



Evaluation of thermal stability and time resolved acoustic fingerprint spectra of 1-(2-methoxy,-3,5-dinitrophenyl)-1H-1,2,3-triazole



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ABSTRACT

The paper reports the study of thermal stability and decomposition mechanisms of the newly synthesized phenyl series energetic molecule named 1-(2-methoxy,-3,5-dinitrophenyl)-1H-1,2,3-triazole (S_5) using time resolved pulsed photoacoustic (PA) pyro analysis technique. The thermal PA spectra of the compound was recorded using a Q-Switched Nd-YAG laser (532 nm, 7 ns, 10 Hz). TG-DTA technique was carried out for ascertaining the melting and decomposition temperature of the compound. The results of these two methods confirm that S_5 is thermally stable in the range of 30–350 °C. We have earlier reported that phenyl series 1,2,3-triazoles require high incident laser energy than that of benzyl series 1,2,3-triazoles [1]. However, our further investigation shows that the change in the position of principal functional groups affects the process of thermal decomposition. Also, the thermal stability of the compound is evaluated on the basis of quality factor (Q) of the PA cavity. Further, we have used GC-MS and FTIR techniques to identify some of the gaseous components released from the compounds.

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1. Introduction

Triazole is a heterocyclic compound of a five-member ring structure, containing three nitrogen atoms and two carbon atoms. These materials have high heat of formation, good thermal stability, high detonation velocity, and resistance to impact, shocks and sensitivity. Therefore, these compounds have potential applications in civil and military as energetic materials [2–5]. Investigation of thermal stability and decomposition of newly synthesized high energy materials (HEMs) have been one of the focused area of the present research [6,7]. Thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Gas chromatography–mass spectrometry (GC–MS), accelerating rate calorimetry (ARC) and heat flow calorimetry (HFC) etc. are some of the well-known analytical techniques, to study the thermal decomposition of HEMs [8–10]. Of these techniques, our group has developed the photoacoustic (PA) pyro analysis technique to understand the thermal decomposition, stability and bond breaking mechanisms of HEMs. The UV–vis wavelengths of pulsed laser radiation are used as an excitation source [11–14].

The photoacoustic technique is a versatile tool to study the non-radiative relaxation transition in solid, gas and liquid sam-

ples [15–18]. Moreover, it offers the advantages of high sensitivity, selectivity, compact setup and fast time response. It is widely recognized for its excellent performance in trace gas measurement [19–24].

The reported compound 1-(2-methoxy,-3,5-dinitrophenyl)-1H-1,2,3-triazole is labeled as S_5 has good thermal stability and shock sensitivity. Its chemical formula $C_9H_7N_5O_5$, and possess molecular weight: 265.20, heat of formation: 253.5 kJ/mol, detonation velocity: 6.34 km/s and density: 1.57 g/cm³ [25]. Theoretical and experimental studies on thermal decomposition of nitro rich HEMs confirms the presence of NO, N₂O, CO, CO₂, H₂O, H₂, HONO and HCN etc. as byproduct gaseous molecule [26,27]. Further investigations revealed that NO₂ is one of the predominant gaseous molecules [28]. It has strong absorption at 532 nm wavelength and excited to ²B₂ state, which is responsible for V-T and V-V relaxations [29]. Therefore, thermal stability of the energetic material can be ascertained based on thermally released NO₂ by employing 532 nm as an excitation wavelength.

2. Experimental arrangements

Fig. 1 shows the experimental design used in the laboratory. A Q-switched Nd: YAG laser (Model Spit, Germany) of 532 nm wavelength, 7 ns duration and 10 Hz repetition rate was used to excite the compound's vapor in a cylindrical PA cell made of stainless steel. It has internal diameter ($d=2R$) of 1.5 cm and length (L) of 7.5 cm.

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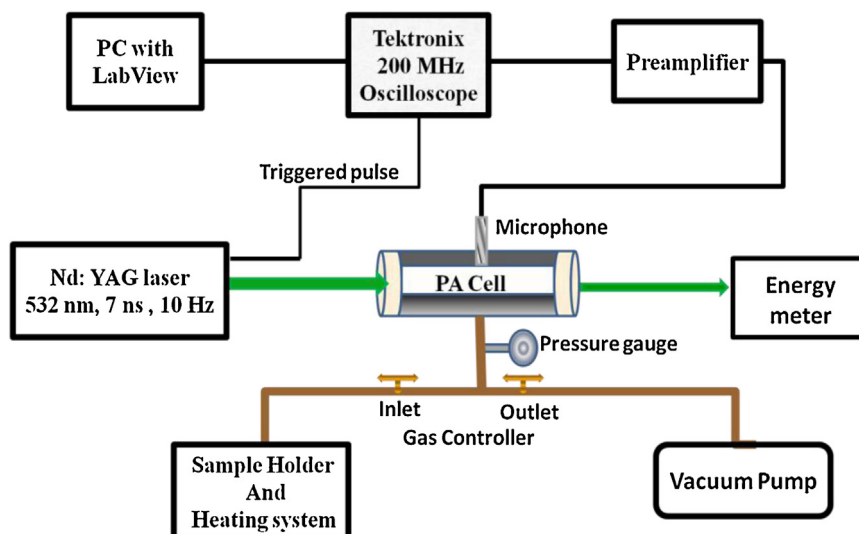


Fig. 1. Experimental set up.

