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THERMAL ANALYSIS OF THE EXTREMELY NITROGEN-RICH SOLIDS BTT AND DAAT

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Abstract

3,6-Bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine BTT and 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) are nitrogen-rich substances considered as new components for energetic applications like gas generators. Therefore, the thermal decomposition behaviour of BTT and DAAT was thermoanalytically characterized.

Both substances decompose at surprisingly high temperatures of >200°C. The decomposition heats released belong to the highest ever measured for energetic materials under similar experimental conditions and are spread over a relatively narrow temperature range. The online monitoring of the decomposition gases reveals the decomposition pathway which is initiated by ring opening reactions of the tetrazole and tetrazine subunits. Subsequent reaction steps could be identified leading to a residue-free degradation of the C–N-backbone of BTT and DAAT.

Keywords: decomposition pathway, energetic materials, nitrogen-rich compounds, tetrazine, tetrazole

Introduction

The synthesis of nitrogen-rich compounds as a unique class of energetic materials has received an increased interest for the past decade [1–5]. In contrast to traditional energetic materials the energy content of nitrogen-rich compounds is essentially derived from their high enthalpy of formation and less from the oxidation of the hydrocarbon backbone. Moreover, good oxygen balances and high densities can be achieved due to the high nitrogen content of such energetic materials which make them highly attractive as components for energetic applications like gas generating airbag formulations.

In this context heterocylic compounds like tetrazoles and tetrazines are of particular interest. For example, the nitrogen content of such compounds can be increased to over 75% by substitution with suitable functional groups [5]. BTT (Fig. 1) is one of these promising new energtic substances with an extremely high nitrogen content of 77.05% [1]. Recently, another promising nitrogen-rich substance based on azo-brigded tetrazine ring structures was synthesized: DAAT with a nitrogen-content of 76.35% [2–4] (Fig. 2). Both BTT and DAAT can be described as new thermally stable and to a great extent insensitive energetic materials.

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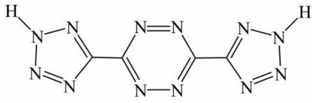


Fig 1 3,6-Bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine (BTT)

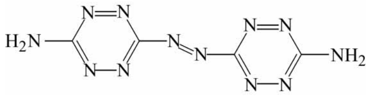


Fig. 2 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT)

This work presents results of a thermoanalytical characterization of BTT and DAAT by applying DSC, TG, TG-MS and fast FTIR spectroscopic Evolved Gas Analysis. Since these new nitrogen-rich substances are considered as components for energetic applications the thermal analysis was focused on their decomposition behaviour. Therefore, this work describes both the decomposition exothermicity and the time-resolved detection of thermal decomposition products. The latter allows the identification of the main decomposition mechanisms of the two heterocycles investigated and points out how differences in molecular structure can significantly influence the thermal decomposition behaviour.

Experimental

BTT was synthesized according to a method first described by Curtius *et al.* [6] and later modified by Sauer *et al.* [1]. The corresponding 3,6-Bis(2H-tetrazol-5-yl)-1,2,4,5-dihydrotetrazine was obtained by the reaction of 5-cyano-tetrazole with hydrazine. In a final step the dihydrotetrazine was oxidized by chromium(VI) oxid, and BTT was obtained as carmine-red crystals. A detailed description of the synthesis procedure is given in [1].

DAAT was obtained in a six-step synthesis following the method described by Hiskey *et al*. [2, 3] which was modified by using triaminoguanidine nitrate (TAGN) as a commercially available starting material [4]. After five reaction steps the bis-DMSO solvate of DAAT was precipitated which was refluxed in water to obtain the solvent-free DAAT as a red crystalline solid. A detailed description of the synthesis procedure is given in [4].

BTT and DAAT were obtained with purities >99.9%, and were therefore used without further purification for thermoanalytical investigations. HPLC and NMR analyses gave no evidence for any impurities or solvent residues in the crystalline samples.

