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Thermal decomposition studies on energetic triazole derivatives

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ABSTRACT

Thermal decomposition studies on two energetic triazole derivatives, viz N-(2,4-dinitrophenyl)-3-nitro-1,2,4-triazole (**1a**) and N-(2,4-dinitrophenyl)-3-azido-1,2,4-triazole (**1b**) have been investigated using simultaneous TG-DTA and TG-GC/MS techniques. Both compounds (**1a**) & (**1b**) showed good thermal stability, with exothermic decomposition peaks at 349 °C and 217 °C, respectively on DTA. Compound (**1a**) was found thermally more stable, and showed gradual weight loss after 250 °C. Kinetic parameters were calculated from the DTA peak temperatures, at different heating rates according to the method of Ozawa and Kissinger and refined for accuracy as per the ASTM E698 standard. Qualitative analysis of gaseous species produced during the decomposition was analysed using mass spectrometry, using the TG–GC/MS techniques. As evident from mass spectrum both compounds showed presence of CO_2, NO_2, NO, HCN, N_2, & H_2O among the products of decomposition.

1. Introduction

Syntheses and thermal investigation of nitrogen containing heterocyclic-based energetic molecules [1–5] have got considerable attention over the last decade. Throughout the literature experimental evidences prove five membered nitrogen heterocyclics as potential energetic molecules, especially azoles of which considerable attention has been given to the development of energetic derivatives of tetrazoles and 1,2,4-triazoles. Though tetrazoles and its derivatives are the most studied as energetic materials [6–8], energetic triazole derivatives (like NTO, ANTA, ADNT, etc.), are also of keen interest, especially owing to its better insensitivity and stability [9].

From the energetic point of view, better oxygen balance (Ω), high positive heat of formation ($\Delta_f H^0$), higher value of density etc., are the most desirable properties. Nitrogen rich heterocyclics are considered suitable candidates for the development of energetic materials due to the inherent high density and high positive heat of formation, when compared to their carbon analogues. By substituting explosophoric groups like azides, nitro etc., on these azoles, the inherent properties of these species can be tailor-made for suitable energetic applications [10]. Incorporation of the azido group increases the heat of formation of the compound (for e.g. $\Delta_f H^0$ of 3-azido-1,2,4-triazole is +458 kJ/mol [11], whereas the unsubstituted 1,2,4-triazole has $\Delta_f H^0$ of +109 kJ/mol [12]), whereas incorporating nitro group increases the oxygen balance as well as detonation properties [13]. The present study involves the development of new energetic molecules by linking the nitro aromatic moiety with nitrogen rich heterocyclics and thus studying its thermo chemical properties. By incorporating nitrogen rich heterocyclics on nitro aromatics, a new class of energetic compounds can be derived, which may exhibit combined properties of both class of energetic molecules [14]. Most of the energy obtained from these compounds results partly through oxidation of the carbon backbone, as traditionally found for carbon rich explosives, and partly from higher positive heats of formation of heterocyclics. Recent studies showed that these compounds can be potential precursors for the synthesis of pentalene systems, an emerging class of high density materials, with high stability and insensitivity [15,16]. Even though the synthesis and initial structural characterisation of the compounds under investigation have been reported, the thermal decomposition characteristics and energetic behaviour of the compounds have not been documented.

Accordingly two energetic azole derivatives, viz., N-(2,4-dinitrophenyl)-3-nitro-1*H*-1,2,4-triazole **(1a)** & N-(2,4-dinitrophenyl)-3-azido-1*H*-1,2,4-triazole **(1b)**, were prepared, characterized (vibrational(FTIR), multi nuclear NMR, friction and combustion values) and studied for their thermal decomposition behaviours as well as the decomposition kinetic analysis.