The explosive vapor was collected from 1.0 mg of solid compound housed in a heating system, which facilitates the controlled pyrolysis between the temperature range of 30–350 °C. A pre-polarized microphone (BSWA, China) of responsivity 50 mV/Pa, having frequency response between 0 and 60 kHz ranges was used to detect the generated acoustic signal. The signal received from microphone was fed to a preamplifier, which was further connected to a 200 MHz oscilloscope (Tektronix, U.S.A.). The oscilloscope shows the generated acoustic signal in time domain mode which was converted into frequency domain using Fast Fourier Transform (FFT) spectra. The data acquisition program written in LabView software is employed for analysis.

The laser pulses of 7 ns pulse duration and 10 Hz repetition rate were allowed to enter the PA cell. The microphone converts the generated acoustic pressure waves into electrical signal. The time domain signal appeared in oscilloscope with respect to laser repetition rate. Since the time gap between two pulses is of the order of 100 ms. Therefore, selection of data acquisition time from the oscilloscope help us to avail the maximum range of the microphone. For example t is set to be 0.5 ms, 1.0 ms, 2.5 ms the corresponding gap between two successive data points is of the order of 200, 100 and 40 Hz respectively. These time scales cover the linear responsivity range (0–60 kHz) of microphone. However, in LabView window the resultant of averaged 1000 time domain signals are recorded, which converted into frequency domain spectra using fast Fourier transform (FFT). These data were exported for further analysis. The compound's vapor at different temperatures and at 600 Torr pressure was allowed into the PA cell and irradiated by incident laser radiation. The PA spectrum was recorded at required incident laser energy (E_{in}) and data acquisition time (t).

The frequency of the acoustic resonant modes generated within the cylindrical type PA cavity can describe as

$$F_{mnq} = \frac{c}{2} \left(\left(\frac{\alpha_{mn}}{R} \right)^2 + \left(\frac{q}{L} \right)^2 \right)^{1/2} \quad (1)$$

Where c , R and L are the sound velocity, radius, and length of the cylindrical resonator, respectively. α_{mn} is the n^{th} zero of the derivative of the m^{th} Bessel function at $r=R$. q , n and m are the longitudinal, radial and azimuthal modes, respectively.

Thermo gravimetric-differential thermal analysis (TG-DTA) was carried out using TA Instrument (Model No. Q600DT). A small quantity (3.8 mg) of the solid compound was placed in an alumina crucible and heated between 25 and 250 °C range under nitrogen

gas (flow rate of 100 cm³/min), which works as the purge and protective gas. An empty alumina crucible was used as a reference. Non-isothermal TGA runs were conducted under the similar range of temperature with the heating rate of 10 °C/min.

Differential Scanning Calorimetry (DSC) analysis was carried out using instrument (METTLER TOLEDO, model: DSC1) between 25 and 400 °C range in the N₂ atmosphere which was purge @ 60 mL/min with flow rate of 10 °C/min.

The compounds were dissolved in chloroform (CHCl₃) to record the GC (Agilent7890a) – MS (AccuTOF GCV) spectra: 0.4 μL solution of the compound was injected after making a saturated solution. The temperature of injector, ion source and transfer line were maintained at 250, 200 and 260 °C, respectively. In addition, infrared spectra of solid compound was recorded using a Perkin- Elmer IR spectrometer between 400 and 4000 cm⁻¹ range in form of KBr pellets.

3. Results and discussions

3.1. FTIR spectra of S_5

Fig. 2 shows the FTIR spectra of S_5 recorded in solid form. Inset table of Fig. 2 shows the structural positions of principal functional groups present in the compound. The strongest absorption peaks of C–O–C, –NO₂, –N=N+=N–, –OCH₃ and C–H are observed at 1300–1000 cm⁻¹, 1550–1300 cm⁻¹, 2400–2000 cm⁻¹ and 2850–2810 cm⁻¹, respectively. The recorded FTIR spectra confirm the presence of different types of functional groups in the compound S_5 .

3.2. Thermal PA spectra and stability of S_5

Fig. 3a shows the chemical structure, electrostatic potential diagram (Density Functional Theory figure) and molecular structure derived from single crystal X-ray diffraction of S_5 . Here, two nitro groups are attached to the *meta* positions, and one methoxy group is present at the *ortho* position of the phenyl ring concerning triazole moiety. Table 1 shows the calculated eigenmode frequencies of 11-longitudinal (q), 2-radial (n) and 2-azimuthal (m) modes of the PA cavity.

Fig. 3b shows the thermal PA spectra of S_5 recorded between 40 and 350 °C temperature range, at E_{in} = 5.25 mJ and t = 5 ms. The excited acoustic modes are located at 3.04, 3.2, 8.7, 9.2, 11.4, 12.6,

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