To characterize the thermal properties and behaviour of BTT and DAAT under conditions of slow pyrolysis thermoanalytical investigations were carried out by applying Differential Scanning Calorimetry (DSC; TA Instruments, MDSC 2920), Thermogravimetric Analysis (TG; TA Instruments, HIRES-TGA 2950) and Evolved Gas Analysis (EGA). EGA experiments were performed by applying either a TG/mass spectrometer system (Balzer Thermostar) or a self-constructed fast infrared spectroscopic EGA equipment based on a heatable optical cell adapted to a rapid scan FTIR spectrometer (Nicolet 60 SX) which allows an on-line monitoring of the gas phase.

Samples weighing between 0.200 and 5.100 mg were analyzed in aluminum pans with pierced lids under argon atmosphere by applying calibrated heating rates between 0.5 and 5.0 K min^{-1}. For statistical reasons all experiments were repeated up to eight times. Stepwise variation of heating rates ensures that characteristic temperatures (e.g. onset temperature, maximum heat flow temperature) can be extrapolated to a formal heating rate of zero. From the measured DSC curves the (integral) heat of decomposition ΔH_{decomp} was calculated based on a sigmoidal base line curvature.

Results and discussion

Besides a high nitrogen content, the low oxygen balance in combination with high heats of formation and acceptable high densities are additional promising properties of BTT and DAAT which make them interesting as new energetic components (Table 1).

Table 1 Relevant properties of BTT and DAAT for energetic applications

Parameter	BTT	DAAT
Nitrogen content/%	77.05	76.35
Oxygen balance/%	–66.01	–72.67
Heat of formation/kJ mol^{-1} (measured by combustion calorimetry)	936±33	1035±48
Density/g cm^{-3} (measured by gas pycnometry)	1.68	1.76

Figures 3 and 4 show characteristic DSC curve of BTT and DAAT recorded at a heating rate of 2.0 K min^{-1} which indicate that both substances decompose at surprisingly high temperatures. Decomposition onset temperatures of 225.2±4.3°C (BTT) and 289.9±7.7°C (DAAT) were calculated by systematic variation of the heating rate.

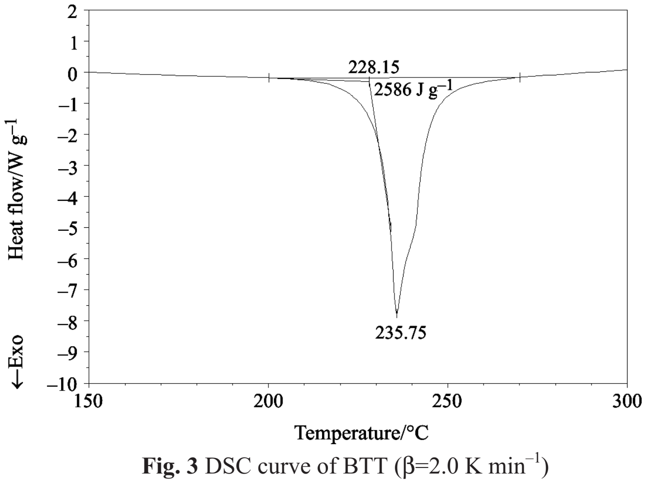


Fig. 3 DSC curve of BTT (β=2.0 K min^{-1})

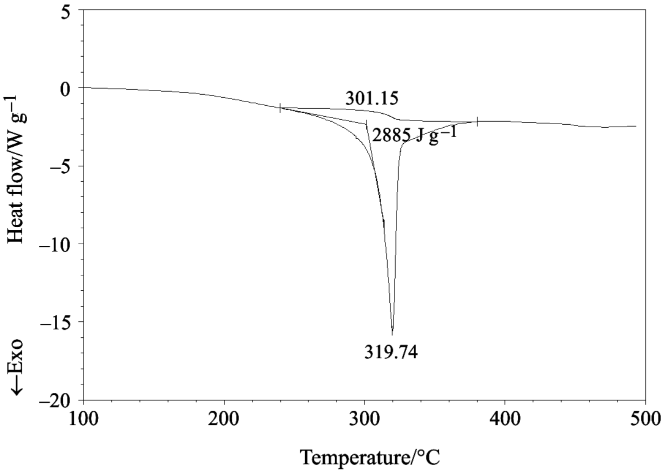


Fig. 4 DSC curve of DAAT (β=2.0 K min^{-1})

