



Studies on characterisation and thermal behaviour of 3-amino-5-nitro-1,2,4-triazole and its derivatives

A.K. Sikder, M. Geetha, D.B. Sarwade, J.P. Agrawal*

High Energy Materials Research Laboratory, Pune- 411021, India

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Abstract

3-Amino-5-nitro-1,2,4-triazole (ANTA) and its derivatives have been prepared in order to carry out the systematic studies on structural aspects, explosive and thermal behaviour. Thermal studies were carried out for ANTA and 4,6-bis-(3-amino-5-nitro-1H-1,2,4-triazole-1-yl)-5-nitropyrimidine (DANTNP) by thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimeter (DSC) and manometric thermal analysis. The results show that (DANTNP) is more thermally stable than ANTA when compared in terms of activation energy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 3-Amino-5-nitro-1,2,4-triazole (ANTA); Triazoles; Insensitive; Isothermal; Activation energy

1. Introduction

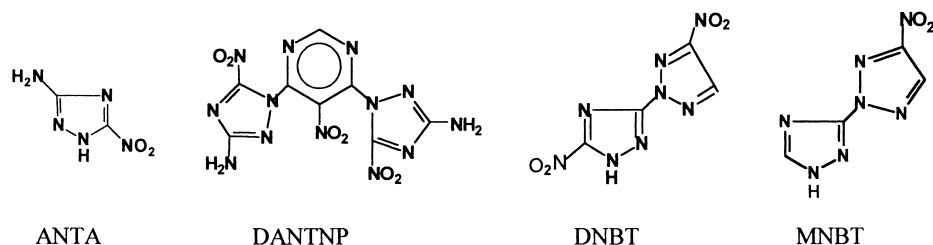
Nowadays, in the area of research of explosives, a lot of emphasis is given to high quality simple compounds, with high energy, high density, heat resistance and low sensitivity. It has been observed that commonly used high explosives such as RDX, HMX, etc. suffer from high sensitivity to impact and shock, which implies that it is necessary to look for new explosives with high energy and low sensitivity.

Literature survey reveal that explosives containing triazole ring are of multipurpose interests [1–4] because the heterocyclic ring system confers a high density, thermal stability, high nitrogen content, high volume of detonation products, and insensitivity to impact. The substituents, combination of amino and nitro groups, provide the inter and intra molecular hydrogen bonding that stabilises the molecule and increases crystal density. In addition, the heterocyclic substrates in many cases contribute to a more positive heat of formation. It has also been reported that 3-amino-5-nitro-1,2,4-triazole (ANTA), an insensitive high explosive (IHE) similar to TATB, has potential as a more energetic alternative to oxynitrotriazole

* Corresponding author. Tel.: +91-20-5889263; fax: +91-20-5881316.
E-mail address: jpa@vsnl.com (J.P. Agrawal).

(NTO) [5] and meets all the above criteria. Furthermore, ANTA had also been proposed by Naval Research Laboratory (NRL), USA to evaluate it as a potential IHE for nuclear weapons applications [6].

In view of the above, and as a part of our ongoing program, in order to understand the thermolysis behaviour of insensitive high energetic materials as regards to their storage, safety and end use, we consider worthwhile ANTA and some of its derived products, for further synthesis, and to study in detail their systematic characterisation on structural aspects and thermal behaviour. These compounds present special characteristics and can be used in various fields [7,8] and we also understand that the thermolysis of these two compounds reported here is not yet mentioned in literature. The structures of ANTA and its derivatives are given below:



2. Experimental

Melting points were determined at $2^{\circ}\text{C min}^{-1}$ by a melting point apparatus and are uncorrected. IR spectra were recorded with Perkin-Elmer infrared spectrophotometer on KBr pellets. $^1\text{H-NMR}$ spectra were recorded on Bruker-90 MHz spectrophotometer. Chemical shifts are reported in δ units parts per million (ppm) down field from tetramethylsilane (TMS) as internal standard. The purity of the compound was performed on silica gel-G plate (CH_2Cl_2 : EtOH, 5:1 as a solvent system).

Impact sensitivity measurement was performed on impact machine using a 2 kg weight, dropped from height as varied according to Bruceton “staircase” method [8]. Friction sensitivity measurement was carried out by Julius–Peters (Berlin-21) apparatus [9].

