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An Improved Safe Method for the Synthesis of Ammonium 5-Nitrotetrazolate (ANT), a Key Intermediate for the Synthesis of Green Energetic Materials (GEMs)

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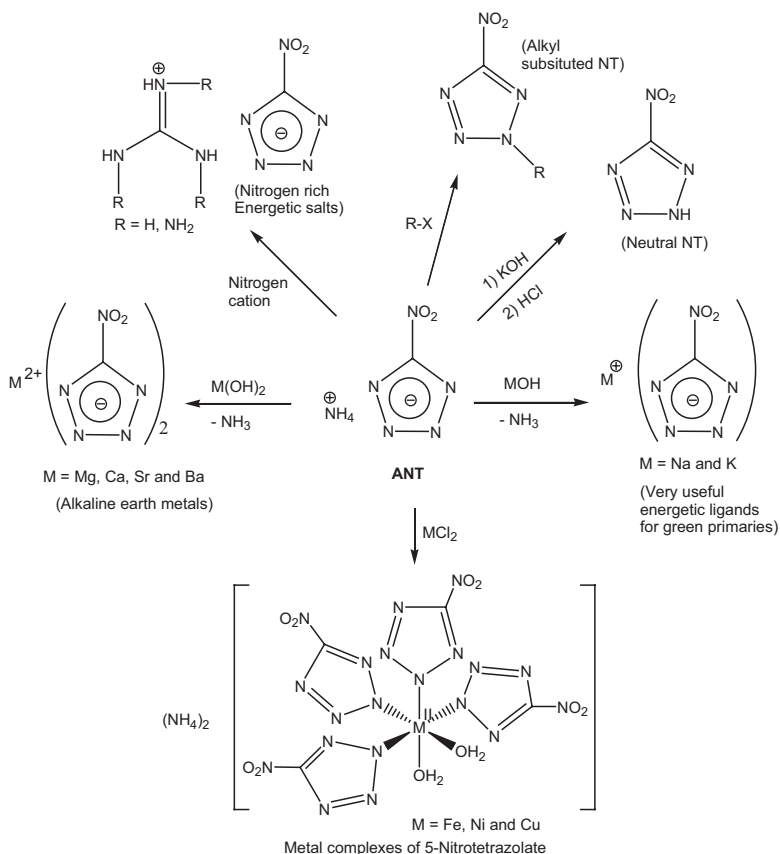
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Abstract: Ammonium 5-nitrotetrazolate (ANT) is an important precursor for the synthesis of green energetic materials (GEMs), including lead/mercury-free environmentally benign primary explosives. The currently employed methods for the synthesis of ANT are hazardous, use an excess of organic solvents/reagents and thus generate effluent. Furthermore, these methods offer low yields of ANT as they involve multistep processes. We describe herein an improved, safe and convenient method for the synthesis of ANT, which greatly improves the process safety and product yield. The advantage of this method is that it avoids hazardous operations, such as the isolation and handling of acidic copper(II) nitrotetrazolate, an extremely sensitive explosive intermediate during the preparation of ANT. In our procedure, 5-aminotetrazole (5-AT) is diazotized with sodium nitrite and nitric acid in the presence of a copper salt. The sensitive copper acid salt thus formed from the reaction mixture is treated *in situ* with aqueous barium hydroxide to convert it to barium 5-nitrotetrazolate and insoluble copper oxide. Finally, the aqueous barium 5-nitro-1H-tetrazolate (BaNT) is treated with ammonium sulfate to yield ammonium 5-nitrotetrazolate (ANT) in good yield. The synthesized ANT was characterized by its physicochemical properties using spectral and thermal techniques. The purity of the ANT was measured by HPLC and ion chromatography (IC). Furthermore, the structure of ANT was confirmed by single crystal X-ray analysis.