The exothermicity itself is in both cases spread over a relatively narrow temperature range appearing as a sharp heat flow peak with its maximum at approx. 235°C (BTT) and 320°C (DAAT), respectively. The released heats of decomposition belong to the highest ever measured for energetic materials and are four to five times the value of the common explosive 2,4,6-trinitrotoluene (TNT) under similar experimental conditions: 578±17 kJ mol^{-1} for BTT and 658±21 kJ mol^{-1} for DAAT. Table 2 summarizes the decomposition data measured by DSC.

Table 2 DSC data of BTT and DAAT

Parameter	BTT	DAAT
Onset temperature of exothermic decomposition $T_{\text{onset (HR 0)}}$/°C	225.2±4.3	289.9±7.7
Maximum heat flow temperature $T_{\text{max (HR 0)}}$/°C	235.1±0.9	319.2±0.7
Decomposition enthalpy/kJ mol^{-1} $\Delta H_{\text{decomp (HR 0)}}$/J g^{-1}	578±17 (2650±78)	658±21 (2989±97)

The TG measurements of the bis-tetrazolyl-tetrazine BTT (Fig. 5) and the azo-bridged bis-tetrazine DAAT (Fig. 6) show a complete, residue-free thermal decomposition of the entire molecules in two main decomposition steps. However, the strong exothermicity is only released during the first decomposition step combined with an approx. 50% mass loss as it is clearly shown by the overlay of the DSC and DTG curves of BTT and DAAT (Figs 7 and 8). In a second weak exothermic decomposition step at higher temperatures complete degradation takes place. Moreover, higher resolved DTG and DSC curves indicate that both the strong exothermic decomposition step and the weak one consists on more complex, partly overlapping degradation processes.

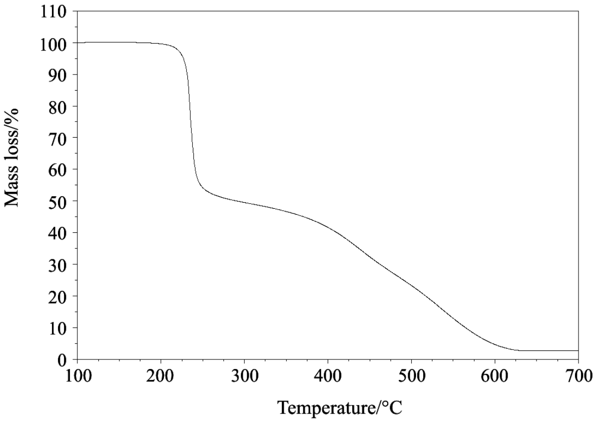


Fig. 5 TG curve of BTT (β=2.0 K min^{-1})

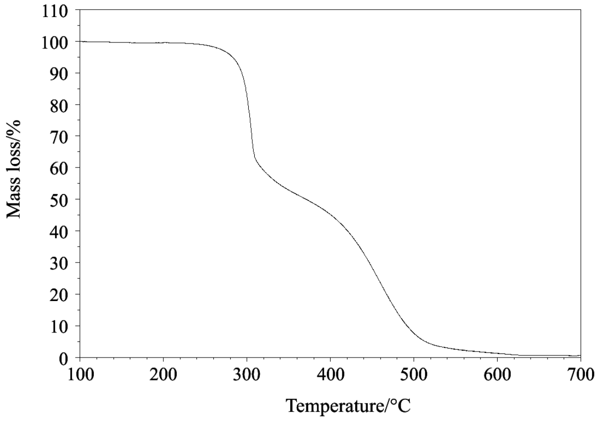


Fig. 6 TG curve of DAAT (β=2.0 K min^{-1})