3. Materials

Chemicals used were of analytical reagent grade (AR). 3,5-diamino-1,2,4-triazole was a product of Aldrich Chemicals Co., USA. Tridodecyl amines were purchased from Emerck (Germany). Hydrazinium monohydrate, acetic anhydride, glacial acetic acid, sodium nitrite, sodium hydroxide, toluene, hydrochloric acid and nitric acid were from Qualigens Fine Chemicals, Mumbai.

3.1. Synthesis

3.1.1. 3-Amino-5-nitro-1,2,4-triazole (ANTA)

3-Amino-5-nitro-1,2,4-triazole (ANTA) was prepared by two different routes starting from commercially available 3-amino-1,2,4-triazole and 3,5-diamino-1,2,4-triazole with the yield ranging from 80 to 73%. The compounds obtained from both the methods [10,11] were fully characterised by spectral data and elemental analysis (Table 1).

3.1.2. 4,6-Bis-(3-amino-5-nitro-1H-1,2,4-triazole-1-yl)-5-nitropyrimidine (DANTNP)

The compound was prepared in 50% yield from the sodium salt of ANTA by following the method of Wartenberg et al. [12]. The spectral data and elemental analysis results are consistent with structure (Table 1).

3.1.3. Preparation of sodium methazonate:

Nitromethane (8.5 ml, 0.15 mol) was run in small portion on cold stirred solution of sodium hydroxide (10 g, 0.25 mol) in water (20 ml). The temperature of the solution was not allowed to reach 40°C. White crystals of sodium salt were formed which slowly dissolved, afforded ultimately a deep cherry red coloured solution. The resulting solution was cooled to 5–10°C. The solid precipitated out, was filtered, washed with alcohol to yield 17 g (91%) of sodium salt of methazonic acid. Recrystallisation was done in minimum volume of water followed by ice-cooled alcohol treatment. The physico-chemical properties and spectral data are in agreement with structure.

3.1.4. 4-Nitro-2-(1,2,4-triazole-3-yl)-1,2,3-triazole (MNBT) and 4-nitro-2-(5-nitro-1,2,4-triazole-3-yl)-1,2,3-triazole (DNBT)

The compounds were prepared from ANTA and 3-amino-1,2,4-triazole, respectively, by sequential diazotization reaction, coupling with methazonic acid and subsequent cyclisation according to the reported methods [13,14]. The spectral data and elemental analysis results are in excellent agreement with the structures (Table 1). Selected properties of these compounds are summarised in Table 2.

3.2. Thermal analysis

3.2.1. Simultaneous thermal analysis

Thermogravimetry (TG), differential thermal analysis (DTA) and derivative of differential thermal analysis (DDTA) were carried out using NETZSCH STA-409 simultaneous thermal analyser. The enthalpy change and mass change measurements were made using about 10 mg of sample in platinum–iridium thermocouples in the temperature range from room temperature to 600°C in static air against equal amount of calcined alumina. The heating rate was 10°C min⁻¹. Pt–Pt (Rh 10%) thermocouple assembly was used for ΔT and temperature measurement.

3.2.2. Differential scanning calorimeter (DSC)

Perkin-Elmer DSC-7 was employed for DSC studies. For this, 2–3 mg of sample was crimped in an aluminium cup which was heated against crimped blank cup at different

Table 1
Spectral data and elemental analysis results of ANTA and its derivatives

Compounds	Molecular formula	IR (KBr) ν (cm^{-1})	^1H NMR (DMSO- d_6 /TMS) δ ppm	Elemental analysis	
				Calculated	Found
ANTA	$\text{C}_2\text{H}_3\text{N}_5\text{O}_2$	3442, 3328, 3260, 2740, 2644, 1512, 1398, 1127, 1036, 786	6.92 (s, NH_2), 13.35(s, NH)	C: 16.30, H: 3.40, N: 47.50	16.67, 3.26, 47.36
DANTNP	$\text{C}_8\text{H}_5\text{N}_{13}\text{O}_6$	3260, 1660, 1548, 1360, 1310, 1030, 840	8.50 (s, 4H), 9.2 (s, H)	C: 25.32, N: 1.31, H: 48.02	25.93, 1.38, 47.44
MNBT	$\text{C}_4\text{H}_3\text{N}_7\text{O}_2$	3114, 2728, 1550, 1414, 1368, 1258, 1028, 738	8.9 (s, H), 8.85 (s, H)	C: 26.50, H: 1.70, N: 54.10	25.92, 1.85, 53.85
DNBT	$\text{C}_4\text{H}_2\text{N}_8\text{O}_4$	3240, 1680, 1552, 1460, 1348, 1045, 830	8.9 (s, H)	C: 21.25, H: 0.89, N: 49.56	21.05, 1.01, 48.98