Keywords: ammonium 5-nitrotetrazolate, harmless synthetic method, less effluent, green energetic materials, characterization

1 Introduction

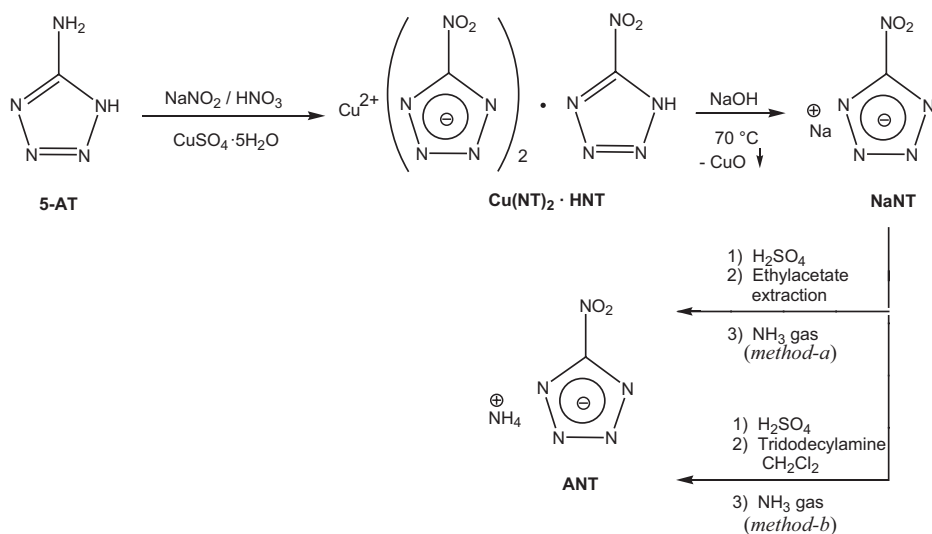
In the continuing search for novel green energetic materials, nitrogen-rich high energy materials based on tetrazoles [1-4] are being investigated by various researchers worldwide. This class of energetic materials has been examined in various applications, such as eco-friendly pyrotechnic compositions [5], non-toxic gas generators [6], chlorine-free propellants [7], insensitive high explosives [8] and lead/mercury-free primary explosives [9]. In particular, 5-substituted tetrazoles [10] is one of the most promising classes of molecules owing to their energetic properties that could be controlled by suitable substituents at the carbon atom [11-14]. Recently, iron and copper complexes of 5-nitrotetrazole have been studied as prospective green primary explosive replacements for the commonly used toxic lead/mercury-based primary explosives [15].



Scheme 1. Preparation of various nitrogen-rich HEMs using ANT

Several high nitrogen, high energy materials starting from ammonium 5-nitrotetrazolate (ANT) have been reported [16, 17]. Furthermore, a literature survey revealed that alkali and alkaline earth metal salts of 5-nitrotetrazolate obtained from ANT are promising candidates for green pyrotechnic compositions (Scheme 1) [18, 19].

In general, ANT is prepared *via* a modified Sandmeyer reaction in the presence of a copper salt. This method produces a very sensitive intermediate, namely the acid salt of copper(II) 5-nitrotetrazolate, $\text{Cu}(\text{NT})_2 \cdot \text{HNT}$ ($\text{NT} = 5\text{-nitrotetrazolate}$) [20]. During this process, the copper salt of NT is removed by filtration, and is reported to be highly sensitive towards spark and mechanical stimuli. The $\text{Cu}(\text{NT})_2 \cdot \text{HNT}$ is then suspended in water and heated in the presence of sodium hydroxide to give insoluble copper(II) oxide and an aqueous solution containing NaNT. The aqueous NaNT is finally converted into ANT. There are several different approaches available in the literature for the conversion of NaNT into ANT, of which two (*methods a & b*) are the mostly commonly used (Scheme 2).