2. Experimental

2.1. Materials and methods

All the solvents used were from Merck and distilled and dried over molecular sieves prior usage. 3-Amino triazole (assay 96%)

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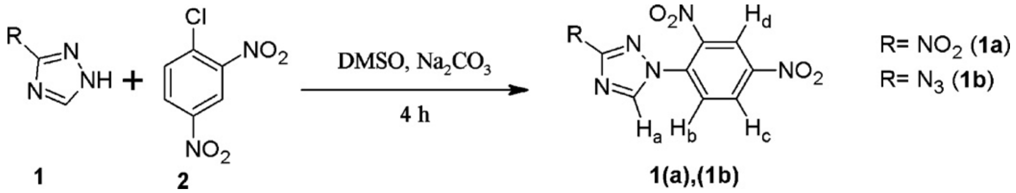

Scheme 1. Synthetic route towards dinitrophenyl triazoles.

and 1-chloro-2,4-dinitrobenzene (assay 98%) were purchased from Alfa Aesar and 3-nitro triazole (assay >98%) was purchased from Sigma–Aldrich and was used as received. FTIR was recorded on a Nicolet 510P spectrophotometer in the wave number range of 4000–400 cm^{-1} with samples made in KBr discs. Elemental analyses (C, H, N%) were determined on a Perkin Elmer Elemental Analyser (model 2400). ^1H and ^{13}C were recorded on a Bruker AC-300 nuclear magnetic resonance spectrometer operating at 300 and 75 MHz, respectively using d_6–DMSO as the solvent and tetramethyl silane (TMS) as the internal reference material. The chemical shifts are reported in ppm relative to TMS.

2.2. Synthesis

Both compounds (**1a** & **1b**) used for the study were prepared as per the procedure explained in the previous communication [17]. 3-Azido-1*H*-1,2,4-triazole was prepared utilizing the procedure explained by Kofman and Krasnov [18], although the procedure was slightly modified in order to prevent the formation of triazenes, which are sensitive energetic molecules. As depicted in Scheme 1, the targeted dinitrophenyl triazoles were realized by reacting the respective triazole derivative with 1-chloro-2,4-dinitrobenzene and Na_2CO_3 in DMSO at 50–70 °C.

2.3. Thermal analysis

Thermal analysis was performed using a simultaneous PerkinElmer® Pyris-Diamond™ TG-DTA. The samples (~1 mg) in Al_2O_3 crucible was subjected to a temperature scanning programme, heating the sample and the reference from 50 to 500 °C, under dynamic argon purging environment (flow rate of 100 cm^3/min). The reference was an empty Al_2O_3 crucible. The TG-DTA was calibrated prior to usage with pure Indium and Zinc {for their melting point as well as for $\Delta_m H$ (enthalpy of melting)}, supplied as standard.Kinetic analysis of the compounds was done by the method of Kissinger and Ozawa, using differential heating rate method, as per the ASTM standard [19]. Energy of activation was calculated from the peak values of exothermic decomposition peaks from the DTA thermogram. Experiments were carried out from 50 to 500 °C at different heating rates of β = 5, 10, 15, 20 & 25 °C. The rate constant for the solid sate decomposition was assumed to follow the Arrhenius rate law, and the first stage exothermic decomposition reaction is used to calculate the kinetic parameters, considering it as a single step.

Accordingly, the simplified rate equation can be expressed as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E}{RT}\right) \qquad (1)$$

or, the logarithmic form of the relation,

$$\ln\left(\frac{d\alpha/dT}{f(\alpha)}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \qquad (2)$$

In the present study activation energies were computed using the logarithmic relations coined by Kissinger [20] and Ozawa [21]. The calculated activation energy from Ozawa relation was refined as per the ASTM procedure. The simplified form of Ozawa (refined form) and Kissinger relations used for activation energy calculation are given in Eqs. (3) and (4).

$$E_a = -2.303 \frac{R}{D} \left[\frac{d \log_{10} \beta}{d(1/T)}\right] \qquad (3)$$

$$E_a = -R \left[\frac{d \ln(\beta/Tp^2)}{d(1/T)}\right] \qquad (4)$$

Qualitative analysis of the evolved gas from thermal decompostion was performed using a simultaneous TG-GC/MS analyser. PerkinElmer® Pyris™ 1 TGA interfaced with PerkinElmer Clarus® 600 GC/MS was used for the analysis. About 1 mg of the sample loaded in platinum crucible were subjected to a temperature programming of 20–400 °C at a heating rate of 20 °C/min inside the TG furnace. The sample is collected from TGA by allowing the high vacuum of the MS to create a pressure drop across the GC column, causing a flow of gas from TGA through analytical column to the MS. The decomposition products were analysed by Mass spectrometer using Electron impact mode (EI) (70 eV, 10–200 amu range).

