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ScienceDirect

Journal of Hazardous Materials 152 (2008) 1317–1324

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Synthesis, characterization and thermolysis studies on 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT): A key precursor in the synthesis of most powerful benchmark energetic materials (RDX/HMX) of today

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Received 1 May 2007; received in revised form 31 July 2007; accepted 1 August 2007

Abstract

This paper reports studies undertaken on 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT). The synthesis of DPT was carried out by the nitration of hexamine based on the lines of reported method with minor modification. DPT was characterized by elemental analysis, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) techniques. Thermal stability of DPT was studied using thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal analysis studies revealed that DPT undergoes decomposition at 211 °C. Decomposition of DPT using TG-FTIR indicated the evolution of carbon dioxide, water and oxides of nitrogen as main gaseous products. The electrochemical behavior of DPT was studied using cyclic voltammetric (CV) studies. The experimentally determined sensitivity parameters indicated the insensitive nature of DPT towards external stimuli. The performance parameters of DPT, RDX and HMX have been computed using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) code. The predicted properties of DPT are interesting and important from the point of process technology and/or safety. The work reported in this paper enriches the existing scanty research and development data on one of the key precursor used for synthesis of important high energy materials (HEMs).

Keywords: 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT); HMX; Molecular orbital calculations; Thermal analysis; Energetic materials

1. Introduction

3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) is one of the most important key precursors in the production of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)/hexahydro-1,3,5-trinitro 1,3,5-triazine (RDX). DPT is synthesized by modified Bachmann process and is considered as a limiting intermediate [1–3] in the synthesis of RDX and HMX. Recently, Vagenknecht and Zeman [4] reported the physicochemical data and basic stability characteristics of the DPT.

The polymorphic forms of HMX are well reported in the literature [5]. The β polymorph of HMX is reported to exist in chair conformation while that of α, γ and δ phases exist in chair—chair conformation [6]. The similar kind of conformational arrangements in DPT has been reported by Oyumi et al. [7]. Differential thermal analysis (DTA) and variable temperature Fourier transform infrared (FTIR) studies were supported the interconvertible solid phase forms between 163 K and the decomposition point (460 K). However, it was noted that preliminary differential scanning calorimetry (DSC) studies showed the absence of solid–solid phase transitions. The understanding of the relation between the structure and decomposition mechanism in energetic materials is complex due to simultaneous formation of several decomposition reactions.

HMX is a powerful military explosive, but its use has been limited by its high cost. Reported manufacturing process for HMX involves the nitration of hexamine. It is known that HMX can be prepared from DPT, and indeed DPT has been identified as a key intermediate in the formation of HMX from the nitration of hexamine, which is also known as the modified Bachmann process [1]. In view of the vital importance of DPT in synthesis of

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doi:10.1016/j.jhazmat.2007.08.006

HMX, a low cost method for producing this intermediate would certainly add significant contribution toward reducing cost of HMX during its production. It was reported that the nitration of DPT gives 75% of HMX [3,8].

In view of the above observations and our continued interest in the area of high energy materials (HEMs) [9], we report here the studies carried out on DPT in our laboratory. The data generated during this work will enrich the existing scanty scientific data on one of the most sought after HEMs precursor (DPT). The present study was also undertaken to understand the various characteristic properties of DPT such as thermal stability, sensitivity to external stimuli and its electrochemical nature.