Scheme 2. Commonly used methods for the synthesis of ANT

The first method (*method-a*) [21] involves extraction of the acidic aqueous NaNT solution using ethyl acetate, followed by treatment with ammonia gas to produce ANT. The drawback of this method is the low solubility of NaNT in ethyl acetate. The process requires repeated extraction with large volumes of ethyl acetate resulting in a poor yield (47%) of ANT. The second method

(*method-b*) [22] involves, extraction of the acidic aqueous NaNT solution using dichloromethane (DCM) in the presence of tridodecylamine (NT transfer reagent), followed by passing ammonia gas to produce solid ANT (yield 51%). The disadvantages of this method are the use of the very expensive tridodecylamine and excess ammonia gas.

The limitations of both methods are the handling of the sensitive acidic copper salt, $\text{Cu}(\text{NT})_2 \cdot \text{HNT}$. In addition, since this acidic copper salt is a sensitive explosive, its separation from the reaction mixture by filtration would lead to increased industrial cost and also low yield of ANT owing to transfer losses. Other major challenge of the traditional ANT synthesis are the lack of purity and the low yield of the resulting NaNT. Moreover, the currently employed processes for making ANT are hazardous, yield less pure material and are expensive for large scale preparation. We report here an improved, safe method for the preparation of ammonium 5-nitrotetrazolate (ANT) using inexpensive reagents, *via in-situ* formation of barium 5-nitrotetrazolate (BaNT) which is treated with aqueous ammonium sulfate to produce ANT in good yield, with high purity.

2 Experimental procedure

2.1 Materials and methods

All chemicals and solvents were purchased from commercial sources (analytical grade) and were used as such. FT-IR spectra were recorded on a Nicolet FTIR-5700 FTIR spectrophotometer, in a KBr matrix. Raman spectra were recorded using a Renishaw in Via Raman microspectrometer (HPNIR laser, 785 nm) and the spectra were collected in the range $100\text{--}3500\text{ cm}^{-1}$. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz instrument. Thermal stability was studied on a DSC-7 Perkin Elmer instrument. Measurements were performed at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ in closed aluminum sample pans under a nitrogen flow of $50\text{ mL}/\text{min}$ with an empty identical aluminum sample pan as a reference. Thermogravimetric Analysis (TGA) studies were carried out on a SDTA-851e Mettler Toledo instrument operating at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere with 1 mg samples. Scanning electron microscopic (SEM) analysis was carried out using a QAUANTA 200 ESEM-FEI, (The Netherlands). The sample was mounted on a stub of metal with adhesive. Ion chromatography (IC), ICS 3000 DIONEX and CS 12A column, was used for purity analysis. Ultraviolet spectra were recorded on a GBC Cintra-10e UV-Visible Spectroscopy instrument, using methanol as solvent.

2.2 Improved method for the synthesis of ammonium 5-nitrotetrazolate (ANT)

A solution containing 5-aminotetrazole monohydrate (5-AT, 2.13 g), copper(II) sulfate(VI) pentahydrate (0.1 g) and nitric(V) acid (1.5 mL, 70%) in distilled water (30 mL) was prepared and cooled to about 10 °C. This solution was slowly added to a solution of sodium nitrate(III) (5.25 g) and copper(II) sulfate(VI) (2.75 g) in distilled water (50 mL) at 5-10 °C, with constant stirring. After the addition, dilute nitric acid (3.5 mL of 70% in 5 mL water) was added to the reaction mixture at a temperature of <10 °C and stirring was continued for a further 15 min. The viscous, green coloured reaction mixture was then stirred at ~25 °C during 2 h, after aqueous barium hydroxide solution had been added. The resultant dark-blue coloured mixture was slowly heated to 75 °C with constant stirring during 1 h. During the heating, the pH of the reaction mixture was maintained at pH ~8 by adding barium hydroxide solution. The precipitated copper oxide was removed by filtration through a silica gel-celite bed and washed with hot water (~20 mL). The aqueous filtrate containing barium 5-nitrotetrazolate was treated with ammonium sulfate sulfate(VI) (2.25 g in 5 mL water) at room temperature; the insoluble barium sulfate(VI) was filtered off. The resulting aqueous filtrate was evaporated to dryness under reduced pressure. The solid residue obtained was re-crystallized from methanol yielding pure crystals of ammonium 5-nitrotetrazolate (ANT) hemihydrate, in 82% overall yield (2.39 g).