3. Results and discussion

3.1. Synthetic aspects

The synthetic route towards the targeted compounds follows the one described for the synthesis of triazolo-pyridines [22]. The prepared compounds were characterized by vibrational (FTIR), multinuclear NMR spectroscopy, elemental analysis as well as friction sensitivity. Both compounds were found to be highly insensitive towards friction, with no ignition of the compound observed for a force of 360 N. Both compounds has high negative oxygen balance, −68.5% (**1a**) and −80.9% (**1b**), comparable to that of TNT (−74%). Combustion energies at constant volume ($\Delta_c U$) were determined using a combustion calorimeter. Samples of both compounds were fired inside an oxygen bomb, pressurized with pure oxygen at 3.0 MPa. The experimentally determined constant volume of combustion energies were −3159 cal/g (**1a**) and −3441 cal/g (**1b**). The average value was deduced from a set of three consecutive measurements made under the same conditions. The molar enthalpy of combustion ($\Delta_c H^m$) was calculated from constant volume energies ($\Delta_c U$) using the relation, $\Delta_c H^m = \Delta_c U + \Delta n RT$, where Δn is difference between the number of moles of gases in products and reactants. Hess's law and combustion reactions were used to calculate the standard molar enthalpy of formation ($\Delta_f H^m$) for each of the compounds at 298.15 K. Heats of formation of the compounds was back calculated from enthalpy of combustion using the relation, $\Delta_f H^m = \{X\Delta_f H^m(CO_2, g) + Y\Delta_f H^m(H_2O, l)\} - \Delta_c H^m$, where *X* & *Y* represents the number of moles of CO_2 and H_2O formed from the products. Molar enthalpy of formation values for $CO_{2(g)}$ (−393.5 kJ/mol), and $H_2O_{(l)}$ (−285.8 kJ/mol) were taken from literature [23]. Compound (**1a**) showed negative heat of formation (−31 $kJmol^{-1}$) and (**1b**) showed higher positive heat of formation (+240 $kJmol^{-1}$).

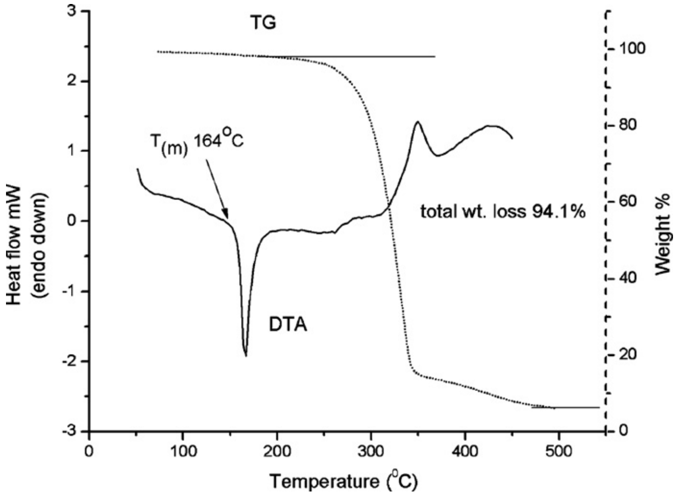

Fig. 1. TG/DTA thermogram of compound (**1a**).

3.1.1. *N-(2,4-dinitrophenyl)-3-nitro-1H-1,2,4-triazole (**1a**)*

Bright yellow micro-crystals (67% yield): mp: 164 °C (DTA) (lit. [24]). FTIR: 3129, 3080, 2890, 1617, 1570, 1542, 1513, 1442, 1350, 1307 and 1091 cm^{-1}. Elemental (C, H, N): found 34.7% C, 1.3% H, 30.1% N; calc. 34.3% C, 1.44% H, 30.0% N. NMR: ^1H (d_6–DMSO), δ 8.36 (d, 1H, Hb), 8.86 (dd, 1H, Hc), 9.06 (d, 1H, Hd), 9.6 (s, 1H, Ha); ^{13}C (d_6–DMSO), δ 121.59, 129.16, 129.77, 132.30, 143.18, 148.18, 148.58, 163.0.

