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Thermal stability study of nitro-rich triazole derivatives using temperature dependent time resolved pulsed photoacoustic (PA) technique

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ABSTRACT

The paper reports the pulsed laser based photoacoustic pyrolysis technique to study the thermal stability of novel nitro-rich 1H-1,2,3-triazole derivatives of high energy materials (HEMs) for the first time. We have employed 532 nm wavelength, 7 ns duration pulses at 10 Hz repetition rate obtained from Q-switched Nd:YAG laser system to record the time resolved temperature dependent PA spectra in a specially designed PA pyrolysis system. The study has been carried out between the 30 and 350 °C temperature range. Thermally stable HEMs are insensitive to temperature and they release very small amount of volatile compounds such as H_2O, NO_2, and NO at high temperatures. The combined results obtained from PA and TG–DTA techniques open a new channel to understand the molecular dynamics of HEMs which is responsible for energy storage mechanism of these compounds in terms of free NO_2 at different temperature ranges. In addition, the experimental findings lead to develop a new tool to scale the efficiency of these molecules as a fuel.

1. Introduction

TNT, RDX, HMX, PETEN, triazole and tetrazole derivatives are well known secondary high energy materials (HEMs) and widely used in the industry and defense applications [1–3]. The present global trend is to develop some new eco-friendly long chain nitrogen or oxygen rich high energy materials which should posses high detonation performance, heat of formation in combination with good thermal and shock stability. These compounds can be used as an efficient rocket fuel and gun propellants [4,5]. Therefore, a lot of quantum chemistry based calculations have been done to develop some new types of HEMs. These materials are not only eco friendly but also thermally stable in nature [6–8]. Moreover, it becomes very important for to understand the molecular dynamics of these compounds under different controlled temperatures.

The recent advances in spectroscopy techniques such as CW, pulsed laser based interferometry techniques, supersonic jet coupled with time of flight mass spectrometer, and ultrafast spectroscopy have opened a new channel for understanding the molecular dynamics of HEMs [9–11]. However, detailed study of intermediate chemical channels of decomposition of these molecules which follow uni and multi-molecular chemical reaction pathways, such as cessation of N—N bonds, concerted ring breaking still need detailed investigation. The laser based experimental results of HEMs provide important basic information which is helpful to develop material models for large scale macroscopic simulations of HEMs [12–15].

In case of HEMs, NO_2 is found as one of the principal volatile by-products which works as an energy marker in the case of thermal decomposition [16–20]. However, some of the initial theoretical models have predicted the bond breaking mechanisms for RDX, which starts above 1200 °C [14]. In addition, some groups have also studied the thermal decomposition (TD) mechanism of these compounds using TG-DSC/DTA coupled with FTIR or GCMS demonstrated that volatile decomposition starts above the melting point i.e. 200 °C. They have identified the NO_2 as an important volatile gas [19]. Main limitations of these instrumentation techniques are their working principle and sensitivity. For example, TG–DTA capable of detecting the weight loss and heat flow of a given compound when it loses weight of the order of few micrograms which ultimately releases significant amount of heat in terms of enthalpy. In addition, their detection and signal processing arrangement can be

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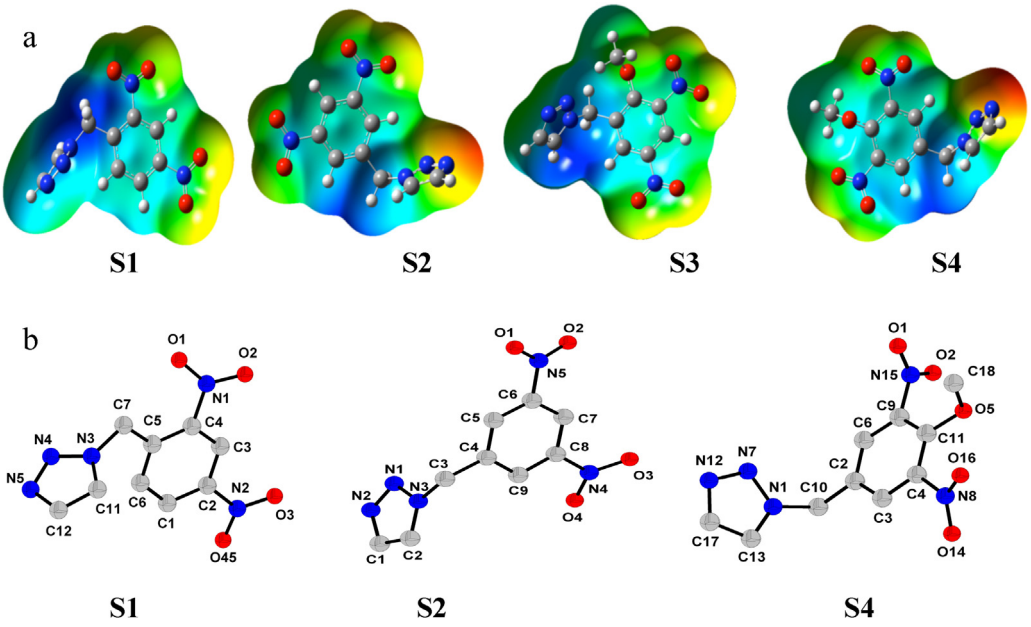