The reaction was finally scaled up starting with varying amounts of 5-AT (21.3 g and 42.6 g) and the corresponding weight ratios of the other reagents. The isolated average yield of ANT from these various experiments was 75-80%.

CAUTION! *Diazotization of 5-aminotetrazole is a highly hazardous process and furthermore ammonium 5-nitrotetrazolate (ANT) is an energetic material sensitive to various stimuli. Although there were no issues in the handling of this material, proper protective measures such as face shield, ear protection, body armour, gloves, anti-static tools and equipment should be used at all times.*

2.3 Characterization of ANT

The purity of the synthesized ANT was determined by HPLC and the results indicated 99.9% purity, with a retention time 1.72 min (methanol/water was used as eluent). In addition, the purity was also determined by ion chromatography (IC) using methanesulphonic acid (20 mM) as the eluent at a flow rate 0.25 mL/min. In duplicate experiments, the purity of ANT was measured to be 99% (based on the ammonium ion). The structure of ANT was confirmed by spectroscopic methods and the data were found to match reported values [22].

The physico-chemical characteristics of ANT are summarized in the Table 1. The Raman spectrum of ANT is shown in Figure 1, and indicates the presence of a nitro group, C=N and N=N groups in the molecule. The scanning electron microscopic (SEM) images of ANT re-crystallized from methanol show randomly shaped or featureless crystals (Figure 2).

Table 1. Physico-chemical properties of ANT

| Method | Results (ANT) |
|---|--|
| IR (KBr) (ν in cm^{-1}) | 3411 (H_2O); 3145, 3084, 2902, 2871 (NH_4); 1544, 1465, 1319 (NO_2); 1448, 1421, 1406, 1319, 1186, 1166, 1068, 1035, 837, 671 (C=N, N=N, tetrazole ring) |
| Raman (25 °C, cm^{-1}) | 2837, 2468, 1543, 1419, 1320, 1065, 1050, 836, 540, 241, 121 |
| UV (λ_{max} , nm) | 258, 217 |
| ^1H NMR (DMSO- D_6) (δ in ppm) | 7.13 (s, 4H, NH_4^+), 3.46 (s, 2H, H_2O) |
| ^{13}C NMR (DMSO- D_6) (δ in ppm) | 168.8 (1C, tetrazole ring) |
| Elemental Analysis for $\text{CH}_4\text{N}_6\text{O}_2 \cdot 0.5\text{H}_2\text{O}$ | Calculated: %C = 8.51; %H = 3.57; %N = 59.61 Found: %C = 8.48; %H = 3.58; %N = 59.69 |
| Purity [%] | 99.9 (HPLC); 99.0 (IC) |
| Crystal habit (SEM) | Randomly shaped or featureless crystals |