3.1.2. *N-(2,4-dinitrophenyl)-3-azido-1H-1,2,4-triazole (**1b**)*

Recrystallisation of the product from ethyl acetate resulted in straw-yellow flaky crystals (70% yield). mp: 145 °C (DTA)(lit. [25]). FTIR: 3136, 3070, 2891, 2154, 1610, 1529, 1458, 1346, 1315, 1087 and 975 cm^{-1}. Elemental (C, H, N): found 34.79% C, 1.5% H, 40.8% N; calc. 34.84% C, 1.46% H, 40.57% N. NMR: ^1H (d_6–DMSO), δ 8.25 (d, 1H, Hb), 8.72 (dd, 1H, Hc), 8.93 (d, 1H, Hd), 9.35 (s, 1H, Ha); ^{13}C (d_6–DMSO), δ 121.79, 127.87, 129.0, 133.05, 143.11, 147.39, 147.46, 159.87.

3.2. *Thermal analysis*

The thermal decomposition studies of the compounds were carried out using TG-DTA under Argon atmosphere. (**1a**) underwent single stage decomposition evident from TG thermogram Fig. 1. The compound showed good thermal stability, with no weight loss observed upto 250 °C. The compound showed single stage decomposition after 250 °C, with a weight loss corresponding to >90% on the TG. DTA of **(1a)** revealed two signals, an endothermic peak corresponding to the melting of the compound at 164 °C (onset) ($\Delta_m H$ 108 Jg^{-1}), followed by an exothermic decomposition peak at 349 °C (peak temperature). Compound (**1b**) showed multi stage decomposition on TG as shown in Fig. 2. TG showed sharp weight loss of 27.4% between 150 °C and 260 °C, followed by a further decomposition of the intermediate products formed, with a weight loss of 34%. The Compound showed a total weight loss of 61.7% at 500 °C, indicative of the poor oxygen balance of the material. DTA of (**1b**) showed three signals, a sharp endothermic peak at 145 °C(onset), corresponding to the melting, with an enthalpy of melting ($\Delta_m H$) 74 Jg^{-1}, and two exothermic peaks at 217 °C and 417 °C, respectively showing the multistep decomposition pattern of the compound. The heat of reaction ($\Delta_r H$) for both exothermic decomposition processes was found to be 840 Jg^{-1} and 758 Jg^{-1}, respectively.

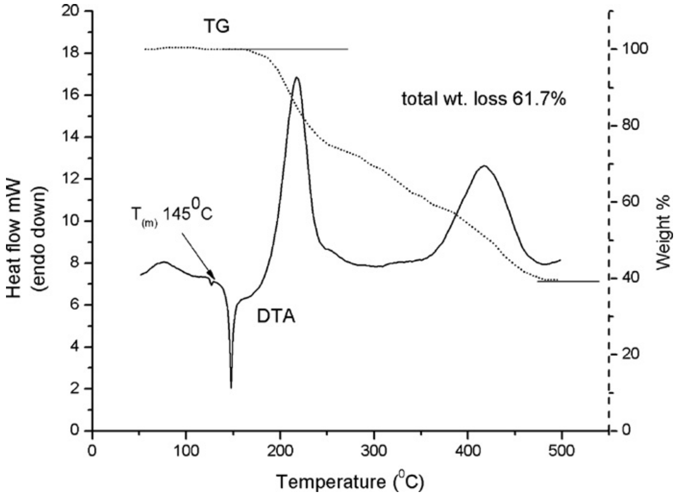

Fig. 2. TG/DTA thermogram of compound (**1b**).

