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Preparation and thermal studies on tetranitrodibenzo tetraazapentalene (TACOT): A thermally stable high explosive

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Abstract

Thermally stable high explosive, tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene (TACOT) was synthesized and characterized during this work. Thermo analytical techniques (TG and DSC) were applied to study the thermal decomposition behaviour of TACOT in comparison with benchmark thermally stable high explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Kinetic parameters such as reaction order, activation energy and pre-exponential factors were computed from the thermal data. The activation energy for TACOT (292 kJ/mol) was found 1.5 times to that of TATB (200 kJ/mol), which can account for its higher thermal stability and can be attributed to pentalene moiety in the former.

Keywords: TACOT; Tetranitrodibenzo tetraazapentalene; Thermally stable high explosive; Triaminotrinitrobenzene; Thermolysis

1. Introduction

Thermal stability is one of the important characteristics of the energetic materials to ensure safe production, desired shelf life of munitions and low vulnerability to accidental initiations. Specific missions demanding thermal stability led to emergence of special class of high energy materials (HEMs) superior to that of benchmark high explosive 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) (>260 °C). Nitro compounds namely 2,4,6-tripicryl-*s*-triazine (TPT), 2,2′,4,4′,6,6′-hexanitrostilbene (HNS), 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl (DIPAM) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) having decomposition temperatures in the range of 290–350 °C have received attention for applications in supersonic missiles where high temperatures are encountered in the space environ [1–3]. Tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene (TACOT) has emerged as one of the most thermally stable HEMs with decomposition temperature of 410 °C. The crystal density of the compound is 1.82 g/cm^3. It can offer velocity of detonation of 7060 m/s and detonation pressure of 203 kbar [4]. Its extraordinary thermal stability and reasonable insensitivity to mechanical stimuli has led to its emergence as HEM of choice for military applications requiring flexible linear shaped charge (FLSC) and sheet explosives as well as civil applications such as oil-well perforating operations [5–7].

This paper reports the synthesis and characterization of TACOT. Detailed thermal studies were conducted by applying differential scanning calorimetry (DSC) and thermogravimetry (TG) to determine the decomposition pattern in comparison to TATB. A mixture of TACOT with 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) was also subjected to DSC with the aim of achieving optimization of decomposition temperature and energetics.

2. Experimental

2.1. Materials and methods

All the reagents and chemicals of AR grade were used as such in the present study. Fourier transform infrared (FTIR) spectra were recorded on Perkin-Elmer FTIR-1600 spectrophotometer in KBr matrix and ^{1}H NMR spectra scanned on a 300 MHz with pulsed Fourier transform system in DMSO-d_6 (TMS as internal standard). Elemental analysis of the sample was carried out on elemental analyzer of CE instruments make (Model CHNO-1110).

Thermal analysis was undertaken on DSC (sample mass: 2 mg, nitrogen flow rate: 40 ml/min, aluminium pan, hermetic

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mode) of Perkin-Elmer make at heating rates of 5, 10, 15 and 20 °C min^{-1} as well as simultaneous thermal analyzer (STA) of Mettler Toledo make at 10 °C min^{-1} in N_2 atmosphere (sample mass: 4 mg, nitrogen flow rate: 40 ml/min, aluminium pan, hermetic mode). Activation energy of the compounds was calculated from DSC results using American Society of Testing and Materials (ASTM) standard method based on Kissinger correlation [8]. Dynamic TG (sample mass: 4 mg, air flow rate: 80 ml/min, aluminium pan) data was analyzed by Coats and Redfern method [9]. The decomposition patterns under the isothermal conditions (sample mass: 4 mg, nitrogen flow rate: 80 ml/min, aluminium pan) were also obtained for TACOT at 370, 375, 380 and 385 °C as well as for TATB at 325, 330, 335 and 340 °C. Activation energy was computed using a Thermal program developed in-house for the prediction of activation energy of energetic systems [10].

The sensitivity to impact stimuli was determined by applying standard Bruceton staircase method using a 2 kg drop weight and the results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) [11]. 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 [12].