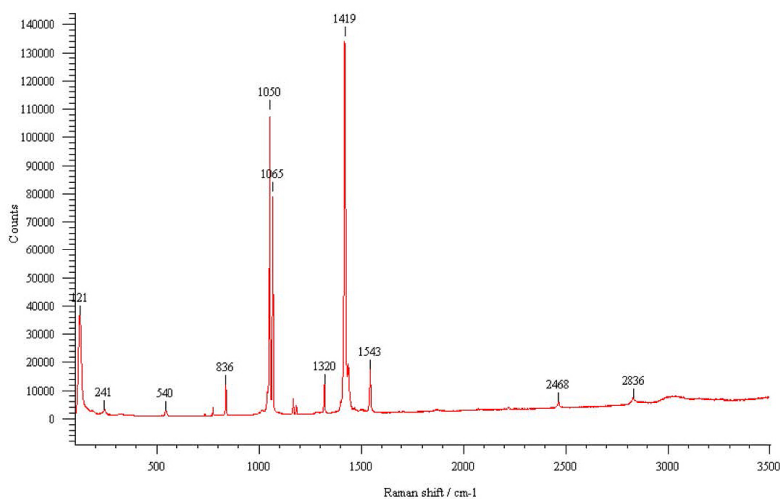


Figure 1. Raman spectrum of ANT

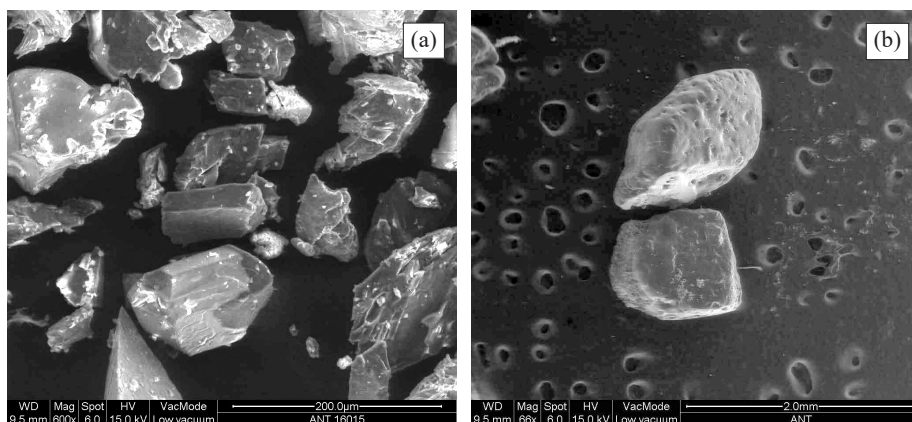


Figure 2. SEM images of crystallized ANT (a and b)

2.4 Single crystal X-ray diffraction analysis

The single crystal X-ray structure of ANT was determined by measuring X-ray diffraction intensity data on a Bruker SMART APEX II single crystal X-ray CCD diffractometer having graphite-monochromatised ($\text{Mo K}\alpha = 0.71073 \text{ \AA}$) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a total of 36 frames. The optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5° increments in φ/ω . Data were collected with a time frame of 15 s keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data acquisition was monitored by the APEX2 program suit [23]. All of the data were corrected for Lorentz-polarization and absorption effects using the SAINT and SADABS programs integrated in the APEX2 package [24]. The structures were solved by direct methods and refined by a full matrix least squares, based on F^2 , using SHELX-97 [25]. Hydrogen atoms were located in the difference Fourier map and refined isotropically. The molecular diagrams were generated using the ORTEP-32 and Mercury programs. Geometrical calculations were performed using SHELX² and PLATON [26, 27].

The crystallographic data and structure determination details are listed in Table 2. The molecular crystal structure of ANT is shown in Figure 3. The ANT crystals obtained in our process were found to be in the hemihydrate form, which is further supported by the single crystal X-ray analysis data. The crystal data obtained in our study for ANT are similar to the literature values reported by Klapötke *et al.* [22].