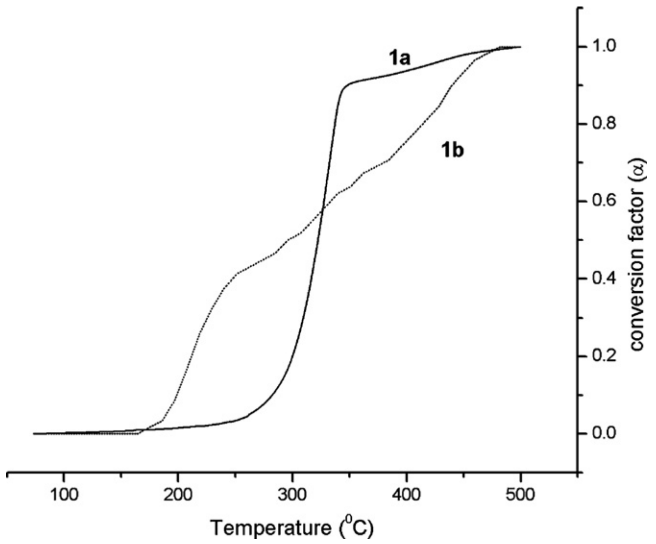

Fig. 3. Dependence of conversion factor (α) on temperature.

The plot of dependence of conversion factor (α) on temperature (Fig. 3) signifies the stability of the compounds as well as the rate of decomposition, over investigating temperature range.

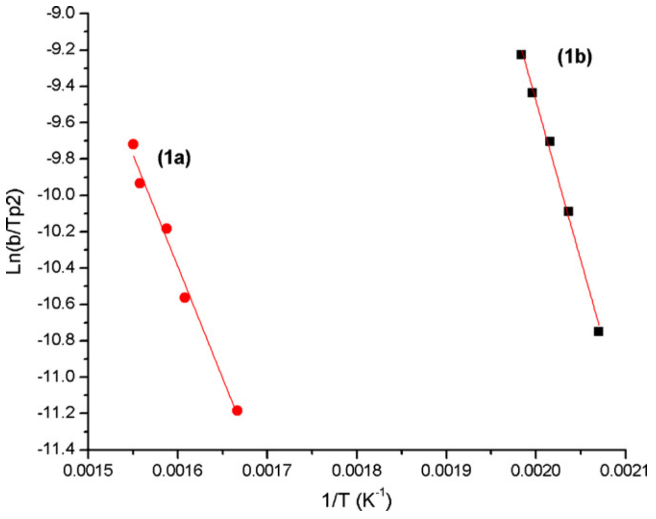

Fig. 4. Kissinger plots for compound (**1a**) & (**1b**).

Table 1
Kinetic analysis data of **(1a)** and **(1b)** using Kissinger and Ozawa relations.

Sl. no	β^a (°C min^{-1})	$T_p{}^b$ (°C)	Frequency factor (ln A, min^{-1})	$E_a{}^c$ Kissinger (kJ mol^{-1})	$E_a{}^d$ Ozawa (kJ mol^{-1})
(1a)					
1	5	327	18.67	102.09	102.24
2	10	349			
3	15	357			
4	20	369			
5	25	372			
(1b)					
1	5	210	35.34	145.73	145.85
2	10	218			
3	15	223			
4	20	228			
5	25	231			

[a] Heating rate from TG/DTA experiment (°C min^{-1}).
[b] Peak temperature of decomposition from DTA thermogram (°C).
[c] Energy of activation calculated from Kissinger relation (kJ mol^{-1}).
[d] Refined value of activation energy using Ozawa relation (kJ mol^{-1}).

