Synthesis and Characterization of Urea Nitrate and Nitrourea

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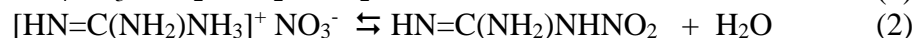**joxley@chm.uri.edu*

Abstract

Although urea nitrate (UN) has not found use as a legitimate explosive, it has been popular as an improvised explosive. In this paper the dehydration product of UN, nitrourea (NU), is characterized for the purpose of distinguishing the two white solids. Although they both melt around 160°C, all other properties differ markedly as might be expected from an inorganic salt (UN) and an organic molecular compound (NU). Two reported routes to the NU product are compared and a decomposition route of UN proposed.

1 Introduction

Dehydration of ammonium nitrate (AN) salts yields nitramine. Nitramine (eq. 1) is relatively unstable compared to nitroguanidine (eq. 2) and nitrourea (eq. 3). The difficulty in the synthesis of nitrourea (NU, CAS 556-89-8) from urea nitrate (UN, CAS 124-47-0) is providing adequate proof of product. Structures of NU and UN are shown in Figure 1. Both NU and UN are white solids with few physical properties available in the literature. Literature melting points are nearly the same, 158-160°C (UN) and 158°C dec (NU)[1]. Herein we report an extensive physical characterization of NU and contrast it with UN. In addition the two reported routes to the NU product are compared and a decomposition routes of UN proposed.

$$NH_4NO_3 \leftrightarrows H_2NNO_2 + H_2O \tag{1}$$
$$[HN=C(NH_2)NH_3]^+ NO_3^- \leftrightarrows HN=C(NH_2)NHNO_2 + H_2O \tag{2}$$
$$[NH_2CONH_3]^+NO_3^- \leftrightarrows NH_2CONHNO_2 + H_2O \tag{3}$$

2 Experimental Section
2.1 Synthesis
NU was synthesized using two different methods, both based on dehydration of UN. In each, the scale of the reaction was designed to make about 1 g of NU. The UN starting material was synthesized by the reaction of nitric acid and urea (U), as previously reported [2].

2.1.1 Method 1: Using UN and sulfuric acid
Sulfuric acid (7.54g, 0.0769 mol) was poured into a round bottom flask equipped with a football stirrer and cooled to -3.0ºC in a salt/ice bath. UN (1.17g, 0.0096 mol) was slowly added, maintaining the temperature between 0 and -3.0ºC. The mixture was allowed to stir for 30 minutes keeping the temperature below +3.0 ºC; then it was poured over ~10g of ice. The white precipitate that formed (NU) was collected on filter paper by vacuum filtration. The product was rinsed with three aliquots of cold water, and dried under gentle flow of air. The NU was re-crystallized from glacial acetic acid [1]. Re-crystallized yield was 125 mg, 1.19 mmol, 13%.

2.1.2 Method 2: Using UN, acetic anhydride and acetic acid
Acetic anhydride and glacial acetic acid were purchased from Fisher Scientific. Acetic anhydride (1.40g, 0.0137 mol) was placed in a round bottom flask with a football stirrer and acetic acid (14.0g, 0.233 mol) was added. The mixture was heated to 60ºC, and UN (1.40g, 0.0113 mol) was slowly added. The mixture was stirred at 60ºC for 15 minutes before removal of heat source. The mixture was allowed to quiescently cool to room temperature. NU was collected on filter paper by vacuum filtration, rinsed with three aliquots of benzene, and oven dried at 40ºC. The NU was re-crystallized from glacial acetic acid to yield 670 mg, 6.45 mmol, 67.2% NU [3].

2.2 Densities, Solubility and Melting Points of UN and NU
Ten density determinations for UN and NU products were obtained using a Micromeritics AccuPyc 1340 gas pycnometer. For each determination a sample cup (1.0 mL) was filled to about 75% capacity, weighed, capped, and inserted into the pycnometer. For each sample, ten helium purges and measurements were taken in succession. Arithmetic means and standard deviations of the UN and NU sets were calculated (Table 1).