Table 2. Crystallographic data and structure determination details for ANT

| | |
|---|--|
| Formula | CH ₄ N ₆ O ₂ ·0.5H ₂ O |
| F. wt. | 141.11 |
| Crystal size [mm] | 0.25×0.20×0.09 |
| Temp. [K] | 296 (2) |
| Crystal Syst. | Monoclinic |
| Space Group | C2/c |
| <i>a</i> [Å] | 10.5292(8) |
| <i>b</i> [Å] | 8.2625(7) |
| <i>c</i> [Å] | 13.8366(11) |
| α [°] | 90 |
| β [°] | 103.875(4) |
| γ [°] | 90 |
| <i>V</i> [Å ³] | 1168.63(16) |
| <i>Z</i> | 8 |
| <i>D</i> _{calc} [g cm ⁻³] | 1.604 |
| <i>m</i> [mm ⁻¹] | 0.146 |
| <i>F</i> (000) | 584 |
| <i>Ab. correct.</i> | multi-scan |
| <i>T</i> _{min} / <i>T</i> _{max} | 0.9644/0.9870 |
| 2 θ _{max} | 50 |
| Total reflns. | 4418 |
| Unique reflns. | 1022 |
| Obs. reflns. | 981 |
| <i>h, k, l</i> (min., max.) | (-12, 12), (-9, 7), (-16, 16) |
| <i>R</i> _{int} | 0.0369 |
| No. of para | 108 |
| <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] | 0.0332 |
| <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] | 0.0848 |
| <i>R</i> 1 [all data] | 0.0345 |
| <i>wR</i> 2 [all data] | 0.0857 |
| goodness-of-fit | 1.132 |
| $\Delta\rho$ _{max} , $\Delta\rho$ _{min} [eÅ ⁻³] | +0.168, -0.134 |
| CCDC no. | 1055350 |

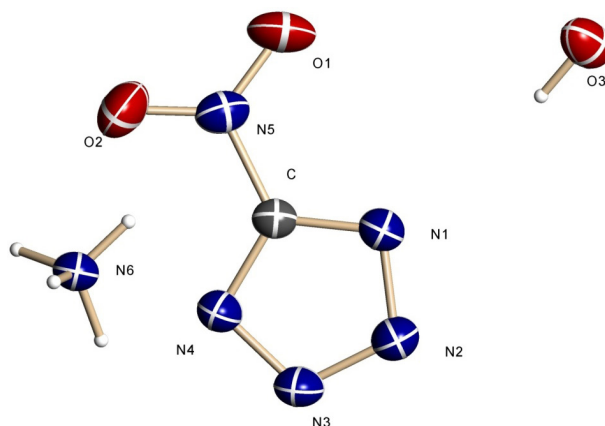
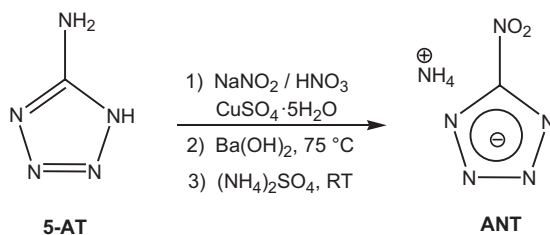


Figure 3. Ortep diagram of ANT

3 Results and Discussion

3.1 Synthesis of ammonium 5-nitrotetrazolate (ANT)

In this work, we have described a simple and convenient method for the synthesis of ANT in high yield starting from 5-aminotetrazole *via* the *in situ* formation of barium 5-nitrotetrazolate as an intermediate (Scheme 3). In our new approach, the copper present in the copper acid salt formed during the reaction was precipitated out *in situ* as its oxide by treatment with barium hydroxide. The resulting aqueous solution containing BaNT was treated with ammonium sulfate(VI) to produce insoluble barium sulfate(VI), which was separated by simple filtration and the resulting filtrate was then evaporated to yield ANT. The prepared ANT was further re-crystallized from methanol.



Scheme 3. Improved synthesis of ANT

The main advantages of this invention are the greatly improve safety of the process, avoiding the handling of the acidic copper salt ($\text{Cu}(\text{NT})_2 \cdot \text{HNT}$), a highly

sensitive explosive intermediate, while producing high purity ANT in good yield. Other additional advantages of this method are that it avoids repeated organic solvent extraction and employs inexpensive reagents, water as the reaction medium, and also the process can be easily scaled up for bulk manufacture of pure ANT. Furthermore, this process avoids the use of dry ammonia gas and expensive tridodecylamine, reflecting the cost effectiveness of the method for producing ANT compared to the reported methods, with less effluent [23].

