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Thermal decomposition and kinetics of 2,4-dinitroimidazole: An insensitive high explosive

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ABSTRACT

2,4-Dinitroimidazole (2,4-DNI) is a novel energetic material with much less sensitive and potential for use as a propellant/insensitive munition (IM) formulations. 2,4-DNI possess high thermal stability and less sensitivity as compared to RDX and HMX which are high explosives extensively used at present. This paper reports a detailed thermal study of 2,4-DNI using various instrumental techniques. The activation energy ($E = 205 \pm 15$ kJ/mol) was calculated from thermal decomposition of 2,4-DNI using DSC at different heating rate. The ignition temperature of pure 2,4-DNI was measured and showed at 285 °C. The TGA experiments demonstrate that 2,4-DNI decomposes in three steps with 92% total weight lose. Moreover, the effect of thermal energy on decomposition of 2,4-DNI in presence of polymeric binders like GAP and HTPB were investigated. Further, decomposition mechanisms of 2,4-DNI based on Electron Impact mass spectra analysis were also reported along with its explosive properties.

1. Introduction

Development of high performance, insensitive energetic materials containing nitrogen hetero-aromatic core units are of current interest to the researchers worldwide [1]. Recently, some of nitroimidazole derivatives have been examined extensively as a possible candidate to meet various aspects of explosive performances with improved safety characteristics [2]. By simple theory, an aromatic imidazole ring may provide significant stability against an impact and thermal stimulus, while a nitrogen-rich chemical composition may enhance explosive performance [3]. Efforts being made by Lawrence Livermore National Laboratory, working together with the Army at ARDEC and LANL for optimizing the synthesis 1-methyl-2,4,5-trinitroimidazole (MTNI) and its evaluation in explosive and propellants formulations [4]. 2,4-Dinitroimidazole (2,4-DNI, Figs. 1 and 2) is a thermally stable, insensitive high energy material and demonstrated less sensitivity than RDX and HMX, which are high explosives extensively used at present [5,6]. Further, it has about 30% more energetic than TATB, which is an important insensitive explosive with relatively low energy output [7,8]. In addition to this, 2,4-DNI can be made from the inexpensive starting material i.e. imidazole. The 2,4-DNI can be used as an energetic monopropellant in propellant formulation to achieve a higher performance characteristic. Relative estimated specific impulse of 2,4-DNI respective to HMX is about 0.94. Comparison of I_{sp} of 2,4-DNI with HMX confirms that it can be used as monopropellant in composite propellants [9–11]. Utility of 2,4-DNI in the joint LLNL-Air Force Hard Structure Munition, high explosive program is under evolution [12]. However, a limited information on thermal characterization of 2,4-DNI could be found in the open literatures [13,14]. We report herein the detailed thermal studies of 2,4-DNI using various instrumental techniques. In addition to this, the effect of thermal energy on decomposition of 2,4-DNI in presence of polymers using DSC analysis were also reported. Further, a decomposition mechanism of 2,4-DNI was predicted based on results obtained from EI Mass spectral analysis.

2. Experimental

2.1. Materials and methods

GAP used in this study was prepared at HEMRL having molecular weight ~2000, density 1.1 g/cc and Tg −45 °C. While, HTPB having molecular weight 2800, density 0.97 g/cc and Tg −72 °C was purchased and used as such. Requisite amounts (1:1) of 2,4-DNI and GAP or HTPB dissolved in methanol and hand mixed in a vacuum chamber at room temperature and the solvent was removed under vacuum then samples were degassed for 1hr prior to testing. FT-IR spectra were recorded on Nicolet FTIR-5700 FTIR spectrophotometer in KBr matrix. ^{1}H and ^{13}C NMR spectra were recorded on Varian 300 MHz instrument. Ultraviolet spectra were recorded on GBC Cintra-10e UV–visible spectroscopy instrument

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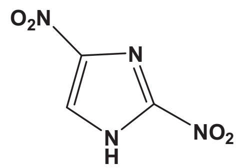

Fig. 1. 2,4-DNI (2,4-dinitroimidazole).

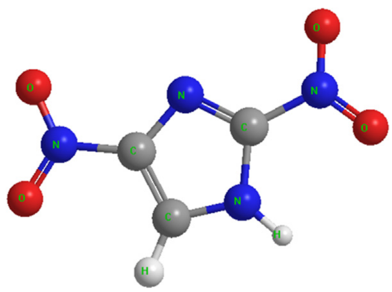

Fig. 2. Energy minimized structure of 2,4-DNI.

in acetonitrile. Thermal analysis was studied on a DSC-7 PerkinElmer instrument under nitrogen atmosphere. Raman spectra were recorded using a Renishaw inVia Raman microspectrometer and the spectra were excited with a Renishaw HPNIR laser (785 nm). Thermogravimetry Analysis (TGA) studies were carried out on a SDTA-851e Mettler Toledo instrument operating at heating rate of 10 °C/min in nitrogen atmosphere. HPLC studies were undertaken on Ultimate-3000 Dionex HPLC system, operating temperature is 25 °C by using reverse phase C-18 column (4 mm × 250 mm), mobile phase: acetonitrile/water (40:60), flow rate 1 ml/min, injection volume 10 μl in isocratic mode. Scanning electron microscope (SEM) analysis was carried out using AUANTA 200 ESEM-FEI, (The Netherlands).