Table 2
Selected properties of ANTA, DANTNP, MNBT and DNBT

Compound	ANTA	DANTNP	MNBT	DNBT
Formula	C ₂ H ₃ N ₅ O ₂	C ₈ H ₅ -N ₁₃ O ₆	C ₄ H ₃ N ₇ O ₂	C ₄ H ₂ H ₈ O ₄
mp (°C)	238	>330	228	
DTA (°C)	240	348		178
Density (g/cc)	1.82	1.84	1.71	1.89
Impact sensitivity(cm)	>170	>170	>170	–
Detonation velocity (km s ⁻¹)	8.46	8.12	8.98	8.98
C–J pressure (kbar)	314	297	289	289

heating rates, i.e. 5, 10, 15 and 20°C min⁻¹. Activation energy of the compound was calculated using Ozawa [15] and Kissinger [16] methods.

3.2.3. Manometric thermal decomposition studies

Manometric measurements of gases evolved during dynamic heating was measured using manometric thermal decomposition apparatus fabricated indigenously similar to reported by Agrawal et al. [17]. The sample was taken in a quartz tube and the same was then connected to the manometer. The system was evacuated by vacuum pump and the instrument was set at zero reading. The furnace, which moves upward and downward, was then raised to the fixed point so that sample tube remains in furnace at the centre and in the vicinity of temperature sensor.

The furnace was heated with a linear heating rate of 10°C min⁻¹. During decomposition, the gases evolved change the level of mercury filled in the manometer due to gas pressure, thereby resulting in a change in the reading. The gas measurement studies were also made isothermally at 210 and 220°C, respectively.

4. Results and discussion

4.1. Structural aspects

ANTA prepared from the reported method was characterised by spectral data and elemental analysis, and was found identical in properties. We also rationalised the results of the experiments accordingly, as observed earlier [11]. IR spectrum in general showed the band at 3443 cm⁻¹ for N–H stretching and that of primary amine exhibits at 3328 and 3260 cm⁻¹, respectively. The absorption of >C=N–NH stretching appears at 2360 cm⁻¹. The spectrum also shows a strong band at 1646 cm⁻¹ corresponds to >C=N stretching. Strong bands at 1512 and 1392 cm⁻¹ are ascribed due to both symmetric and asymmetric stretching frequencies of NO₂ ions. Other characteristic bands at 1308, 1136, 1080, 842 and 722 cm⁻¹ correspond to the skeletal vibrations of triazole ring (N–N stretching, C–N bend, etc.). Nevertheless, absorption associated with NH deformation mode is expected to appear near 1600 cm⁻¹ but these are greatly masked by other strong absorptions in the same region.

In the ¹H-NMR spectrum of ANTA, the signals for NH and NH₂ protons show two singlets at δ 13.35 and 6.92, respectively, and the NH proton signal disappears with the

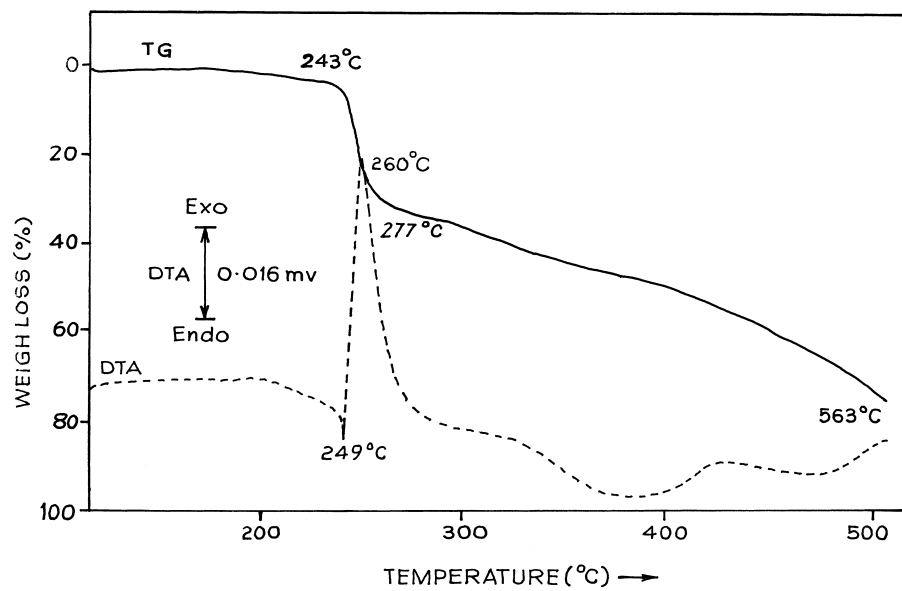


Fig. 1. TG/DTA curve of ANTA.