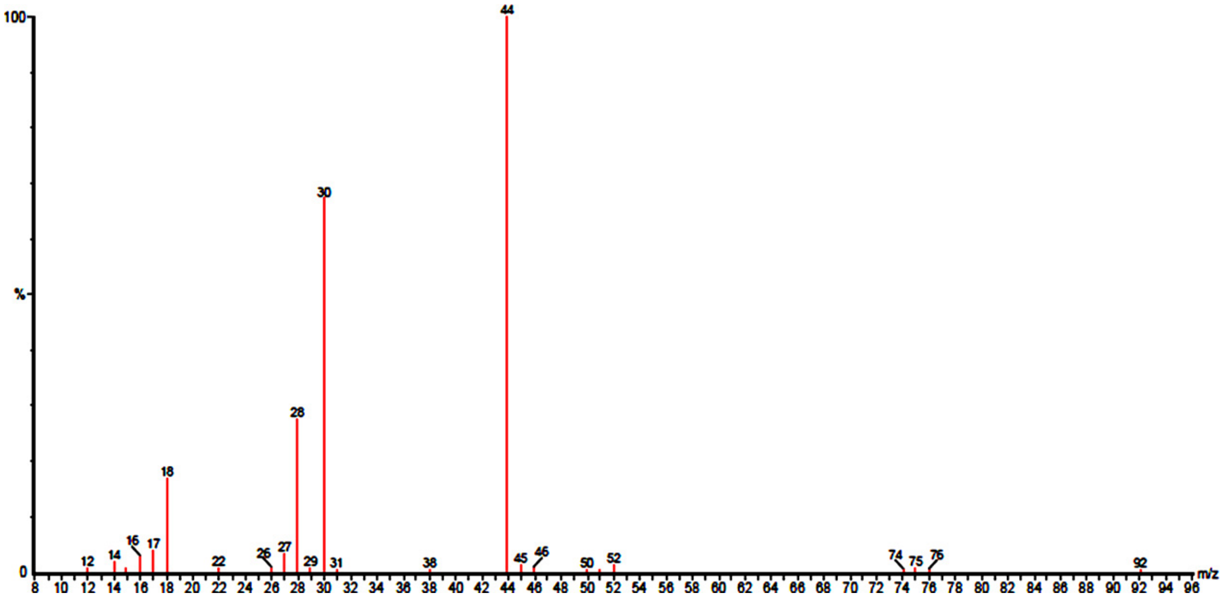

Fig. 5. Mass spectrum of decomposition products of compound **(1a)** at 16.03 min.

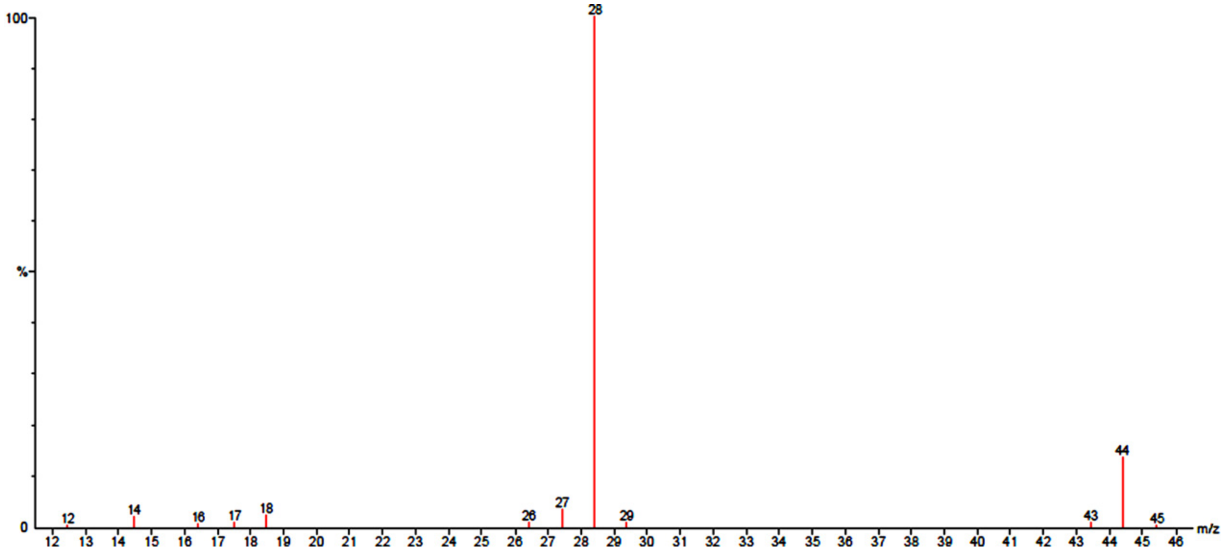

Fig. 6. Mass spectrum of decomposition products of compound **(1b)** at 10.40 min.