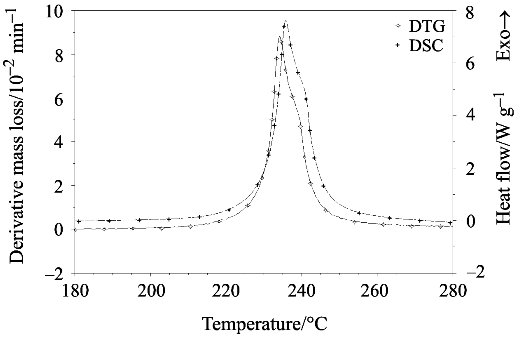


Fig. 7 Comparison of DTG and DSC curves of BTT (first decomposition step)

To get a closer view on the chemism of the thermal decomposition processes of BTT and DAAT infrared spectroscopic and mass spectrometric Evolved Gas Analyses were carried out during pyrolysis.

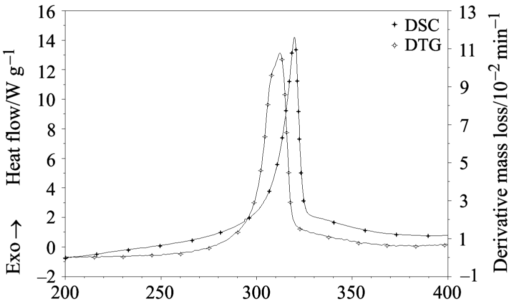


Fig. 8 Comparison of DTG and DSC curves of DAAT (first decomposition step)

Figures 9 and 10 show the decomposition gases detected by IR spectroscopy which are released during heating of BTT and DAAT with 5.0 K min^{-1} under argon atmosphere. Right from the beginning of thermal decomposition ammonia (NH_3), hydrogen cyanide (HCN) and cyanamide ($H_2N{-}CN$) are detected as IR-active gaseous decomposition products (Figs 11 and 12). Residues of water (H_2O) and carbon dioxide (CO_2) appearing in the gas phase are due to residues within the sealings of the optical cell and are also detected during blank trials.

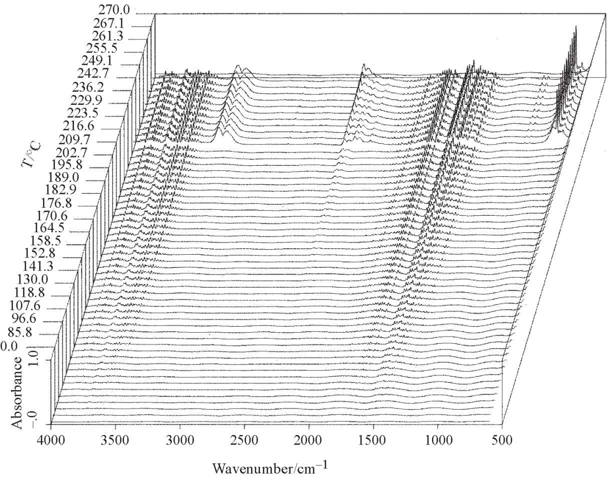


Fig. 9 Infrared spectroscopic Evolved Gas Analysis of BTT (β=5.0 K min^{-1})

Cyanamide, which could be undoubtedly identified by comparison EGA measurements of the pure reference, is more released during decomposition of DAAT than of BTT. On the other hand, the IR spectrum of the BTT decomposition gases show an additional gaseous product with an absorption band centered at 2162–2164 cm^{-1}, which was not detected during DAAT decomposition. It was assumed that this additional absorption band is derived from the release of cyanogen ($N{\equiv}C{-}C{\equiv}N$) which is described in literature having an IR-active absorption band at

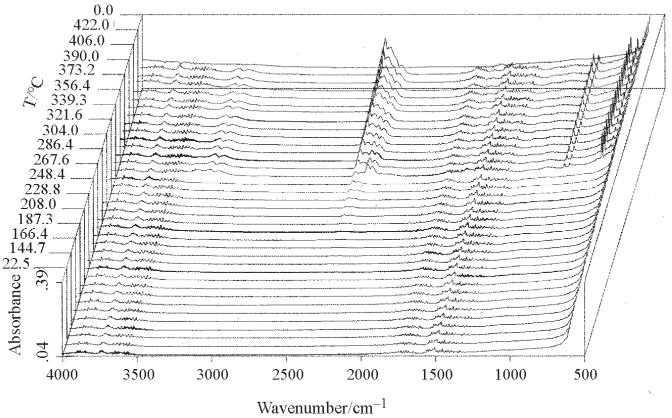


Fig. 10 Infrared spectroscopic Evolved Gas Analysis of DAAT (β=5.0 K min^{-1})