The solubility of UN and NU in water, ethanol, methanol and acetone are reported in Table 1. Samples of 10-20 mg were weighed into two 10 mL glass vials and capped. Approximate solubility was determined by adding 1.0 mL and 2.0 mL aliquots to the first and second vial, respectively, and followed by sonication for 5 minutes. Samples were removed and visually inspected for presence of solid. If solid was still present, an aliquot of 2.0 mL was added to each vial and the process repeated until dissolved or 10.0 mL of solvent had been added. If the analyte was still not dissolved it was classified "insoluble." Once approximate solubility was obtained, the process was repeated for new samples near the estimated solubility with small aliquots of solvent ranging from 0.05 mL – 0.75 mL using 100 µL and 1.0 mL syringes. Arithmetic means and standard deviations (5 replicates) were calculated for the UN and NU sets.

Melting points of UN and NU are given in Table 1. Small amounts (~0.5-1.0 mg) of UN or NU were loaded into melting point glass capillaries and positioned into a MelTemp melting point apparatus. At a setting of 4, samples were observed as they heated. Temperature was recorded to the nearest degree as crystals of UN started to melt (range about 3-4ºC). The melting temperature was taken as the mid-point of the melt range. For NU, decomposition without melting was observed.   No solid residue was observed after completion of this procedure. The

decomposition temperature was recorded to the nearest degree. Arithmetic means and standard deviations (10 replicates) were calculated for the UN and NU sets.

2.3 Infrared (IR), Raman and Nuclear Magnetic Resonance (NMR) Spectroscopy

Fourier Transform Infrared (FTIR) spectra were obtained with Nicolet 6700 FTIR Spectrometer employing DTGS TEC detector and KBr beam splitter. Spectral range was 650 to 4000 cm^{-1} at resolution of 4.0 cm^{-1}. For attenuated total reflectance (ATR) of solids 22 scans was sufficient. An IR gas cell (pathlength 10 cm), with MCT/A detector, was used to monitor decomposition gases at 290°C from a transfer line (250°C) connected to a TA Instruments Q5000 thermogravimetric analyzer (TGA). Raman spectra were obtained on a Bruker Sentera Raman Microscope. The microscope module was a Olympus BX51. Excitation source was a 785 nm diode laser. A Bruker Advance III nuclear magnetic resonance spectrometer (NMR) was used to collect both proton and carbon NMR spectra (^1H at 300 MHz and ^{13}C NMR at 75 MHz). In the proton mode 16 scans were collected; carbon mode was run proton decoupled and 512 scans were collected.

2.4 Gas Chromatography Mass Spectrometry (GC/MS)

Gas chromatograph (Agilent model 6890) coupled with mass selective detector (Agilent model 5793) (GC/MS) was used to characterize the samples. The GC/MS inlet was operated in splitless mode with inlet temperature of 125°C and a flow of 11.2mL/min (helium carrier gas). A 15 meter VF200MS column (J&W) with a 0.25mm inner diameter and a 0.25μm film thickness was operated under a constant flow condition of 1.5mL/min. The oven program had an initial temperature of 40°C with a 5 min hold followed by a 20°C/min ramp to 250°C and a post-run at 310°C for 1 min. The transfer line temperature was 250°C and the mass selective detector source and quadrupole temperatures were 230°C and 150°C, respectively. Chemical ionization (positive mode) was used with methane as the reagent gas.

2.5 Liquid Chromatography High-Resolution Mass Spectrometry (LCMS)

Both UN and NU were analyzed using liquid chromatography/high-resolution mass spectrometry (LCMS). The mass spectrometer was operated in both negative and positive ion mode under multiple ionization conditions coupled with the HPLC or direct injection into the atmospheric pressure chemical ionization (APCI) source via syringe pump. The vaporizer temperature was set at 150°C, and capillary was set to 125°C. The discharge current ranged from 5-10 μA, and the sheath gas and auxiliary gas were operated at 25 and 10 arbitrary units, respectively, for negative mode, and 20 and 0 for positive mode. When directly injected into the ionization source via syringe pump, sample flow rate was ~10 μL/min, and the material was dissolved in a 50:50 methanol-water solution. If adduct formation was desired, 0.25wt% carbon tetrachloride or 0.23wt% aqueous ammonium acetate was added to the methanol-water mixture. MS resolution was set to high (50,000 at 2 Hz), and the maximum injection time was 250 ms.