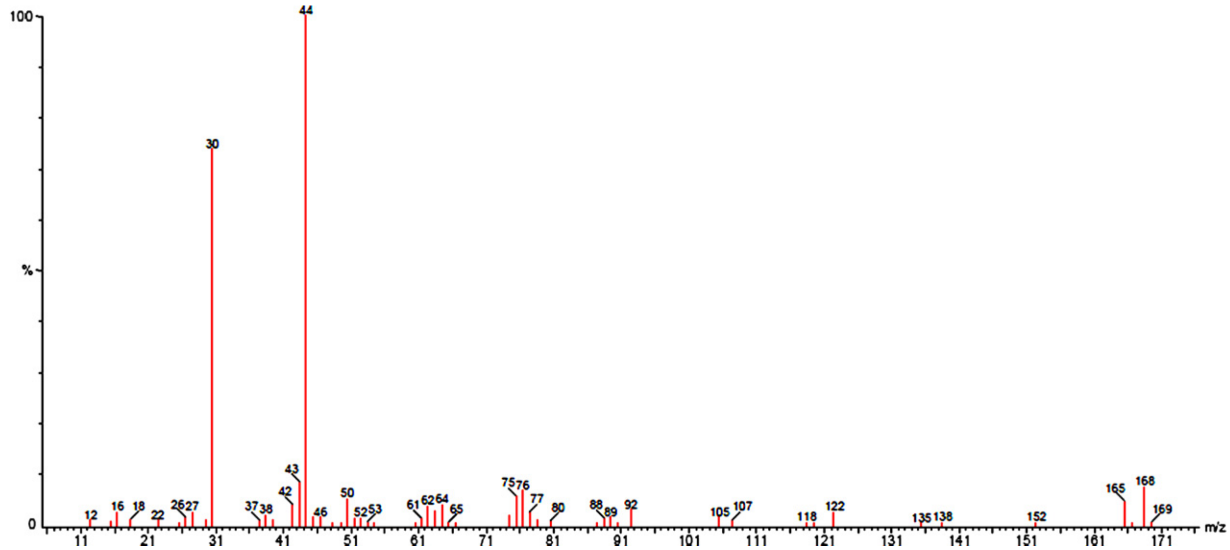

Fig. 7. Mass spectrum of decomposition products of compound **(1b)** at 16.99 min.

From the plot the rate of decomposition seems to be auto catalytically increasing over temperature for **(1a)**, whereas **(1b)** seems to decomposing slowly over the whole range of temperature.

The peak temperature from the DTA thermograms were utilized for kinetic analysis. DTA analysis was carried out at five different heating rates so as to obtain five peak values (T_p), to generate the kinetic parameters using Kissinger and Ozawa methods. As observed for many energetic materials, the decomposition temperature of both compounds increased with increase in temperature [26]. In order to have good correlation, the E_a value obtained by Ozawa method is refined as per the ASTM E-698 standard. A correction factor, D was introduced into the simplified Ozawa relation, which depends up on the E_a/RT value, obtained from the unrefined relation. The activation energies and frequency factor was calculated using the Eqs. (3) and (4). Activation energies were calculated from the slope of the linear plots of $\ln(\beta/T_p^2)$ against $1/T$ (Kissinger plot, Fig. 4), and $\log\beta$ against $1/T$ (Ozawa method) respectively. The activation energy values obtained from Kissinger and Ozawa method, with a correlation factor of >0.99 ($-r$), showed good correlation {(**1a**) −102.23 kJ/mol Ozawa & 102.09 kJ/mol Kissinger} for both compounds. The activation energy of compound **(1a)** was found to be lower than that of **(1b)** (102.09 kJ/mol & 145.72 kJ/mol, respectively). The calculated kinetic parameters like, E_a, frequency factor (A), ln A are tabulated in Table 1.

3.3. *Decomposition experiments*

Both compounds were subjected to thermal analysis (TG), and gaseous species produced during the decomposition was analysed using mass spectrometry.