Table 3. Reaction parameters *vs.* ANT yield*

| Batch No. | Addition of 5-AT [mL/min] | Temperature [°C] | Stirring speed [RPM] | Yield [%] |
|-----------|---------------------------|------------------|----------------------|---|
| ANT-1 | 5 | 0 to 5 | 300 | 75 |
| ANT-2 | 5 | 0 to 5 | 200 | 70 |
| ANT-3 | 2 | 5 to 10 | 200 | 80 |
| ANT-4 | 3 | 5 to 10 | 300 | 82 |
| ANT-5 | 2 | 0 to -5 | 200 | 65 |
| ANT-6 | 3 | -10 to -5 | 300 | Low yield (viscous reaction mixture) |
| ANT-7 | 1-2 | -20 to -10 | 200 | Less or no product, reaction mixture decomposed |

* Reagents: 5-AT (2.13 g) + CuSO₄ (0.1 g) + NaNO₂ (5.25 g) + HNO₃ (1.5 mL) + CuSO₄ (2.75 g)

3.2 Effect of reaction parameters on ANT yield

Table 3 shows the effect of varying the reaction parameters on the product yield. Diazotization of 5-aminotetrazole is an exothermic reaction and must be performed in the temperature range 0 °C to 10 °C. It is mandatory to perform this reaction safely. There is a possibility for a runaway reaction if the reaction is carried out below -5 °C. This is due to the increase in viscosity of the reaction mixture consisting of sodium nitrate(III), nitric(V) acid and copper(II) sulfate(VI). Addition of a further reactant *viz.* 5-AT solution, to this viscous reaction mixture results in an increase in the concentration of both reagents. At some point the reaction may become very fast and vigorous (Note: on one occasion we observed a small explosion in our laboratory, during a small scale synthesis). As also reported in the literature, the rate of addition of 5-AT in the presence of the CuSO₄ solution and the stirring speed also play very important roles in avoiding any micro detonation during the reaction. This is due to the formation of the less stable diazonium salt, which is instantaneously converted to the copper acid salt. The pre-cooled (<10 °C) aqueous solution of 5-AT was

added to the reaction vessel at the rate of ~ 2 -3 mL/min with constant stirring (300 RPM) using a Teflon[®] propeller stirrer. At the initial stage, the reaction temperature rises very rapidly and needs very effective temperature control. The reaction progress can be monitored visually by observing the formation of a greenish-blue coloured precipitate with the evolution of nitrogenous gases.

3.3 Thermal analysis by DSC and TGA

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are versatile techniques for understanding the thermal decomposition process of a molecule. The DSC thermograph (Figure 4) of ANT measured at $5\text{ }^{\circ}\text{C}/\text{min}$ showed a small endothermic peak at $76.0\text{ }^{\circ}\text{C}$ (ΔH , 20.4 J/g) due to dehydration of the water of crystallization. Another endothermic peak was also seen at $199.1\text{ }^{\circ}\text{C}$ (ΔH , 438.2 J/g), followed by a broad exothermic peak maximum at $215.9\text{ }^{\circ}\text{C}$ (ΔH , -2528.2 J/g). The TGA study of ANT showed (Figure 5) a single step decomposition starting at 181 - $240\text{ }^{\circ}\text{C}$; this decomposition corresponded to a mass loss of 71.35% .

