display probably maximal variability of the conversion mechanisms due to their unique structure. Being highly reactive and multifunctional species the compounds as constituents of multicomponent compositions are able to react with several components simultaneously. At the process the different active sites of the same molecule can be involved at the same time. Beforehand the behavior and result of such reactions can't be in all cases predicted. The problem is complicated by the fact that active components of natural or technogenic composition are not always known. Taking the above mentioned facts into account importance of the investigations dealing with identification of the conversion products of compounds of VX group in various media increases. It is supposed that destruction of the compounds is initiated by addition of an electron by the phosphorus atom as a result of the reaction with anionic nucleophile [3]. Hydroxyl anion, water, alcohols, amines, unsaturated organic compounds can serve as a nucleophile. Determination of RVX in

composition of the complex mixtures as well as identification of the conversion products of RVX are difficult tasks also due to some deficit of available reference information.

With the help of integrated chromatographic and spectral methods composition of the destructive products of VX together with its impurities was characterized in detail. Review [4] presents the systematic information about the composition of the conversion products of VX together with the data on their persistence and toxicity. Concerning RVX the systematic data are absent. Composition of the destructive products of RVX in different media is always complex and in most cases includes tens of both volatile and non-volatile organic compounds. For instance, 44 compounds were registered as components of bitumen neutralizer of RVX [5]. Alkyldiethyl aminoethyl- mono and polysulfides which do not contain phosphorus atom in the structure are the major compounds among volatile conversion products of RXV. Mass spectra of electron impact (MS EI) of the compounds are difficultly distinguished and in most cases contain only one intensive signal with *m/z* 86 corresponded to ion $[(Et)_2NCH_2]^+$. Such low informativeness of the EI mass spectra of the conversion products of RVX restricts possibility of usage of the data bases of mass spectra and retention time indexes which are able to reproduction between the laboratories [6]. Among the phosphorus-containing products methylphosphonic acid (MPA) is almost always determined together with its mono- and diisobutyl esters. The compounds were proposed to consider as retrospective markers which indicate the fact of contact of objects with RVX in the past [7]. By means of gas chromatography-mass spectroscopy (GC-MS) MPA and its acidic isobutyl ester can be developed only in form of their derivatives. The technical samples of RVX always contain these compounds as impurities but their content differs from tenth part to few per cent. As a result of P–S bond rupture in molecule RVX diethylaminoethane thiol and isobutyl methylphosphonic acid are formed; the latter is slowly hydrolyzed providing MPA. The conditions which promote rupture of P–O bond with formation of highly toxic S-2-diethylaminoethylmethyl thiophosphonic acid are not definitely found out.

Systematic information on behavior of the destruction products of RVX in the objects of the environment, their acute and chronic toxicity for people and mammals and their eco-toxicity on the whole are absent. Similarly to VX and as distinct from organophosphorus pesticides, the structure of RVX does not have strong electron-acceptor center which is able to activate decomposition; besides that RVX is not an absolute analog of VX. Being in dilute neutral aqueous solutions RVX occurred to be substantially more persistent than VX (half-life time 12.4 days compared to 4.8 days for VX) [8]. The mechanism of neutralization of VX with equimolar amount of water was firstly described in work [9]. It was found that autocatalytic hydrolysis is possible only in the case of organophosphorus compounds of V-type because of participation of protonated amino group.



Structure of RVX.

We performed the experiment on estimation of stability of RVX and identification of the products of its hydrolysis with equimolar and excessive amount of water. For analysis the most simple and available method was used, namely, gas chromatography in regime of electron ionization (GC-MS-EI).

Identification of the hydrolysis products of RVX with excessive amount of water in acidic medium was done after incubation of 1% solution of RVX in 5% aqueous solution of phosphoric acid for 20 days at room temperature and natural lightning. An aliquot part of the aqueous solution was extracted with acetonitrile using extracting freezing regime, the extract was dried with anhydrous sodium sulfate and treated with silylating agent, bis(trimethylsilyl)trifluoroacetamide (Merck, Germany) at 70°C for 30 min. An aliquot part of the sample (2 μL) was analyzed on the instrument complex by Shimadzu (Japan), GC-17A-QP 5000, in a regime of registration of the complete ionic stream within an interval of the mass numbers *m/z* from 73 to 450. Energy of ionized electrons was 70 eV. The ionic source temperature was 280°C. The capillary column DB-5 of 25 m length, 0.20 mm × 0.33 μm was used. The column temperature