2.2. Synthesis of 2,4-DNI

Synthesis of 2,4-DNI was achieved by stepwise nitration of imidazole according to the literature method [3]. The synthesized product always contains 4-nitroimidazole as impurity which could be removed by crystallization method. In our study, the crude product was re-crystallized from hot methanol to give pure crystalline 2,4-dinitroimidazole. The pure 2,4-DNI was subjected to various instrumental techniques like IR, NMR, UV and elemental analysis. FT-IR (KBr, cm^{-1}): 3149 (N—H), 3014 (C—H), 1549 (C=N), 1512 and 1341 (NO_2); UV (λ_{max}, nm): 221, 260, 324 for NH and NO_2; ^{1}H NMR (δ) (DMSO-d_6): 14.4 (s, 1H, NH), 8.5 (s, 1H, C_5-H); ^{13}C NMR δ (DMSO-d_6): 144 (C_2), 143 (C_4), 122 (C_5); Anal. Calcd for $C_3H_2N_4O_4$: C, 22.79%; H, 1.28%; N, 35.44; Found: C, 22.90%; H, 1.29%; N, 35.23%.

3. Results and discussion

3.1. Structural and purity analysis

IR spectrum of 2,4-DNI showed strong band at 3149 cm^{-1} which correspond to N—H bond presences in the imidazole ring. Further strong and weak bands appear in the range of 1512–1546 cm^{-1} and 1328–1354 cm^{-1} respectively corresponding to nitro groups present in the imidazole ring. The Raman spectrum ($\Delta\nu$) of 2,4-DNI is shown in Fig. 3. A strong peak at 1435 cm^{-1} for the >C=N bonds, another strong peak at 1273 cm^{-1} corresponding to bending vibrations of the ring. A peak appeared at 1339 cm^{-1} which assigned for NO_2 groups present in the molecule. Other peaks for C=N, C—N, C—H and N-O observed at 273, 817, 1014, 1106, 1216, 1399, 1509, 1554 cm^{-1}. The UV spectrum revealed that presence of $n \rightarrow \pi^*$ transition at 324 nm attribute to nitro groups present in the imidazole ring and band at 221 to 260 indicates that presence of NH. Further, ^{1}H NMR spectra showed chemical shift (δ) at 14.4 ppm corresponding to acidic N-H, and the ring C_5-H proton gives a singlet at 8.5 ppm. Similarly, ^{13}C NMR spectra showed three peaks for imidazole ring carbons at 144 (C_2), 143 (C_4), 122 (C_5).

Purity of 2,4-DNI was determined by HPLC method using methanol/acetonitrile system as mobile phase and found to be greater than 98%. The SEM image of 2,4-DNI presented in Fig. 4, it reveals that rod/plate shaped layered crystalline morphology with particle size ranging 100 to 400 μm. Indicates that it require a morphological modification before use in the explosive composition for better performance.

3.2. Thermal analysis

The DSC traces of 2,4-dnitroimidazole showed a broad exothermic peak 288 °C (T_{max}) with decomposition energy (ΔH) = −1732 J/g. In addition to this, a small endothermic peak was observed at the temperature 228 °C (T_{max}, ΔH = 42 J/g), this may be attributed to the phase transition occurred in the 2,4-DNI crystal structure (Fig. 5, heating rate 10 °C/min). This is different from

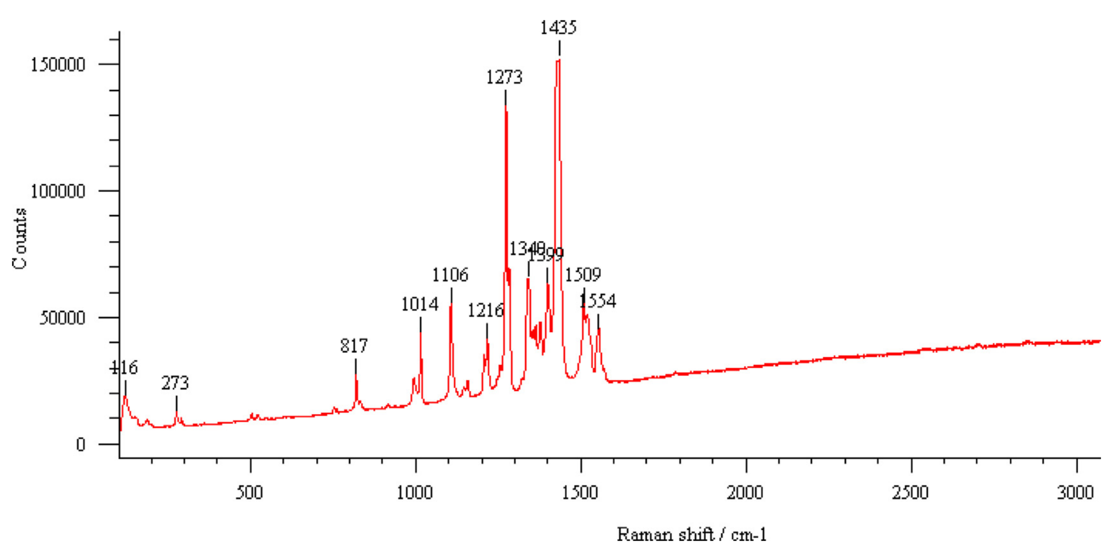

Fig. 3. Raman spectra of crystallized 2,4-DNI.