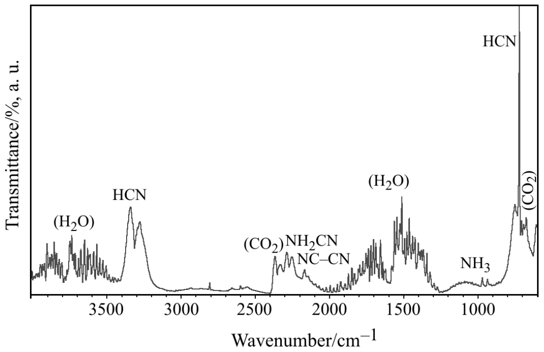


Fig. 11 IR spectrum of BTT decomposition gases detected at 250°C

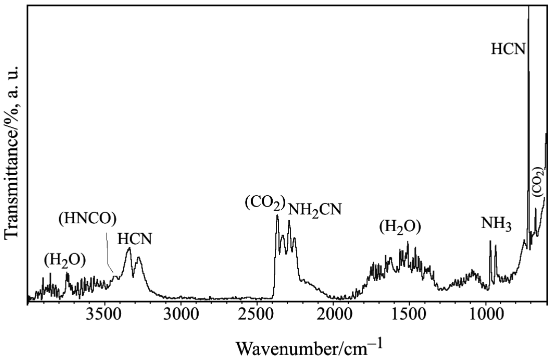


Fig. 12 IR spectrum of DAAT decomposition gases detected at 340°C

2165–2167 cm^{-1} [8, 9]. To confirm the release of cyanogen and to detect further potential decomposition gases which are not IR-active like elemental nitrogen (N_2) TG-MS experiments were carried out. A mass fragment of m/z=52 was detected with

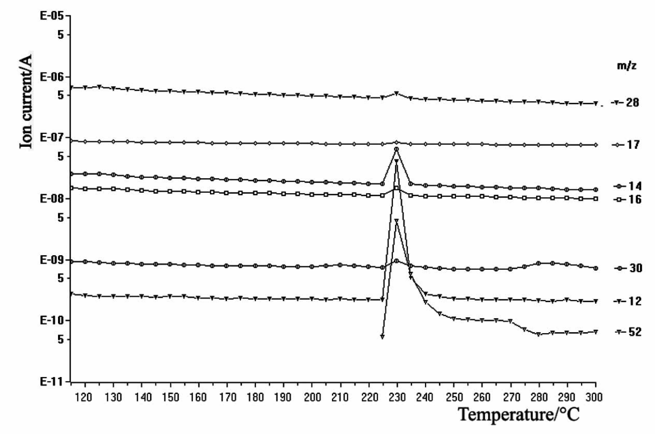


Fig. 13 Mass spectrometric detection of BTT decomposition gases (TG-MS run with β=5.0 K min^{-1})