2.6 Differential Scanning Calorimeter (DSC)

Analyses were performed using a TA Instruments model Q-100 DSC. Samples were run under nitrogen flow (50mL/min), and the system was calibrated against indium (m.p. 156.60°C, H_f 28.71 J/g). Sample amounts ranged from 0.2 to 0.5mg and were sealed in glass micro-ampoules (1.5mm O.D., 0.28mm wall thickness, and 8mm length) [4]. Samples were run in triplicate.

2.7 Thermal Gravimetric Analyzers (TGA)

The TGA (TA Instruments Q5000) used nitrogen purge gas to constantly sweep the balance (10 mL/min) and furnace (25 mL/min). Samples (10 mg) were held in open platinum pans (110 uL). Runs were performed in duplicate or triplicate, ramping the temperature at 20 ^{o}C/minute from 40°C to 400°C. For some samples decomposition gases were transferred via a heated (250°C) transfer line to a Nicolet 6700 FTIR spectrometer.

3.0 Results

3.1 Infrared Spectroscopy

Figures 2 and 3 show the IR spectra of UN and NU, respectively. There were no significant changes in spectra of NU prepared using sulfuric acid or acetic anhydride. Both UN and NU had bands around 1700 cm^{-1} (CO) and in the high and low end of 1300 cm^{-1} (NO), but UN is clearly distinguished by the broad band around 2400 cm^{-1}. NU differs from UN between 3400 cm^{-1} and 2765 cm^{-1} where at least five bands are resolved. Both the Israeli Police Laboratory [5]. and a Canadian government laboratory [6] have reported IR of UN. The Canadian facility assigned bands at 3402 cm^{-1} (NH$_2$ asymmetric stretch), 3354 cm^{-1} (NH stretch), 3198 cm^{-1} (NH$_2$ symmetric stretch), 1704 cm^{-1} (CO stretch), 1568 cm^{-1} (N–H), 1426 cm^{-1} (C–N), 1298 cm^{-1} (NO$_3$−). They suggested the peak at 2410 cm^{-1} in UN was OH symmetric stretching from hydrogen bonding of adjacent UN molecules, C=O--H-ONO$_2$. This is consistent with our comparison of IR spectra for UN and NU (Figures 2 and 3) where we found this band only in UN.

3.2 Raman Spectroscopy

Raman spectra of UN, NU, U and AN are given in Figure 4. Literature assignments are available for the prominent 1043 cm^{-1} and 1057 cm^{-1} lines in AN and UN, respectively. They are due to internal symmetric stretching of the NO$_3^-$ anion [7,8]. The 715 cm^{-1} in AN and the 537 cm^{-1} in UN may also be due to internal covalent stretches of NO$_3^-$ anion. A C-N symmetric stretching mode has been assigned to the 1011 cm^{-1} line in urea and is likely responsible for the 1020 cm^{-1} line in UN and possibly the 989 cm^{-1} line in NU. The weak lines in urea at 1625 and 1649 cm^{-1} have been assigned to NH$_2$ deformations. A similar assignment is possible in UN and NU. The 1540 cm^{-1} line in urea has been assigned to C-O stretching. Raman lines at 1583 cm^{-1} (NU) and 1574 cm^{-1} (UN) may also result from C-O stretches.

3.3 ^{1}H and ^{13}C NMR Spectroscopy

Proton NMR spectra of NU in d^6-acetone showed 2 broad peaks--one around 12 ppm, assigned to the proton adjacent to nitro group, and one around 7 ppm, assigned to the proton attached to the amino group. In contrast, UN showed a single peak at about 8 ppm; indicating that the hydronium ion exchanges with amino protons and cannot be observed by proton NMR. Proton decoupled ^{13}C NMR in d^6 acetone yielded a single peak-at 151 ppm for nitrourea and at 163 ppm for UN. The latter is higher due to proton-bonding on the oxygen site of the carbonyl group.

