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Characterisation of oxidation products of 1,1-dimethylhydrazine by high-resolution orbitrap mass spectrometry

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HIGHLIGHTS

- Orbitrap mass spectrometry was used to study the oxidation of 1,1-dimethylhydrazine.
- Hundreds of toxic nitrogen containing products of CHN and CHNO classes were found.
- Most of them have not been previously detected among rocket fuel degradation products.
- The reaction proceeds through intermediates containing up to ten nitrogen atoms.
- The elemental composition of all intermediates and final products was determined.

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ABSTRACT

1,1-Dimethylhydrazine is used as a fuel for carrier rockets in the majority of countries implementing space exploration programs. Being highly reactive, 1,1-dimethylhydrazine easily undergoes oxidative transformation with the formation of a number of toxic, mutagenic, and teratogenic compounds.

The use of high-resolution mass spectrometry for the study of the reaction of 1,1-dimethylhydrazine oxidation with hydrogen peroxide in aqueous solution allowed us to find hundreds of nitrogen-containing products of the CHN and CHNO classes, formed via radical processes. The vast majority of the compounds have not been previously considered as possible products of the transformation of rocket fuel.

We have shown that the oxidation of 1,1-dimethylhydrazine proceeds in two stages, with the formation of a great number of complex unstable intermediates that contain up to ten nitrogen atoms. These intermediates are subsequently converted into final reaction products with a concomitant decrease in the average molecular weight.

The intermediates and final products of the oxidative transformation of 1,1-dimethylhydrazine were characterised on the basis of their elemental composition using van Krevelen diagrams and possible compounds corresponding to the most intense peaks in the mass spectra were proposed. The data obtained are indicative of the presence of the following classes of heterocyclic nitrogen-containing compounds among the oxidation products: imines, piperidines, pyrrolidines, dihydropyrazoles, dihydroimidazoles, triazoles, aminotriazines, and tetrazines.

The results obtained open up possibilities for the targeted search and identification of new toxic products of the degradation of rocket fuel and, as a result, a more adequate assessment of the ecological consequences of space-rocket activity.

1. Introduction

1,1-Dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) is widely used as a fuel for carrier rockets in the majority of countries implementing space exploration programs (Buryak and Serdyuk, 2013). Being highly toxic, UDMH entering the environment can cause serious ecological damage (Carlsen et al., 2007, 2009a,b). The hazard is increased by the high reactivity of UDMH, which results in the rapid formation of a number of dangerous oxidative degradation products when it contacts oxygen in the air. Like unsymmetrical dimethylhydrazine, these products exhibit

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mutagenic and teratogenic properties (Carlsen et al., 2009a). An important aspect of this problem is the wide use of different oxidants (hydrogen peroxide, potassium permanganate, hypochlorites, ozone, and Fenton's reactant) for the detoxification of soils polluted by rocket fuels, as well as the application of catalytic oxidation in the purification of natural and sewage waters containing alkylhydrazines (Abilev et al., 2015).

The range of possible transformation products formed on the arrival of rocket fuel in the environment has been determined in numerous publications devoted to the ecological consequences of space-rocket activity, mainly using GC–MS. This range was most fully presented in the work by Kenessov et al. (2012), who used solid-phase microextraction and found 56 compounds of different classes in extracts from soils polluted by 1,1-dimethylhydrazine. The formation of only about 20–30 of these compounds has been confirmed by the experimental data of other researchers. The main products of UDMH transformation are supposed to be, first of all, *N,N*-nitrosodimethylamine (NDMA), tetramethyltetrazene (TMT), hydrazine and its methyl derivatives, *N,N*-dimethylformamide (DMF), formaldehyde dimethylhydrazone (FADMH), formyl dimethylhydrazide (FDMH), 1-methyl-1H-1,2,4-triazole (MT), and dimethylguanidine (DMG). Almost all current procedures for the analytical control of environmental samples polluted by hydrazines are designed for targeted determination of these compounds (Kenessov et al., 2011; Kosyakov et al., 2014, 2015; Payen et al., 2015; Rodin et al., 2010; Smirnov et al., 2010; Ul'yanovskii et al., 2014; Yegemova et al., 2015). The efficiency of oxidants proposed for detoxification has also been estimated mainly based on specific searches for the most important compounds, and the published data on the composition of hydrazine degradation products, summarised in Table 1, are extremely incomplete. This might lead to erroneous conclusions about the actual level of environmental pollution after spills of toxic fuels and also after the treatment of polluted areas with different reagents.

