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Investigations of bis(methyltetrazolyl)triazenes as nitrogen-rich ingredients in solid rocket propellants – Synthesis, characterization and properties

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ABSTRACT

The energetic nitrogen-rich compounds 1,3-bis(1-methyltetrazol-5-yl)triaz-1-ene (**4**) and 1,3-bis(2-methyltetrazol-5-yl)triaz-1-ene (**5**) were synthesized by diazotation of 1-methyl-5-aminotetrazole (**2**) and 2-methyl-5-aminotetrazole (**3**), respectively, by using half an equivalent of sodium nitrite. The reaction of **4** and **5** with diluted ammonia solution yields ammonium bis(1-methyltetrazol-5-yl)triazenate (**6**) and ammonium bis(2-methyl-tetrazol-5-yl)triazenate (**7**). Treating of **4** and **5** with aqueous sodium hydroxide solution yields sodium bis(1-methyltetrazol-5-yl)triazenate (**8**) and sodium bis(2-methyltetrazol-5-yl)triazenate (**9**) almost quantitative. Compounds **8** and **9** were methylated using methyl iodide and dimethyl sulfate, respectively, originating bis(1-methyltetrazol-5-yl)-3-methyltriaz-1-ene (**10**) and bis(2-methyltetrazol-5-yl)-3-methyltriaz-1-ene (**11**). The products **4**–**11** were characterized by Raman, IR, multinuclear NMR and UV–Vis spectroscopy, mass spectrometry, elemental analysis and differential scanning calorimetry. The structures of the crystalline state of **4** · H_2O, **5**, **8** · MeOH, **10** and magnesium bis(2-methyltetrazol-5-yl)triazenate (**12**) were determined by low temperature single crystal X-ray diffraction. The heats of formation $\Delta_f H^\circ$ of **4**–**7**, **10** and **11** were calculated using energies of combustion $\Delta_c U^\circ$ determined by bomb calorimetry, resulting in strongly endothermic values. With these data and by using calculated (**4**, **5**, **10**) as well as measured (**6**, **7**, **11**) crystal densities, several detonation parameter (heats of explosion, detonation pressure, detonation velocity, explosion temperature) were calculated by the EXPLO5 software. In addition, the specific impulse of different propellant mixtures of the most promising compound **6** with ammonium dinitramide (ADN) were computed. Furthermore the *n*-octanol/water partition coefficients of **4**, **5**, **6** and **7** were determined and the long-term stability of **6** was tested by thermal safety calorimetry. Lastly the sensitivities toward impact and friction as well as electrical discharge were determined by the BAM drophammer, friction tester and a small scale electrical discharge tester.

1. Introduction

In contrast to high explosives, propellants need to release their energy in form of deflagration. In this way they produce high pressure without fracturing the containment chamber. Black powder [1] was one of the first propellants used in guns and motors. Today it is still used in pyrotechnic goods, especially small rockets. However the use of black powder as propellant for larger objects like missiles and space rockets contain too much disadvantages. There is a certain unpredictability of the behavior and development of extremely dirty gases [2]. Rocket propellants need to fulfill a couple of requirements: (i) The explosives must have a high energy content and slow burning rate to sustain impulse over a period of time. (ii) The substance additionally needs to be stable over a long time period and in a wide as possible temperature range. To compare different propellants in their performance the specific impulse I_{sp} is used. It is defined as the thrust divided by the mass flow rate of the explosive (Eq. (1)):

$$I_{sp} = \frac{\text{thrust of motor}}{\text{mass flow rate through nozzle}} \tag{1}$$

The specific impulse is also a function of the temperature in the combustion chamber and the average molar mass of the gases:

$$I_{sp} \approx \sqrt{\frac{\text{temperature of combustion chamber}}{\text{average molar mass of gaseous products}}} \tag{2}$$