3.4 Gas Chromatography Mass Spectrometry (GC/MS)

No attempt was made to obtain GC/MS of UN. NU in acetonitrile solution was analyzed by chemical ionization GC/MS. NU, made by methods 1 and 2, as well as crude and recrystallized NU, were examined. The chromatographic peak of NU was broad and asymmetric with mass fragments: 44 (medium), 63 (large), 91 (small), 106 (small, NU+H$^+$).

3.5 Liquid Chromatography High-Resolution Mass Spectrometry (LCMS)

Mass spectra for UN and NU (HPLC and direct injection) are given in Figures 5 and 6. The solvent system was equal portions water and methanol spiked with 0.25 wt% carbon tetrachloride (CCl_4) for adduct formation. Most of the major peaks remained the same for NU spectrum whether the sample was introduced via HPLC or direct injection. The negative ion spectrum with CCl_4 (Figure 5) provided the best comparison of UN and NU. In the negative mode, the principle anionic fragments from NU were $NU + Cl^-$ (139.986), $NU - H^+$ (104.010) and nitrate (61.987), and for UN, $urea + Cl^-$ (95.002), $2\ urea + Cl^-$ (155.034), nitrate (61.987), and $nitric\ acid + NO_3^-$ (124.983), the latter two being observed with direct injection. In positive mode (Figure 6) the major fragment for both NU and UN was about m/z 61.040. For UN, in addition to 61.040 fragments, m/z 121.072 and 181.104 values suggest that the 61.040 m/z fragment be assigned as $urea + H^+$; and the other two fragments as $2x\ urea + H^+$, and $3x\ urea + H^+$ (Tables 2 & 3). The NU spectra did not have m/z 121.072 and 181.104 peaks leading to the assignment of the 61.040 fragment as cyanic acid complexed with ammonium ion.

Direct injection spectra of NU and UN in equal amounts of methanol/water with and without 0.23% ammonium acetate for adduct formation. With the ammonium acetate the negative ion spectrum of NU has 3 major m/z values (61.003, 61.987, 104.009). Tentative assignments are $nitramide - H^+$, nitrate, $NU - H^+$ (See Tables 2 & 3). The corresponding negative ion spectrum of UN produced only a nitrate peak at 61.987 m/z. The ammonium acetate positive ion spectra for NU and UN, both have a prominent m/z at 61.040 believed to be $cyanic\ acid + NH_4^+$ in NU and $urea + H^+$ in UN (for the same reasons as the positive CCl_4 spectra). The direct injections in methanol/water without adduct former for both NU and UN did not provide useful information.

Mass spectrum of nitrourea changed as the solution aged. In a freshly made methanol/water solution, $NU - H^+$ (104.010) was the largest peak in the negative mode of the MS fragmentation pattern. However, when a methanol/water solution of NU is allowed to sit one week under ambient conditions all evidence of the $NU - H^+$ fragment disappears and essentially only $dicyanic\ acid - H^+$ (85.044) becomes the major peak. This corresponds to the decomposition of NU previously reported [9].
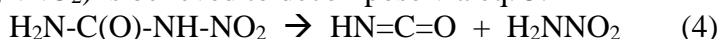
3.6 Differential Scanning Calorimeter (DSC)

Figure 7 shows thermograms of UN and NU. The thermogram of UN showed a melt near 162°C and a sharp exotherm immediately thereafter at 167°C. A second broader exotherm was observed around 380°C (Table 4). At the completion of each DSC run samples were re-weighed to ensure there had been no leaks from the sealed capillaries. A small amount of white residue was observed in all UN samples. A sharp exotherm for NU was observed at about 162°C. While the DSC of UN showed a melt, the NU did not. The NU energy released, according to DSC, was about double the energy of UN (1100 vs. 480 J/g). For NU samples a trace amount of black residue remained.