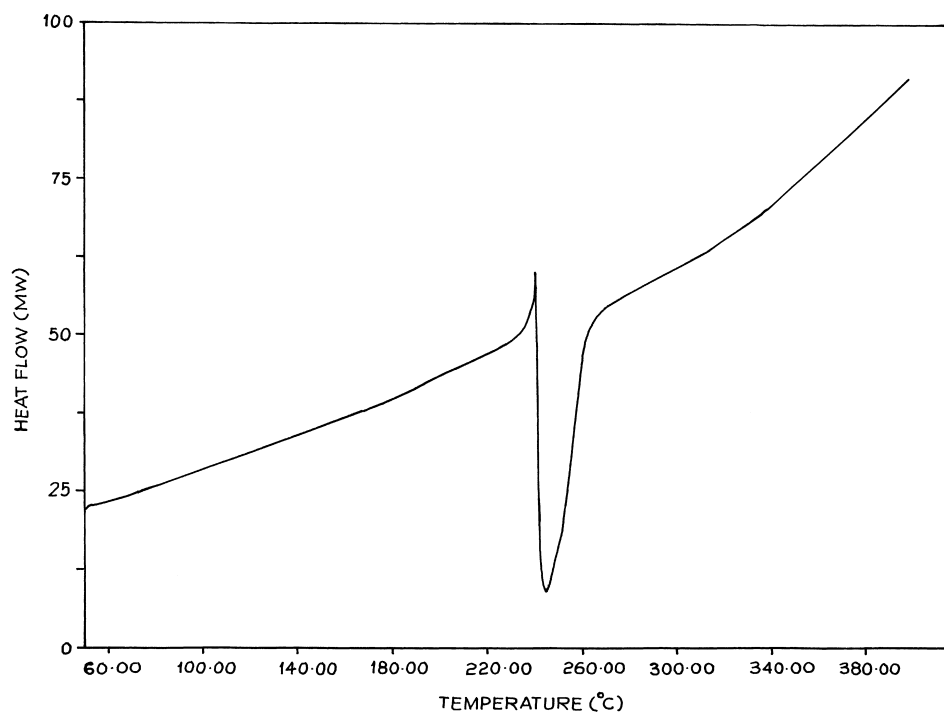


Fig. 2. DSC curve of ANTA.

addition of D₂O. ANTA was further characterised for its preliminary explosive properties like friction sensitivity (insensitive up to 36 kg); deflagration temperature, 258°C and impact sensitivity (>170 cm).

Since ANTA has got two reaction centres allowing a further chemical conversion where ring nitrogen may form anion capable to react with suitable chloro-compounds, thus the compound DANTNP was prepared and characterised by elemental analysis and spectral data. The IR spectrum show diagnostic peaks at 3260 cm⁻¹ due to NH₂ stretching and 1548 and 1310 cm⁻¹ for –NO₂ group. The ¹H-NMR shows two singlets at δ 8.50 and 9.2 ppm for aromatic and NH₂ protons, respectively.

The explosive properties of the compound appear to be more suitable as thermally stable insensitive high explosives and, therefore, this explosive can be handled without any restriction.

The mono- and dinitro-bitriazole derivatives were prepared with the expectation to be an explosive of greater performance than ANTA because of more favourable oxygen balance. It was observed that the yield was too low (yield 45%) while making the compound as per the reported method. The IR spectra in general of the compounds showed the characteristic peaks of stretching frequencies in the range at 3154–3114 and 2994–2978 cm⁻¹ for NH and triazole –CH, respectively (Table 1). The spectra also displayed the corresponding nitro group stretching frequencies of compounds at 1552–1534 and 1374–1358 cm⁻¹. The spectral data and results of elemental analyses show excellent confirmity with structures. The ¹H-NMR spectra were also taken in DMSO-d₆ at room temperature in 90 MHz instrument. The signal of the proton attached to the ring nitrogen was not always found. This phenomenon is common with analogous triazole derivatives and is explained by proton exchange with solvents at room temperature. The NH proton in the spectra appears to be missing in case of dinitro-bitriazole but is present in mono-nitrobitriazole. The chemical shifts of ring CH protons in bitriazole resonated at δ 8.9 and for mono-nitrobitriazole, two C–H protons in both the triazole rings were observed at 8.9 and 8.85 δ, respectively.