The prevailing approaches for the control of the consequences of pollution of waters and soils with unsymmetrical dimethylhydrazine are usually guided by the postulated simple schemes of UDMH transformations, including some of the main products mentioned above. At the same time, it has long been known that the oxidation of alkylhydrazines proceeds to a substantial extent via radical mechanisms, with the formation of a number of intermediates bearing unpaired electrons (Bard and Atkinson, 1971; Goodwin et al., 1996). The fact that oxidation can give not only nitrogen-containing but also alkyl radicals seems extremely important. Thus, Netto et al. (1988) found by ESR spectrometry that the oxidation of 1,2-dimethylhydrazine can give up to 8% of methyl radicals compared to the amount of absorbed oxygen. Taking these facts into account, the initial stage of the oxidative transformation of UDMH can be represented by the scheme shown in Fig. 1 for the reaction of 1,1-dimethylhydrazine with hydrogen peroxide. Radical species of eight types formed (including resonance structures) can play key roles in the formation of very complex nitrogen-containing organic molecules, to give an almost unlimited range of products. Many of them may be thermally labile or non-volatile and can be hardly detected by gas chromatography. In addition, information about a great number of potential analytes may not be contained in commercial mass spectrum libraries, which explains the rather narrow range of the known transformation products of UDMH. These assumptions were indirectly confirmed by a recent publication about the catalytic oxidation of unsymmetrical dimethylhydrazine in aqueous media on the surface of a solid catalyst (Liang et al., 2016), in which a mass spectrum of a solution of reaction products formed within 5 min of the beginning of the reaction, including not less than 50 peaks of individual compounds in the *m/z* range from 50 to 200, was obtained by low resolution HPLC–MS. Based on the recorded MS/MS spectra, the authors proved the presence of four widely known products (NDMA, DMG, TMT, and FDMH) in the mixture, but the majority of the

Table 1
Known transformation products formed in the reaction of 1,1-dimethylhydrazine with different oxidants.

Compound	Oxidant	Method of analysis	Reference
N-Nitrosodimethylamine	H_2O_2, O_3, $KMnO_4$, chlorine reagents	GC-FID, GC-MS, GC-MS/MS	Pestunova et al., 2002, Lunn and Sansone (1994), Buryak et al., 2011, Mach and Baumgartner (1979), Andrzejewski et al., 2012, Mitch et al., 2003, Sgroi et al., 2014.
Tetramethyltetrazene	H_2O_2, $KMnO_4$, chlorine reagents	GC-FID, GC-MS, GC-MS/MS	Pestunova et al., 2002, Lunn and Sansone (1994), Buryak et al., 2011, Mach and Baumgartner (1979)
Dimethylamine	H_2O_2, chlorine reagents	GC-FID, GC-MS, GC-MS/MS	Pestunova et al., 2002, Lunn and Sansone (1994), Mach and Baumgartner (1979)
Dimethylformamide	$KMnO_4$, chlorine reagents	GC-MS, GC-MS/MS	Buryak et al., 2011, Mach and Baumgartner (1979)
Formaldehyde dimethylhydrazone	H_2O_2, chlorine reagents	GC-FID, GC-MS	Pestunova et al., 2002, Lunn and Sansone (1994), Mach and Baumgartner (1979)
Acetaldehyde dimethylhydrazone	Chlorine reagents	GC-MS	Mach and Baumgartner (1979)
Pyridine	Chlorine reagents	GC-MS	Mach and Baumgartner (1979)
Tetrazine	H_2O_2	GC-MS	Pestunova et al., 2002
1,1,5-trimethylfarmazane	H_2O_2	GC-MS	Pestunova et al., 2002
Formic acid	Fenton's reagent	UV–Visible Spectroscopy, GC-MS	Makhotkina et al., 2006, Angaji and Ghiaee (2015)
Acetic acid	Fenton's reagent	UV–Visible Spectroscopy, GC-MS	Makhotkina et al., 2006, Angaji and Ghiaee (2015)
Nitromethane	Fenton's reagent	UV–Visible Spectroscopy, GC-MS	Makhotkina et al., 2006, Angaji and Ghiaee (2015)
Unidentified components	$KMnO_4$	GC-MS	Buryak et al., 2011