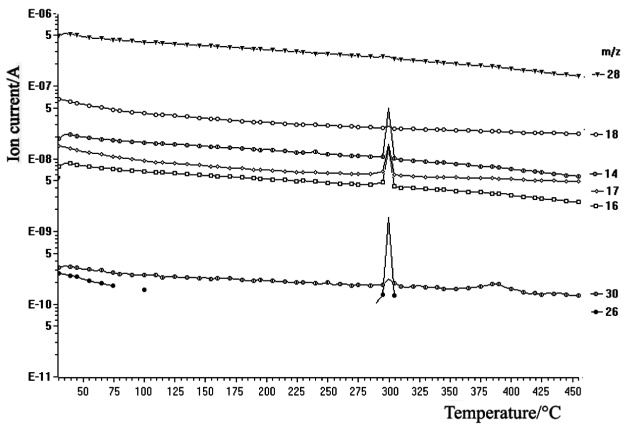


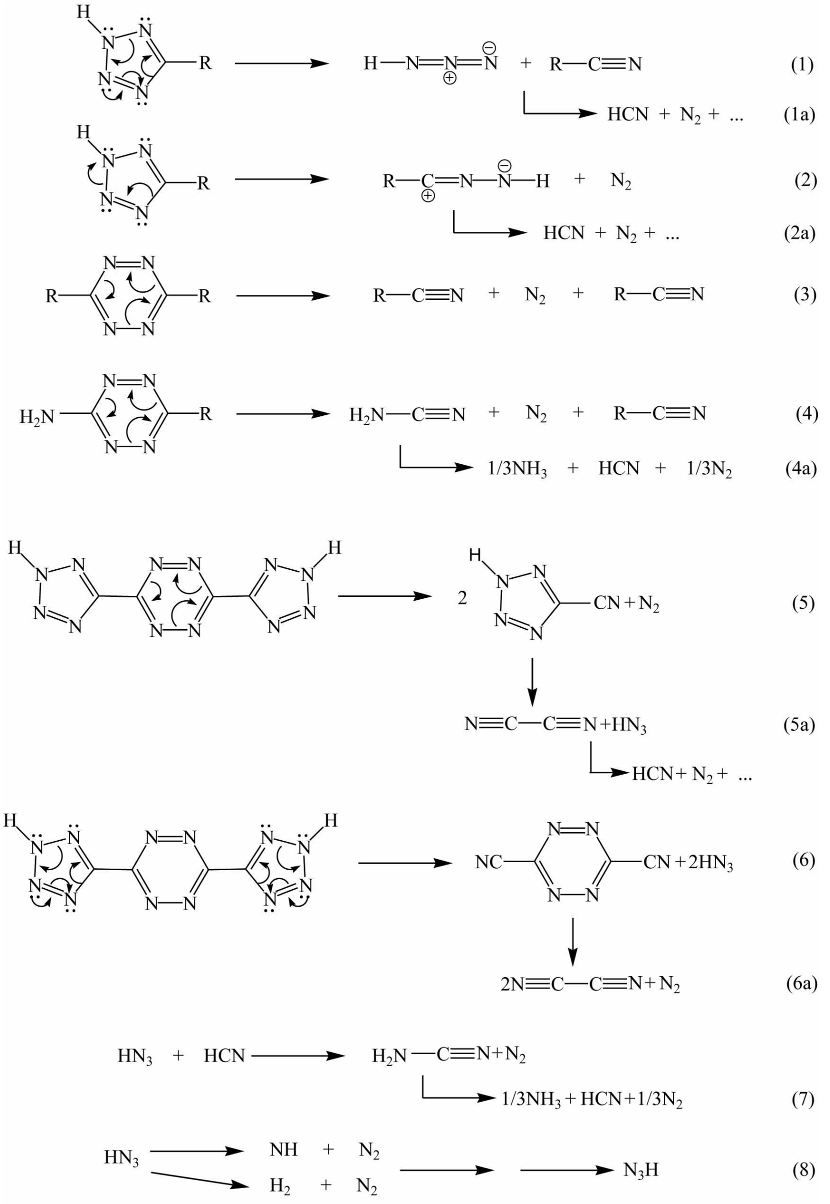
Fig. 14 Mass spectrometric detection of DAAT decomposition gases (TG-MS run with β=5.0 K min^{-1})

high intensity confirming clearly the evolution of cyanogen (M=52.03 g mol^{-1}) during the pyrolysis of BTT (Fig. 13). Moreover, m/z=52 in combination with the normally unspecific mass fragment m/z=12 is a typical pattern for the presence of cyanogen. However, in the TG-MS experiments of DAAT cyanogen was not detected (Fig. 14).

Mass fragments which were detected in the decomposition gases of both nitrogen-rich compounds were m/z=14 (N^+, N_2^{++}), 16 (NH_2^+), 17 ($NH_3{\cdot}^+$), 26 (CN^+), 27 ($HCN{\cdot}^+$), 28 ($N_2{\cdot}^+$, $HCNH^+$), and 30 ($N_2H_2{\cdot}^+$). They confirm the infrared spectroscopic detection of HCN, NH_3 and H_2N–CN. Traces of oxygen containing species like H_2O or CO_2 were not detected in the TG-MS experiments.