4.2. Thermal studies

Fig. 1 shows DTA and TG of ANTA. The TG curve reveals that the decomposition reaction is a two stage process: first stage starts from 243 to 277°C with 38% weight loss and the second stage which is very slow, begins immediately at 277°C and ends at 563°C with 51% loss. Thus, the calculated weight loss due to overall reaction is 89%. DTA curve shows that there is an endotherm immediately followed by a sharp exotherm. The endotherm peak at

Table 3
Maximum exothermic responses as a function of scan speed and activation energy

	Heating rate (°C min ⁻¹)					Activation energy (kcal mol ⁻¹)	
	5	10	15	20	25	Ozawa	Kissinger
ANTA peak maxima	214	245	250	253	256	53.0	53.7
DANTNP peak maxima	–	341	344	347	349	84.0	85.9

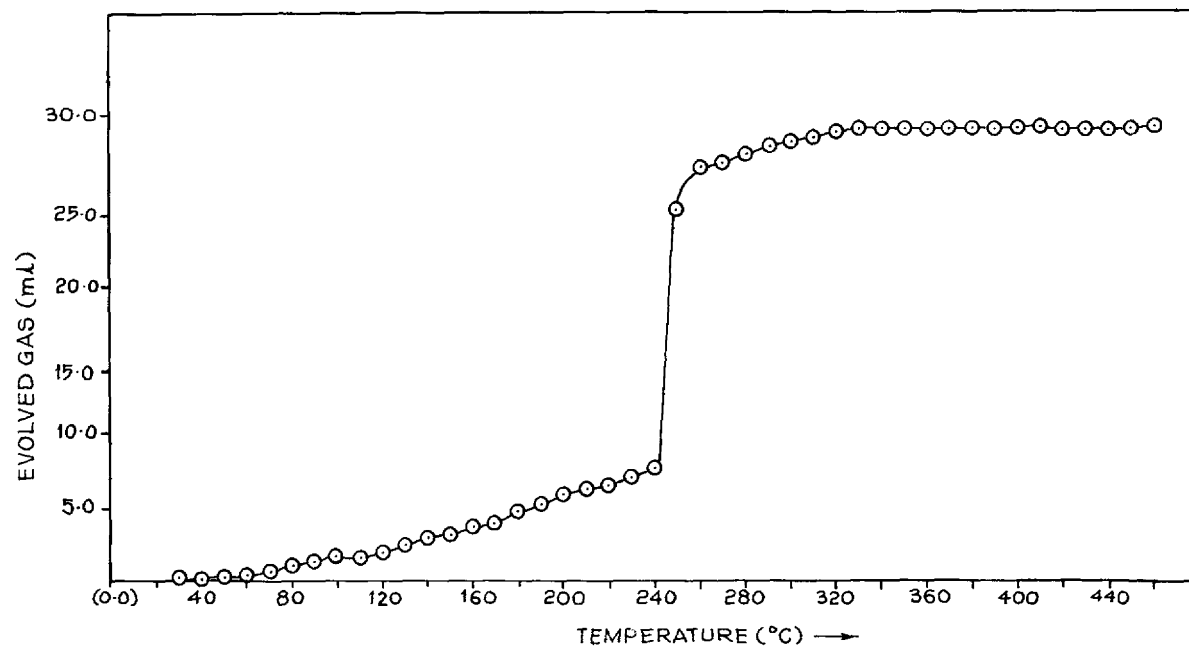


Fig. 3. A plot of evolved gas vs. temperature for ANTA.