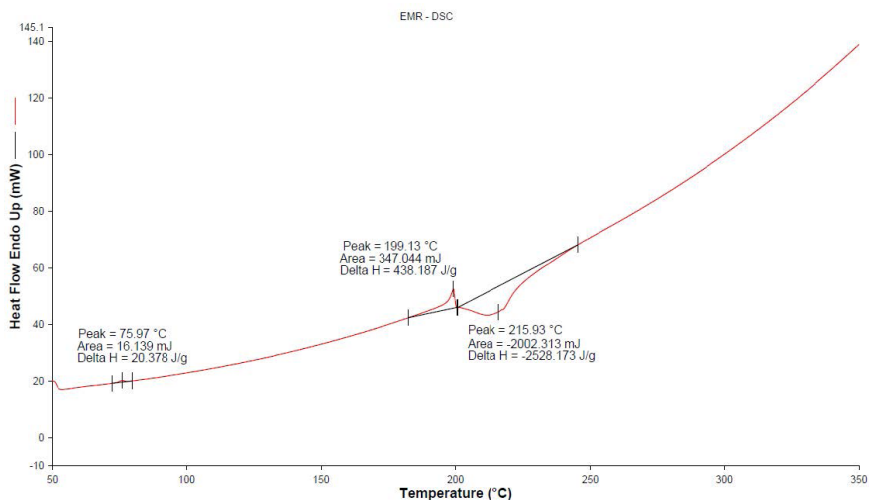


Figure 4. DSC trace of ANT crystals ($5\text{ }^{\circ}\text{C}/\text{min}$)

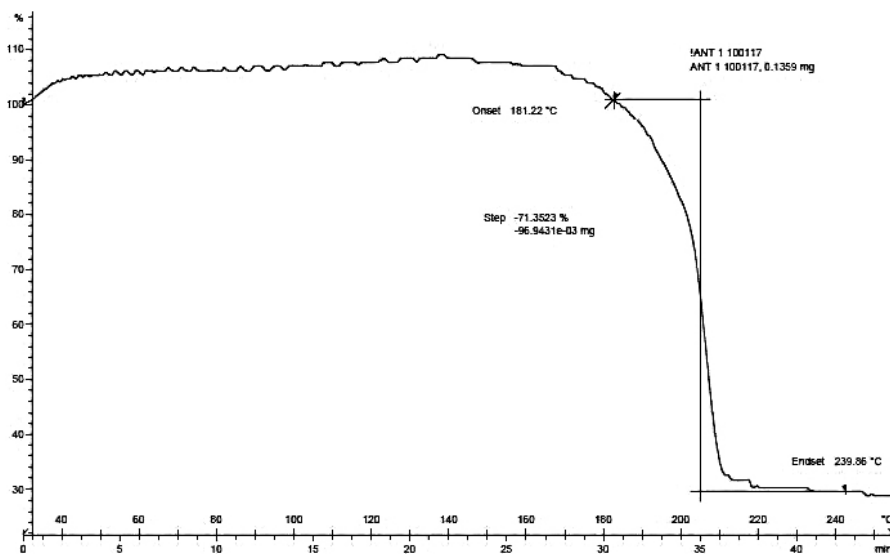


Figure 5. TGA trace of ANT crystals (5 °C/min)

4 Conclusions

The present work describes an improved safe process for the preparation of ammonium 5-nitrotetrazolate (ANT), an important precursor for green energetic materials, in good yield (82%) and high purity (>99%). The structure and purity of the ANT were confirmed by spectroscopic and thermal techniques and single crystal X-ray analysis. The main advantages of the present method are to provide a safe and simple process for the preparation ANT, *via* the formation of barium 5-nitrotetrazolate, which is treated *in situ* with ammonium sulfate to produce highly pure ANT. Furthermore, this method does not involve isolation of the highly sensitive intermediate $\text{Cu}(\text{NT})_2 \cdot \text{HNT}$. Instead the intermediate is treated *in situ* with barium hydroxide solution at elevated temperature to generate barium 5-nitrotetrazolate and copper(II) oxide. This process also avoids the use of dry ammonia gas and expensive tridodecylamine, as used in conventional methods, thereby minimizing hazardous byproducts and effluent. Other advantages of this method are the use of inexpensive reagents and a minimized number of hazardous steps. The process could be easily scaled up for the preparation of pure ANT.

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