Fig. 1. (a) Electostatic potential surfaces of compounds **S1**–**S4**. (b) Molecular structures of compounds **S1**, **S2**, and **S4** confirmed by X-ray crystallography.

used only to monitor the changes in ppm level. Thermal stability of HEMs is ascertained by heating these compounds up to 100 °C for long hours under vacuum and tested on the basis of color change which is mainly due to release of H_2O molecules [21]. However, evaluation of thermal stability on the basis of NO_2 which releases much below 100 °C opens a new channel for thermal study. This technique is more effective, less time consuming and efficient as compared to other existing conventional techniques.

There is another class of HEMs such as imidazole, pyrazole, triazole, and tetrazole with high nitrogen content, heat of formation, detonation velocity and pressures. Our group has synthesized thermally stable energetic 1,2,3-triazole derivatives such as 1-(2,4-dinitrobenzyl)-1H-1,2,3-triazole (**S1**), 1-(3,5-dinitrobenzyl)-1H-1,2,3-triazole (**S2**), 1-(2-methoxy-3,5-dinitrobenzyl)-1H-1,2,3-triazole (**S3**), 1-(4-methoxy-3,5-dinitrobenzyl)-1H-1,2,3-triazole (**S4**) in the laboratory [22]. The electostatic potential surfaces of compounds **S1**, **S2**, **S3** and **S4** are shown in Fig. 1a, and the molecular structures of compounds **S1**, **S2** and **S4** are confirmed by X-ray crystallography and are shown in Fig. 1b. The respective position of $-NO_2$, $-OCH_3$ functional groups and triazole moieties was observed clearly in the electostatic potential surfaces.

The photoacoustic pyrolysis technique offers main advantages such as of high sensitivity, selectivity, compact setup and fast time-response, and is widely recognized for its excellent performance in trace gas detection from ppb to ppt level [23–33]. Several groups have reported the photoacoustic studies of NO_2 gas using second harmonic of pulsed Nd:YAG laser; however, our group has extended this work to understand the thermal decomposition mechanism of HEMs. The PA signal in NO_2 is produced by nonradiative decay process. It is due to strong coupling between the high vibrational levels of the X^2A_1 ground state and the $^2B_2$ or $^2B_1$ state. NO_2 is excited to the $^2B_2$ state due to absorption of 532 nm and its excitation energy is lost to photo-acoustic signal generation by *V–T* and *V–V* relaxation [17,18].

In the present report, we discuss the new multidimensional aspects of our improvised form of existing pulsed PA technique which has motivated us to study the thermal stability mechanism of newly synthesized nitro-rich 1H-1,2,3-triazole derivatives for the first time. These compounds have wide gap between the melting and decomposition temperature. For example, while compound **S1** has melting point (T_m) 145 °C and decomposition point (T_d) 225 °C, as well as it takes more time to release the heat and volatile gaseous products like H_2O, NO_2 NO, N_2O, HCN and so on each of these gases has its own absorption wavelength in UV–vis range which can only generate photoacoustic signal from the given gas molecules. For example, H_2O, NO and N_2O have strong absorption range between 0–195 nm, 6.5–207 nm and 170–223 nm wavelengths, respectively. Similarly, other gases can also produce PA signal in their suitable absorption wavelengths range.

However we successfully recorded their acoustic fingerprints and identified some new NO_2 thermal windows just above the room temperature. Finally, our experimental observations combined with TG–DTA analysis provide a new tool to identify some of the important features of the HEMs such as thermal gaseous bi-products, and relationship between residual amount of the compounds and the efficiency of the fuel.

2. Experimental details

The second harmonic of Q-switched Nd:YAG laser (Model Spit, Germany) is used to excite the vapors of newly synthesized nitro-rich molecules in a specially designed photoacoustic pyrolysis system. The PA cell with an internal diameter of 1.5 cm and length of 7.5 cm made of stainless steel is used to record the PA spectrum. The compounds are heated in a round bottom flask housed in a temperature controlled oven. A needle valve is used to control the flow rate of vapor through inlet. The photoacoustic signal (PA signal) was detected by pre-polarized microphones of 50 mV/Pa (BSWA, China). The microphone was placed in the center of the cell. The output signal of the microphone has been given as feedback to the preamplifier which is coupled to the 200 MHz Oscilloscope (Tektronix, U.S.A.). The USB/GPIB interfacing is used for data acquisition through Boxcar integrator (Stanford Instruments Inc., USA). Schematic layout of photoacoustic experiment is shown in Fig. 2. The compound vapors are collected from solid compound in a specially designed heating system provides temperature 25–350 °C for all compounds.

A special type of needle valve is used to control the inlet vapor which helps to protect the microphone diaphragm. The collected vapor is sent into the PA cell which is irradiated by 532 nm

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