Therefore I_{sp} depends on the properties of the propellant, on the design of the combustion chamber and the rocket motor, respectively [3]. The two main types of solid rocket propellant are double-base propellants and composite propellants. Double-base propellants are homogenous and composed of nitrocellulose with nitroglycerine or other nitroglycols as energetic plasticizers. Because the dimension of propellant grains based on this type of mixture is

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limited, composite propellants were developed during the second world war. The most important composite propellant today is a mixture of aluminum as fuel and ammonium perchlorate as oxidizer. As binding agent serves a polymer, e.g. hydroxy- or carboxy-terminated polybutadiene. This type of mixture is used for example as solid rocket boosters at the US Space Shuttle (and also in Ariane rockets ESA). Depending on the kind of binder and other additives used the specific impulse reaches about 2400–2600 Ns/kg (engl. (I_{sp}/g): 245–265 s) and the flame temperature is about 2850–3500 K [3].

Although the performance of ammonium perchlorate is highly suitable as rocket propellant, it has one big disadvantage. As it can be seen from the decomposition Eq. (3) a high amount of HCl is produced.

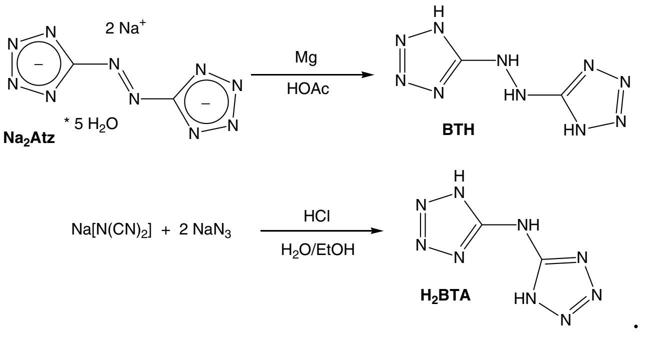
$$2NH_4ClO_4 \rightarrow N_2 + 3H_2O + 2HCl + 2.5O_2 \tag{3}$$

With the fact of 500 kg propellant per booster for the Space Shuttle there is a total output of 217 tons of HCl per launch. With the humidity in the air a huge quantity of acid mist is released, which leads to acid rain. In addition the resulting Al_2O_3 is harmful for living creatures and plants. Some endeavors were made to reduce the environmental pollution, especially, concerning the HCl impact. One possibility is to add $NaNO_3$ to build up NaCl [4]:

$$\begin{aligned} NH_4ClO_4 + NaNO_3 &\rightarrow NH_4NO_3 + NaClO_4 \\ &\rightarrow \text{production of NaCl} \end{aligned} \tag{4}$$

The simplest way to reduce the environmental pollution would be using propellants which contain no chloride and do not produce any other harmful residues. Many scientists today are searching for new energetic materials with good performance and at the same time having environmental friendly properties. Examples for this new class of energetic materials are 5,5′-bis(1*H*-tetrazolyl)amine (H_2BTA) [5] and salts of 5,5′-bis(1*H*-tetrazolyl)hydrazine (BTH) [6] as well as 5,5′-azotetrazolates (ATZ), which syntheses are illustrated in Scheme 1.