2. Experimental

2.1. Materials and methods

The starting materials used in the present study were of analytical grade (AR) grade and used directly as purchased from the trade. Melting point of the synthesized compound was measured using Thomas Hoover capillary melting point apparatus. Elemental analysis was carried out using Perkin-Elmer instrument (model 240C). The purity of DPT was ensured by high performance liquid chromatography (HPLC) (Waters Alliance HPLC system) with reverse phase micro C18 column. The eluent used was the mixture of acetonitrile, methanol and water (5:35:60) with the flow rate 1 ml/min. The IR spectrum was recorded on Perkin-Elmer FTIR-1600 spectrophotometer in KBr matrix and ^{1}H NMR spectrum was scanned on a 300 MHz Varian instrument in deuterated chloroform at 30 °C using trimethyl silane (TMS) as an internal standard. The DSC studies were undertaken on a Perkin-Elmer DSC-7 instrument at the heating rate of 10 °C/min. Differential scanning calorimeter was calibrated using indium and zinc standards and baseline corrections were also performed. Experiments were carried out in nitrogen atmosphere (nitrogen flow rate is 40 ml/min). The thermal decomposition studies were also undertaken on simultaneous thermo gravimetric/differential thermal analyzer of Mettler Toledo (model 8551). Thermo gravimetric Fourier transform infrared (TG-FTIR) studies on DPT was carried out using Bruker (EQUINOX-55) instrument. Mass spectra were obtained with Waters Micromass-Q-Tof micro (YA105) spectrometer using electro spray ionization (ESI) method. Electro spray ionization is the method of choice for analyzing thermo labile compounds using mass spectrometer. This method uses and electrical stress between the ESI probe exit (e.g. capillary) and the counter electrode (located few millimeters from the probe). This process results in the generation of highly charged droplets directly from the infused solution. The formation of positive or negative ions occurs in high yield. In the positive ion mode protonated and/or alkali adduct analyte molecules are generally observed in the mass spectra. Cyclic voltammetric studies were carried in acetonitrile solvent using a CHI-620A electrochemical analyzer. The sensitivity to impact stimuli was determined by applying standard staircase method using a 2 kg drop weight and the results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample [10]. Figure of insensitivity (F of I) was computed by using tetryl (composition exploding; CE) as reference. The friction sensitivity of the compound was determined on a Julius Peter's apparatus until there was no explosion/ignition in five consecutive test samples at that weight. The results obtained for impact and friction sensitivity were within the uncertainty limits of ±5 cm and ±0.2 kg, respectively. The crystal morphology was recorded using Scanning Electron Microscope (SEM) Instrument of Philips (FEI XL-30 model). The performance parameters of the synthesized compounds were predicted using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) code [11]. Geometrical parameters were calculated using Gaussian'03 package [12]. Semi-empirical molecular orbital calculation at parametric model 3 (PM3) level has been performed to optimize the geometry of the molecule.

2.2. Synthesis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT)

The DPT was synthesized based on the lines of modified Bachmann route [3]. In a five necked round bottomed flask equipped with stirring assembly, 150 ml of glacial acetic acid, 15 ml of acetic anhydride and 2 g of para formaldehyde were taken. The flask with the stirrer assembly was kept in a water bath. The temperature of the bath maintained at 44 ± 1 °C. Solution A consisting of 50 g of hexamine dissolved in 80 ml of glacial acetic acid and solution B consisting of 43.2 g of ammonium nitrate dissolved in 32 ml of 98% nitric acid were prepared. Solution A, B and 150 ml of acetic anhydride were added simultaneously to the reaction flask with the help of pre-calibrated peristaltic pumps over a period of 15 min. After the complete addition of the above reactants, the reaction was quenched by stirring the mixture for 15 min at a temperature of 44 ± 1 °C. The reaction mass was filtered immediately and the solid obtained was washed repeatedly with water and then dried. The yield obtained was 72% (57 g). The synthesized DPT was purified by recrystallising in nitromethane solvent, dried and characterized; melting point (MP): 203–206 °C; HPLC: retention time; 3.29 min (wavelength of 254 nm); IR: 3031, 2974, 2937, 2880, 1602, 1524, 1456, 1289, 1207, 1077, 935, 816 and 780 cm^{-1}; ^{1}H NMR (δ, ppm) = 4.1 (2H, singlet); 5.7, 4.8 (8H, AB quartet).

Table 1
Nitration of hexamine to DPT

Hexamine (g)	Hex/AcOH solution volume (ml)	Ac_2O (ml)	HNO_3/NH_4NO_3 solution (1:0.93 wt ratio) (ml)	DPT (g)	Percent conversion
50.17	485	150	60	55	70.3
50.69	490	150	60	58	73.4
50.59	489	154	60	57	72.3