Products of RVX hydrolysis with excessive amount of water in acidic medium

RI	Compound	Formula	Content in the reaction mixture, %
930	*N,N*-Diethylformamide	$HCOEt_2$	1
952	2-(Diethylamino)ethanethiol	$Et_2NCH_2CH_2SH$	10
976	*N,N*-Diethylacetamide	$HCOEt_2$	< 1
1147	MPA (diTMS ether)	$MePO[OSi(Me)_3]_2$	5
1221	Isobutyl MPA (TMS ester)	$CH_3PO(OiBu)OSi(Me)_3$	22
1269	Isobutyl methylphosphono thiolate (S-TMS ether)	$CH_3PO(OiBu)SSi(Me)_3$	11
1298	Diisobutyl methylphosphonate	$MePO(OiBu)_2$	3
1307	Isobutyl *S*-2-diethylaminoethyl methylphosphonothiolate	$Et_2NCH_2CH_2$-S-iBu	10
1337	Butyl *S*-2-diethylaminoethyl methylphosphonothiolate	$Et_2NCH_2CH_2$-S-Bu	1
1510	Isobutyl *S*-2-diethylaminoethyl methylphosphonodithiolate	$Et_2NCH_2CH_2$-S-S-iBu	2
1675	RVX	$MePO(OiBu)SCH_2CH_2NEt_2$	26
1744	Bis-(2-Diethylaminoethyl) disulfide	$(Et_2NCH_2CH_2)_2S_2$	1

was programmed from 40°C (1 min) to 270°C (15 min) with rate 5 deg/min. The gas-career (helium) expense was 1 ml per min. Linear-logarithmic retention indexes (RI) were calculated relatively to *n*-alkanes, whose mixture was subjected to the analytic chromatography under the same conditions.

Composition of the identified conversion products of RVX in diluted aqueous medium in the presence of phosphoric acid is presented in the Table. Residual amount of RVX after 20 days was 2.7 mg/mL or 27% from initially introduced quantity; 100 days later content of RVX in the solution was still more than 1% from the initial amount that evidences sufficiently even proceeding of the hydrolytic destruction process. Important characteristics of the identified components are the presented in the table values of retention times on stationary phase DB-5 which are absent in the available data bases of reference information. Non-volatile products were identified in a form of their trimethylsilyl (TMS) ethers.

To reveal composition of the hydrolysis products of RVX with equimolar amount of water, 74 μL of RVX was mixed with 5 μL of water, the mixture was kept at room temperature for 100 days without stirring constantly taking an aliquot part for GC-MS-EI analysis. The sample gradually thickened and presented homogeneous paste of ash grey color completely dissolved in acetonitrile. After 100 folder dilution the acetonitrile solution was treated with silylating agent and analyzed as described above. The auto-catalytic hydrolysis of RVX by the time of the experiment termination was practically finished since the residual content of RVX in the sample after 20 days did not exceed 0.01%, and by the end of the experiment (100 days) RVX was not determined even qualitatively. The reaction mixture composition was much more concise than in the case of hydrolysis with excessive amount of water. As volatile products of RVX transformation after 20 days of the mixture exposition by the means of GC-MS-EI were identified: 2-diethylaminoethanethiol (4%), diisobutyl methylphosphonate (2%), bis(2-diethylaminoethyl) sulfide (2%), RVX (<0.01%), bis-(2-diethylaminoethyl) disulfide (40%). Methylphosphonic acid (1.5%) and isobutyl methylphosphonic acid (48%) were identified among the nonvolatile products in a form of trimethylsilyl ethers. Isobutyl methylphosphonic acid catalyzed destruction of RVX is present in the reaction mixture as one of two main components. The second main component according to work [9] should be 2-diethylaminoethanethiol but as we showed it practically completely converted to bis-(2-diethylaminoethyl) disulfide. The obtained result looks quite logic because after termination of auto-catalytic destruction of RVX there is no barrier for conversion of the mercaptan to disulfide. In diluted aqueous solution of RVX conversion of the mercaptan to disulfide is much slower: even 100 days later

amount of mercaptan, 2-diethylaminoethanethiol, in the solution was significantly lower than amount of the corresponding disulfide, bis(2-diethylaminoethyl) disulfide.

Hydrolysis of RVX with equimolar amount of water is therefore simple and effective method for its detoxification since the formed products are low toxic.

At standardization in water was revealed that RVX in concentration within interval 0.01–1.0 mg/L did not negatively influenced the processes of reservoirs self-cleaning, development and dying off of saprophytic and pathogenic microflora, did not affect the nitrification. Afunctional dose was 10^{-7} mg/kg, threshold dose was 10^{-6} mg/kg, and functional dose was 10^{-5} mg/kg [10].

At investigation of RVX effect on soil microflora was established that the most sensitive occurred to be micromycetes and actinomycetes, less sensitive, nitrifying bacteria [11]. The investigations in the field of ecological chemistry of the conversion products of compounds of VX group are in progress [12].

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