Thermochimica Acta 535 (2012) 48–57

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal behavior and combustion mechanism of high-nitrogen energetic materials DHT and BTATz

V.P. Sinditskii*, V.Yu. Egorshev, G.F. Rudakov, A.V. Burzhava, S.A. Filatov, L.D. Sang

Mendeleev University of Chemical Technology, 9 Miusskaya Square, 125047 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 18 January 2012
Received in revised form 8 February 2012
Accepted 8 February 2012
Available online 17 February 2012

Keywords:
Energetic materials
Decomposition kinetics
3,6-Dihydrazino-1,2,4,5-tetrazine (DHT)
3,6-Bis(1H-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine
(BTATz)
Combustion mechanism
Surface temperature

ABSTRACT

The thermal stability of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT) and 3,6-bis(1H-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine (BTATz) have been examined by isothermal and nonisothermal methods. The research conducted allow considering that the first stage of DHT decomposition is an unique, from viewpoint of thermal decomposition, redox process, in which tetrazine ring is reduced by hydrazine group forming diaminodihydrotetrazine and molecular nitrogen. In the case of BTATz, the decomposition begins with less thermostable tetrazole fragments, which captures the tetrazine ring also. The presence of preliminary reactions of isomerization during tetrazole ring decomposition is the reason for the large observable activation energy of decomposition (240.6 kJ/mol or 57.5 kcal/mol) in the temperature interval 250–334 °C. In the combustion wave at higher temperatures, the activation energy of BTATz decomposition has considerably lower value (128.4 kJ/mol or 30.7 kcal/mol), which is close to theoretically calculated one.

Burning characteristics of DHT and BTATz have been investigated. The temperature distribution in the combustion waves of DHT and BTATz have been measured at low pressures, which allows obtaining the surface temperature dependence vs. pressure. The research conducted allow considering that the burning of investigated compounds controls by a combustion model with leading reaction in the condensed phase.

1. Introduction

In the past decade, there has been an interest in the research and development of the high-nitrogen compounds with high positive heats of formation and containing a high percentage of nitrogen. These high-nitrogen materials have been shown to be useful as high explosives, components of propellants, and gas generators. Among polynitrogen energetic materials 1,2,4,5-tetrazine derivatives (also known as s-tetrazine) are of particular interest owing to their high density, thermostability, and remarkable insensitivity to electrostatic discharge, friction, and impact [1–11].

One of such compounds, 3,6-dihydrazino-1,2,4,5-tetrazine (DHT), calculates to perform well in both rocket and gun propellant applications, which is partly attributed to its high hydrogen makeup [6]. DHT is an example of a high-nitrogen explosive that relies entirely on its heat of formation for sustaining a detonation. DHT, having a measured heat of formation of +536 kJ/mol (128 kcal/mol), detonates with rate of 7.54 km/s in the unconfined pressed pellets of 1.25 cm in diameter ($\rho = 1.56\ \mathrm{g/cm^3}$) [6]. Another tetrazine relative, 3,6-bis(1H-1,2,3,4-tetrazolyl-5-amino)-1,2,4,5-tetrazine, known as BTATz, is treated as the key component for new generation propellants [6,12], fire suppressing gas generators [13,14] and automobile airbags [15]. BTATz burns at impressive rates, producing a large amount of relatively cool nitrogen gas upon ignition. As a gas-generating solid BTATz is a candidate for use in automobile airbags [15]. The properties of BTATz rank it among the more promising components for cooled propellant formulations in new highly efficient, environmentally acceptable fire suppressant capabilities based upon solid propellant gas generators [13,14]. BTATz can sustain a burn front when packed in glass tubes as small as 250 microns in diameter [6], which may well find an application as monopropellant for microthrusters [16,17]. In addition, BTATz is ballistic modifier for propellants: addition of 22% BTATz to ammonium dinitramide (ADN) increases burning rate 1.5 times, at the same time reduces the pressure exponent [18]. As a substitute of hexogen (RDX) in the composite modified double base (CMDB) propellant, BTATz can improve the burning rate and reduce the pressure exponent [19].

The thermal stabilities of the tetrazine derivatives, as well as DHT and its salts with perchloric and nitric acids, dinitramide and bisdinitroimidazole were examined in works [20,21]. Thermal decomposition was initially evaluated using differential scanning calorimetry (DSC) in nonisothermal conditions. Isothermal thermolyses were performed on samples (0.1–0.6 mg) in tubes 4 mm

---

* Corresponding author. Tel.: +7 495 4966027; fax: +7 495 4966027.
E-mail address: vps@rctu.ru (V.P. Sinditskii).

0040-6031/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2012.02.014

outside diameter. Investigation conducted showed that tetrazine ring possesses high thermostability and decomposes by elimination of N_2 followed by cleavage of the remaining N–N bond. The thermal stabilities of DHT and tetrazines, having pyrazole ring as substituent are somewhat lower, that can be explained by primary decomposition of the exocyclic substituent or by its loss. For DHT an external deuterium kinetic isotope effect (DKIE) was found [20], which was attributed to protonation enhancing the rate of substituent loss.

The explanation of lowered thermostability of DHT by primary decomposition of the exocyclic substituent is not very clear, since hydrazine moiety itself is stable enough. The kinetic parameters of BTATz decomposition were measured with the help of DSC under nonisothermal conditions only, and the activation energy obtained has anomalous high value [11,22,23].

Combustion behavior of some tetrazine derivatives were studied in works [5,14,18]. The burning rate of DHT is considerably higher than the burning rate of HMX and strongly depends on small additive of binder. Mixture of DHT with 3% estane-based binder has higher burning rate at low pressure than pure DHT and as a result, the mixture has reduced pressure exponent in the burning rate law. BTATz also burns faster than HMX and with low burning- rate pressure exponent (0.49). Combustion studies of BTATz showed a strong influence of purification method on burning rate. However, detailed studies on the combustion mechanism of tetrazine derivatives were not carried out.

The goal of the present work was to evaluate the thermal decomposition and combustion mechanism of high-nitrogen DHT and BTATz, as well as 3-hydrazino-6-(1H-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine (HTATz), which is likened as a hybrid of the two molecules, having hydrazine moiety as DHT and tetrazolylamino substituent as BTATz.

2. Experimental

Preparation. The energetic compounds based on the s-tetrazine ring, DHT and BTATz, have been synthesized by methods published elsewhere [2–4] after treatment of the precursor, 3,6-bis-(3,5-dimethylpyrazol-1-yl)-s-tetrazine (BDT) by hydrazine hydrate or 5-aminotetrazole (5-AT), correspondingly. Elemental analysis and NMR spectroscopy confirmed the assigned structure.

During synthesis of HTATz the hydrazine salt of 3-hydrazino-6-(1H-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine ($HTATz{\cdot}N_2H_4$) firstly is formed, which is transformed then to HTATz by conversion to hydrochloride followed by neutralization by equimolar amount of water solution of NaOH.