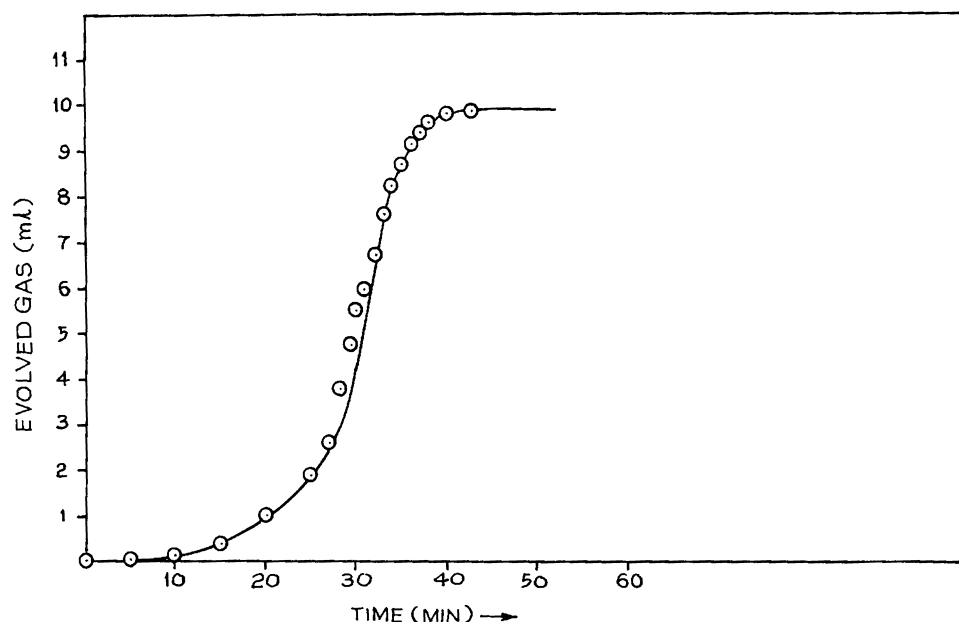


Fig. 4. A plot of evolved gas vs. time for ANTA at 210°C.

249°C is due to the melting of the compound. After melting, immediately there is a sharp exotherm peak at 260°C which corresponds to first stage degradation.

The DSC measurements of ANTA at 10°C min⁻¹ shows a single sharp endotherm at 240°C (Fig. 2) indicates the melting of the compound followed by an exotherm at 245°C with an energy of 1680 J g⁻¹ involved during this change in the decomposition reaction. This change may be attributed to exothermal decomposition of ANTA.

Differential scanning calorimetric studies have been carried out at five different heating rates viz. 5, 10, 15, 20 and 25°C min⁻¹ to calculate the energy of activation by following the methods of Ozawa and Kissinger. The calculated activation energy for both the methods have been found to be 53.0 kcal mol⁻¹ and 53.7 kcal mol⁻¹, respectively, (Table 3) which are in excellent agreement.

Fig. 3 depicts a typical plot of temperature on x-axis against quantity of evolved gas on y-axis. This dynamic manometric gas measurement curve shows that as the temperature increases, the evolution of gases starts significantly with linearity from 80 to 240°C. There is a sudden change at 240°C where decomposition of the compound takes place rapidly with the change in the volume of the gas from 8 to 28 ml at 250°C. After 250°C, there is not much change till 450°C. This suggests that the decomposition occurs between 240 and 250°C.

Isothermal gas measurement studies have been carried out at two different temperatures, 210 and 220°C, respectively. It is seen that the curve (Fig. 4) at 210°C is sigmoidal in nature and three stages can be discerned: induction, acceleration and de-acceleration. It is also observed that, at any time, the quantity of gas evolved is more at 220 than at 210°C.