Therefore, the main qualitative difference in the composition of the gaseous pyrolysis products of BTT and DAAT is the absence resp. presence of cyanogen. Quantitative differences were observed in higher concentrations of H_2N–CN and NH_3 during DAAT pyrolysis and a higher concentration of HCN during BTT pyrolysis.

The differences in pyrolysis gas evolution can be explained by the differences in the decomposition pathways of BTT and DAAT. In previous studies it was already shown



Schemes 1–8 Simplified scheme of initial decomposition pathways of tetrazine and tetrazolering structures that the decomposition of substituted tetrazole and tetrazine structures is initiated by ring opening reactions [5]. For the pyrolysis of BTT and DAAT different formal decomposition pathways are simplistically illustrated in Scheme. Monosubstituted tetrazole rings collaps either by forming nitriles under release of hydrogen azide or by forming nitrilimines under release of elemental nitrogen (Schemes (1) and (2)). Consecutive reactions lead to the formation of hydrogen cyanide, further amounts of nitrogen as well as ammonia. The ring opening reaction of tetrazines is driven by the release of N_2 forming two equivalents of nitriles, Schemes (3) and (4). In the case of the amino group substituents of DAAT cyanamide is formed, Scheme (4), as it was detected by EGA experiments. As for the tetrazoles, consecutive reactions like the degradation of cyanamide lead to the formation of NH_3, HCN and N_2.

On closer inspection of the BTT molecule which consists of both tetrazole and tetrazine ring units two formal and idealized pathways have to be considered, Schemes (5) and (6). One is solely based on the tetrazine ring opening by forming cyanotetrazole which consecutively collapses to cyanogen and HN_3, Scheme (5). The other considered pathway is solely based on the tetrazole ring opening by forming bis-cyanotetrazine which immediately collapses again to cyanogen and N_2, Scheme (6). Although these two pathways are considered in a very idealized way they show clearly that cyanogen is an inherent decomposition product of BTT and can not be released by DAAT as it was observed in the EGA experiments.

Although hydrogen azide (HN_3) is a key intermediate during tetrazole ring degradation it could not be clearly proved in the decomposition gases of BTT. Due to the low thermal stability of HN_3 at the high decomposition temperature of BTT only its consecutive reaction products were certainly detected. However, in comparison EGA experiments of cyanotetrazole which decomposes at lower temperatures of >100°C [5] the evolution of cyanogen and HN_3 according to Scheme (5a) was clearly confirmed. HN_3 was IR spectroscopically proved by its characteristic absorption bands at 2153, 2127, 1165 and 1135 cm^{-1} as they were observed in previously measured reference spectra of in situ synthesized HN_3 (by H_2SO_4+NaN_3).

A number of consecutive gas phase reactions can be formulated, like Schemes (7) and (8), which explain the evolution of further amounts of NH_3, HCN, N_2 and also $H_2N–CN$ as they were IR spectroscopically and mass spectrometrically detected in the decomposition gases of BTT and DAAT. The higher amounts of cyanamide and ammonia that were detected in the decomposition gases of DAAT are due to the amino groups which are absent in the molecular structure of BTT. In the case of DAAT, additional amounts of elemental nitrogen arise from the azo-bridge.

Conclusions

The thermal decomposition behaviour of the two nitrogen-rich compounds BTT and DAAT was thermoanalytically characterized showing complete degradation accompanied by very high heats of decomposition which are released in a relatively narrow temperature range. These strong exothermicities combined with surprisingly high thermal stabilities make BTT and DAAT very interesting for gas generating energetic applications. The decomposition pathways of BTT and DAAT, which are initiated by ring opening reactions of the tetrazole and tetrazine structures, as well as subsequent gas phase reactions were identified. The understanding of thermal properties and decomposition pathways will give access to more tailor-made nitrogen-rich energetic materials.

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