Compounds containing the 5,5′-azotetrazolate anion are particularly suitable target molecules, since these salts have a considerable nitrogen content and are expected to have appropriate stabilities toward friction, impact and heat. Metal salts of 5,5′-azotetrazolates have been extensively studied [7] and also N-rich guanidinium derivatives of 5,5′-azotetrazolate are described in literature as possible additives in solid propellants [8]. The main disadvantage is the incompatibility toward acids. Suitable alternatives for 5,5′-azotetrazolates are derivatives of bis-tetrazolyl-triazenes, which are also stable toward acid conditions. Derivates of bis-tetrazolyl-triazenes have also high-nitrogen contents and a very high positive heat of formation. Due to their high-nitrogen content the main decomposition product is also dinitrogen. In 1910, Hofmann and Hock synthesized bis(1*H*-tetrazol-5-yl)triaz-1-ene for the first time [9], which decomposes slowly by simple exposure to air but can be used as precursor producing 5-tetrazolylhydrazones. A great deal better are the methylated derivatives of bis(1*H*-tetrazol-5-yl)triaz-1-ene since they are thermally stable and show lower sensitivities. toward outer stimuli. These properties can be still improved by deprotonation of the triazene group forming triazenates. Bis(1-methyl-tetrazol-5-yl)-triazene is unknown in literature. Bis(2-methyltetrazol-5-yl)triaz-1-ene was synthesized accidentally by Hattori et al. during the attempt producing methylated 5-hydroxytetrazole, but was not further described [10]. It has been also mentioned in literature as intermediate in synthesis of arylidene-2-methyl-2*H*-tetrazol-5-yl-hydrazones [11] and 1,3,4,6-tetrakis(2-methyltetrazol-5-yl)hexaaza-1,5-diene [12]. In the work of A. Lyakhov deprotonated bis(2-methyltetrazol-5-yl)triaz-1-ene was used as a chelate ligand for Ni(II) [13]. In this work we present facile synthetic routes to several bis(methyltetrazolyl)-triazenes, bis(methyltetrazolyl)-triazenates and bis(methyltetrazolyl)-methyltriazenes, which were fully characterized and also tested with regard to their energetic properties.



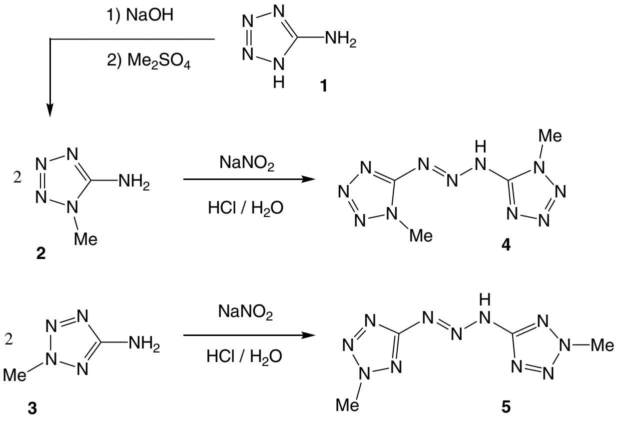
Scheme 1. Syntheses of the nitrogen-rich materials 5,5′-bis(1*H*-tetrazolyl)amine (H2BTA) and salts of 5,5′-bis(1*H*-tetrazolyl)hydrazine (BTH).

2. Results and discussion

2.1. Synthesis

1-Methyl-5-aminotetrazole (**2**) and 2-methyl-5-aminotetrazole (**3**) were synthesized by methylation of 5-aminotetrazole (**1**) using dimethyl sulfate according to the literature [14]. The diazotation of **2** was carried out in water, according to Scheme 2. A matter of particular interest is the sequence of addition. In this case a solution of 1-methyl-5-aminotetrazole in diluted hydrochloric acid is slowly dropped to an ice cold solution of half an equivalent of sodium nitrite. Bis(1-methyltetrazolyl)triazene (**4**) starts to precipitate after a few minutes (from this solution) and was isolated by filtration. Recrystallization from hot water yielded single crystals of the monohydrate suitable for XRD. Bis(2-methyltetrazolyl)triazene (**5**) can also be synthesized via this route, but also, due to its solubility in organic solvents, by the reaction in THF as solvent and *i*-pentylnitrite as the diazotation agent. Recrystallization from hot water yielded also light yellow single crystals. A small amount of single crystals of magnesium bis(2-methyl-tetrazolyl)triazenate dodecahydrate (**12**) was accidentally obtained on working up one of the reactions originally carried out to establish the reaction conditions toward **5** using $MgSO_4$ as drying agent.

Deprotonation (Scheme 3) of **4** and **5** can be performed in water by adding common bases e.g metal hydroxides or carbonates. The reactions with conc. ammonia solution yielded the water free salts



Scheme 2. Synthesis of bis(1-methyltetrazolyl)triazene (**4**) and bis(2-methyltetrazolyl)-triazene (**5**).