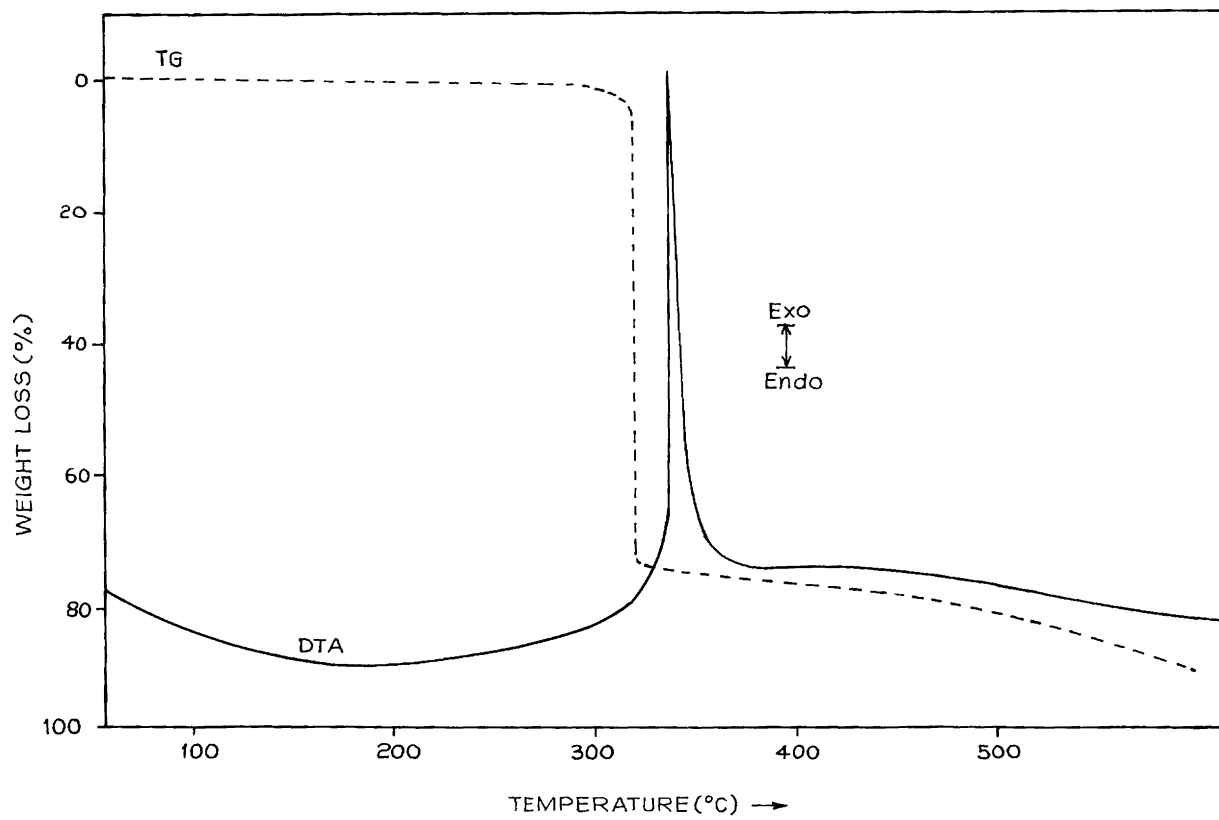


Fig. 5. TG/DTA curve of DANTNP.

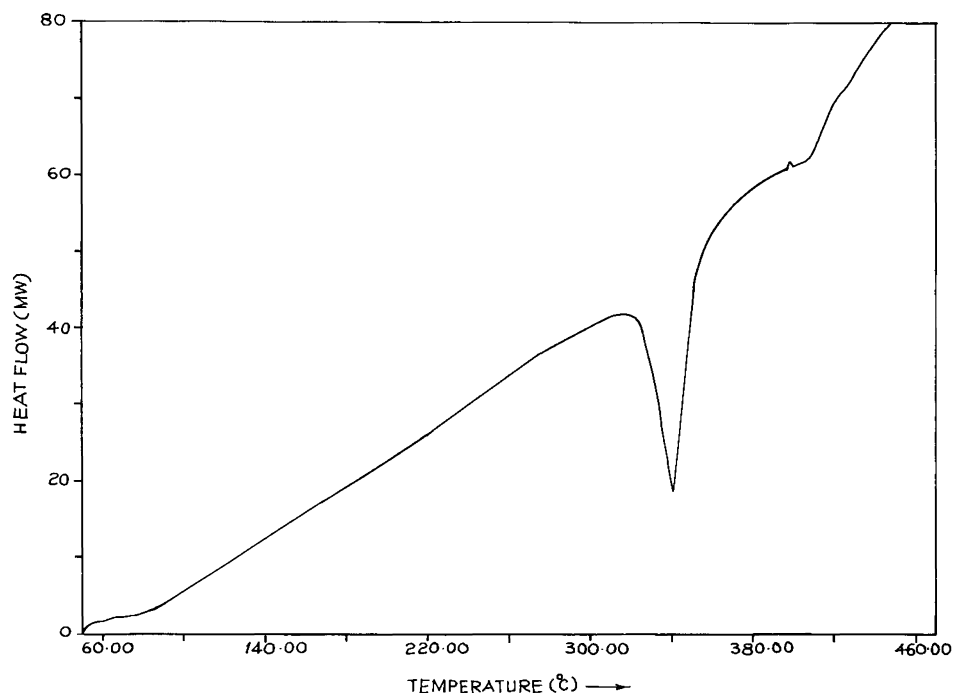


Fig. 6. DSC curve of DANTNP.

indicating the rate of decomposition is higher at 220°C. The decomposition is found to be auto-catalytic.