In accordance with the single stage decomposition pattern of the compound **(1a)** in TG, the TIC (total ion chromatogram), obtained from the mass spectrometry, showed a single peak at a retention time 16.03 min. Mass spectrum (Fig. 5) for the max TIC (at 16.03 min) showed signals of higher intensity at m/z values of 44, 30, 28 and 18, which can be attributed to the formation of CO_2 (m/z 44), N_2 (m/z 28), NO (m/z 30) and H_2O (m/z 18). The base peak was that of CO_2 (m/z 44). The spectrum reveals the possible decomposition mechanism to be oxidation of the carbon back bone, by oxygen from nitro groups within the molecule. Formation of NO (m/z 30) also ascertains the fact that the first cleavage site could possibly be the nitro group, which further oxidizes the molecule. Similar decomposition behaviour of nitro aromatics have already been documented in literature. TG-FTIR studies on TNT revealed the presence of CO_2, NO_2 & H_2O among the decomposition products [27]. The single step decomposition pattern of the compound observed in TG also points out this possible decomposition behaviour. The signal at m/z 28 can be due to N_2 and CO. Since the molecule is oxygen deficient (negative oxygen balance), incomplete oxidation of carbon can be expected, resulting in the formation of CO. Similarly, the triazole nucleus in the molecule can generate N_2 on decomposition. Hence the signal at 28 could be due to the formation of both these species. The spectrum showed trace amounts of methane (m/z 16), HCN (m/z 27), NH_3 (m/z 17). The analysis results are in good agreement with the literature values obtained for substituted triazole derivatives [28].

The multistep evolution of the decomposition products from **(1b)** were resolved and separated out in the TIC. The first peaks in the mass spectra were observed during the retention time 9.00–11.00 min in the TIC. The mass spectrum recorded at 10.40 min (Fig. 6) showed only a very few signals, with a base peak at m/z 28 (N_2) and a less intense peak at m/z 44(CO_2/N_2O). The second stage decomposition (retention time 16.99 min on TIC) showed decomposition products of m/z 44, 43, 30, 27, 18 and 16 on the mass spectrum. It can be understood from the mass spectrum that the initial decomposition site is the azido group in the triazole nucleus, as the first stage decomposition resulted in liberation of N_2 (m/z 28) as the major decomposition product. As expected for nitrogen rich heterocyclics with azido linkage (both chain and ring), the predominant decomposition product is N_2, with traces of HCN and cyanamide [29]. The spectrum for the second stage decomposition (Fig. 7) was devoid of the signal at m/z 28, indicative of no N_2 liberation. This may be due to the complete decomposition of the azido triazole within the first stage itself. The spectrum showed a base peak at m/z 44(CO_2/N_2O) and signals at m/z 30(NO), 43(HNCO), 27(HCN). The presence of peak at m/z 168 (dinitrophenyl gp.), proposes the possible cleavage of triazole nucleus from the molecule.

Comparing the decomposition patterns for both compounds, it is observed that the decomposition pattern for compound **(1b)** is different from that of **(1a)**, with azido triazole being the initial spot of decomposition, followed by decomposition of dinitrophenyl moiety. Whereas, decomposition of **(1a)** is assisted by the rupture of NO_2 from the molecule and thereby oxidising the carbon backbone, resulting in the release of CO_2, as one of the major product.

4. Conclusions

The energetic derivatives of triazole, viz., N-(2,4-dinitrophenyl)-3-nitro-1,2,4-triazole (**1a**) and N-(2,4-dinitrophenyl)-3-azido-1,2,4-triazole (**1b**) was characterized and studied for their thermal decomposition behaviours, using TG-DTA analysis. Both compounds (**1a)** & (**1b**) showed good thermal stability with high insensitivity, with the former being more thermally stable. The kinetic parameters of the compounds were derived using non-isothermal method. The gaseous species produced during the decomposition were analysed using mass spectrometry. Both compounds showed presence of CO_2, NO_2, NO, HCN, N_2, & H_2O among the products of decomposition. (**1b**) showed multistage decomposition, with generation of N_2 in the initial stage and CO_2 in the later stages of decomposition. The parameters like good thermal stability, generation of nitrogen gas, and strong exothermicities, shown by these compounds make them interesting candidates for gas generating energetic applications.

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