2.2. Synthesis

The compound was synthesized and characterized on the lines of the method reported by Carboni et al. [13] with little modifications. All the starting materials were of >97% purity and solvent used were dried by standard procedure. The first step involved the oxidation of *O*-phenylenediamine by lead oxide/potassium superoxide in benzene/toluene under reflux to obtain 2,2′-diaminio azobenzene (I) which was doubly diazotized and treated with excess sodium azide in the second step to realize 2,2′-diazidoazobenzene (II). The third step involved the cyclization of (II) to dibenzotetraazapentalene (III). Nitration of III with HNO_3 and H_2SO_4 led to the formation of tetranitrodibenzo tetraazapentalene (IV) in 50% yield. The various reactions that are involved in the synthesis are given in Scheme 1. TATB and CL-20 used in the study were synthesized in house and are of required purity.

3. Results and discussion

3.1. Spectral studies

The FTIR spectrum of TACOT exhibited absorption at 1530 and 1325 cm^{-1} attributable to asymmetric and symmetric stretching of –NO_2 group and at 3100 cm^{-1} due to aromatic –CH stretching. In ^{1}H NMR, TACOT gave two signals at 9.98 δ and 9.31 δ which can be assigned to C_1–H and C_7–H protons. The IR and NMR patterns obtained during this work are concurrent with the reported values [13]. The elemental analysis results for TACOT (C: 37.3, N: 28.73, H: 1.01) were close to the theoretical values (C: 37.12, N: 28.86, H: 1.03).

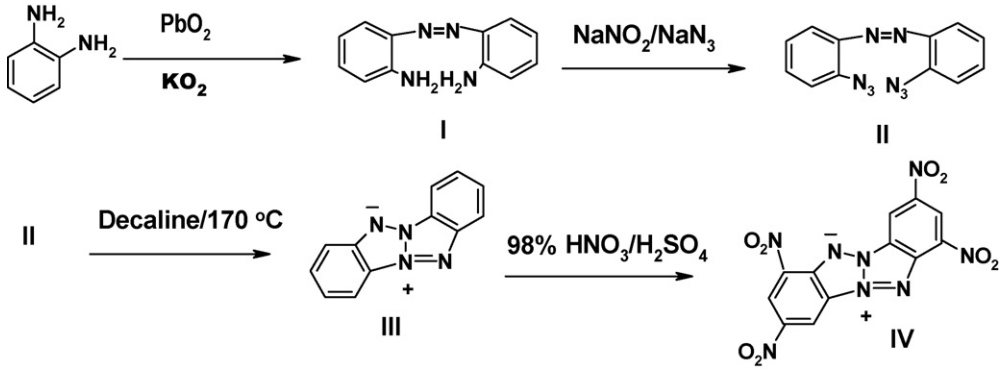
3.2. Sensitivity

The experimentally obtained impact sensitivity of TACOT is 68 cm and it is friction insensitive upto 36 kg. TATB is insensitive to impact (>170 cm) and friction (up to 36 kg). The results revealed that TACOT is completely insensitive to friction stimuli and reasonably insensitive to impact.

3.3. Thermal studies

The DSC of both TACOT and TATB exhibited single stage exothermic decomposition with decomposition maximum (T_{max}) at 403 and 376 °C, respectively. The heat evolved during exothermic decomposition of TACOT was 1795–2712 J/g in comparison to that of 832–1409 J/g for TATB at heating rates of 5, 10, 15 and 20 °C. The DSC curves were analyzed by Kissinger method. In this method, $\ln(\beta/T_m^2)$ is plotted against $1/T_m$ (where β is the heating rate, T_m is maximum decomposition temperature). From the slope of the curve, activation energy is calculated. The activation energy of TACOT computed from DSC results obtained was 292 kJ/mol whereas that obtained for TATB was 200 kJ/mol (Table 1).

Dynamic TG of TACOT in conjunction with DTG also revealed single stage exothermic decomposition at 403 °C (Fig. 1). Coats and Redfern plot of the dynamic TG data gave straight line with order parameter of zero. The slope of plot ($-E/2.3R$) corresponded to E_a of 330 kJ/mol whereas E_a obtained for TATB was 221 kJ/mol.



Scheme 1. Synthesis of TACOT.