Fig. 5 represents the TG/DTA of DANTNP. It is seen from the DTA curve that there is only one sharp exotherm peaking at 317°C. TG curve shows no weight loss till 290°C. Beyond 290°C, the weight loss is very sharp with 73% loss upto 320°C. After 320°C, the weight loss continues very slowly and the total loss becomes 89% up to 600°C. The above observation suggests that the compound is stable up to 290°C and it decomposes rapidly and exothermically beyond 290°C. The slow and continuous loss after 320°C may be due to the residual oxidative decomposition.

Differential scanning calorimetric studies (Fig. 6) at 10°C min⁻¹ shows that there is only one exotherm at 340°C. The energy associated with this exotherm is 1356 J g⁻¹ which is less than ANTA. This further concludes that the compound is less energetic than ANTA, which also correlates well with explosives properties as given in the Table 2. In order to determine the energy of activation, the DSC studies have been carried out at four different heating rates, i.e. 10, 15, 20 and 25°C min⁻¹. It is observed that the temperature of decomposition increases with the increased rate of heating of the sample. The energy of activation was calculated using Ozawa and Kissinger equations and it is found to be 84.0 and 85.9 kcal mol⁻¹, respectively, with an excellent correlation. The activation energy values also suggest that the DANTNP is more thermally stable than ANTA, when compared in terms of calculated activation energy, 53.5 kcal mol⁻¹ of ANTA.

5. Conclusions

3-Amino-5-nitro-1,2,4-triazole (ANTA) and some of its high energetic derivatives have been prepared and characterised systematically. The data on the explosive and thermal properties suggest that ANTA and DANTNP may find application to a propellant and explosive formulation where insensitivity coupled with thermal stability is of prime importance.

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References

- [1] M.D. Coburn, K.Y. Lee, *J. Heterocycl. Chem.* 27 (1990) 57–77.
- [2] J. Li, Y. Ou, Modified preparation and nitration of 3-picylamino-1,2,4- triazole, in: *Proceeding of the 17th International Pyro. Seminar*, Vol. 1, Pbul., Beijing, Int. Tech. Press, Beijing, 1991, pp. 196–99.
- [3] M.M. Stinecipher, K.Y. Lee, M.A. Hiskey, in: *Proceedings of the 31st AIAA/ASME/SAE/ Joint Propulsion Conference*, 10–12 July 1995.
- [4] C.X. Lu, *Kayaki Kogyo* 51 (1990) 275–279.
- [5] F. Bugaut, S. Benard, R. Chirat, Thoretical prediction of high explosives efficiency: application to NTO, in: *Proceedings of the 9th International Symposium on Detonation*, Public Office of the Chief of Naval Research, Arlington, Virginia, 1989, pp. 489–497.
- [6] K.Y. Lee, R. Glidardi, M.A. Hiskey, J.R. Stine, *Material Res. Soc. Sym. Proc.* 418 (1998) 43–48.
- [7] K.Y. Lee, C.B. Storm, M.A. Hiskey, M.D. Coburn, *J. Energetic. Mater.* 9 (1991) 415–428.
- [8] R. Meyer, J. Kohler, *Explosives*, 4th revised and extended edition, Weinhein, VCH Publishers, New York, 1993, pp. 149–150.
- [9] R. Meyer, J. Kohler, *Explosives*, 4th revised and extended edition, Weinhein, VCH Publishers, New York, 1993, pp. 197–199.
- [10] M.S. Pevzner, T.N. Kulibabina, N.A. Povarova, L.V. Kilina, *Khim. Gereo. Soed.* 8 (1979) 1132.
- [11] R.L. Simposon, P.F. Pagoria, A.R. Mitchell, C.L. Coon, *Propellant. Explos. Pyrotech.* 19 (1994) 174–179.
- [12] F. Laval, Ch. Wartenberg, P. Charre, *Propellant. Explos. Pyrotech.* 20 (1995) 23–26.
- [13] H.H. Licht, H. Ritter, *J. Energetic. Mater.* 12 (1994) 223–235.
- [14] E.J. Browne, *Aust. J. Chem.* 22 (1969) 2251.
- [15] T. Ozawa, *Bull. Chem. Soc. Jpn.* 38 (1965) 1831–1836.
- [16] H.E. Kissinger, *Anal. Chem.* 29 (1957) 1702–1707.
- [17] S.P. Agrawal, J.P. Agrawal, *Ind. J. Chem.* 7 (1969) 1264–1267.