3.7 Thermal Gravimetric Analyzer

A DSC trace of NU is shown is Figure 7. There was no discernable difference between the TGA traces of the crude and re-crystallized NU or between the NU made by the first or second synthesis methods. The TGA traces of UN (Figure 8, bottom) and NU (Figures 7) were distinctly different. Weight-loss of both UN and NU started at ~140°C; NU exhibited a single weight-loss event, while UN experienced three thermal events. The TGA trace of urea (Figure 8, top) also exhibited three thermal events before being completely consumed. FT-IR spectra of the gases from decomposition of NU, UN and urea are compared in a stack plot (Figure 9) that also includes a mixture of CO_2
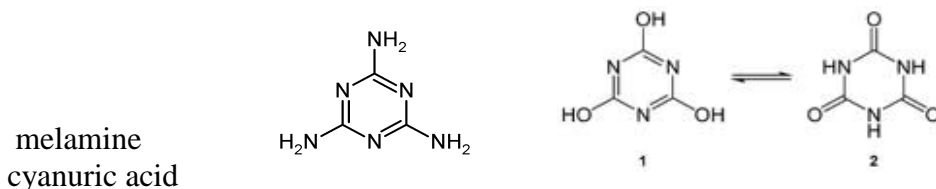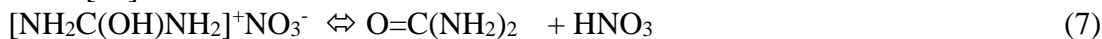
and N_2O gas (second spectrum from top). Overlapping spectra of neat CO_2 and N_2O gases and a mixture of the two, shown in Figure 10, distinguish peaks associated with these two gases. Comparison of the IR spectral region between 2100 cm^{-1} and 2400 cm^{-1} (Figure 11) for UN, NU, U and CO_2/N_2O mixture suggest that UN decomposition produced significant amounts of CO_2 while NU and urea decomposition did not. Further, N_2O gas appeared to be present in UN, NU and urea as demonstrated by prominent peak at 2240 cm^{-1} and an isolated doublet centered at 1288 cm^{-1} (Figure 10). The 1355 cm^{-1} peak in Figure 10, adjacent to the doublet and only appearing in UN was not assigned. Closer inspection of all three materials (Figure 11) reveals another peak centered between the N_2O peak (2240 cm^{-1}) and CO_2 peak (2360 cm^{-1}). This peak (2283 cm^{-1}) is assigned to gas phase isocyanic acid, literature value 2269 cm^{-1}[10]. Since NU was completely consumed, a suggested mechanism is as shown by eqs. 4 and 5. Isocyanic acid (HN=C=O) was also observed in the mass spectrum fragmentation pattern of NU and UN (Table 3). The other product nitramide (H_2NNO_2) is believed to decompose via eq. 5.

$$H_2N\text{-}C(O)\text{-}NH\text{-}NO_2 \rightarrow HN\text{=}C\text{=}O + H_2NNO_2 \qquad (4)$$
$$H_2NNO_2 \rightarrow H_2O + NNO \qquad (5)$$

The formation and subsequent hydrolysis of isocyanic acid to ammonia and carbon dioxide has been demonstrated[9]. This hydrolysis had been observed by mass spectrometry in the aging of aqueous methanol solutions of NU via eq. 6.

$$HN\text{=}C\text{=}O \text{ -- } H_2O \rightarrow NH_3 + CO_2 \qquad (6)$$
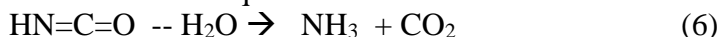
The first weight-loss event for UN (~140°C) only consumed about 40% of the sample (Figure 8). The weight-loss events for NU and UN do not appear to proceed via the same mechanism as their decomposition products are notably different. The decomposition gases of UN exhibit peaks at 2400 and 1350 cm^{-1} not observed in the spectra of the NU off gases. Formation of urea from UN (eq. 7) and the subsequent reactions of urea (eqs. 8-13) to form melamine, cyanourea, biuret and cyanuric acid results in species which are likely to survive at high temperatures [10].

$$[NH_2C(OH)NH_2]^+NO_3^- \Leftrightarrow O\text{=}C(NH_2)_2 + HNO_3 \qquad (7)$$
$$O\text{=}C(NH_2)_2 \rightarrow NH_3 + HCNO \qquad (8)$$
$$NH_3 + HCNO \rightarrow NH_4CNO \qquad (9)$$

$$\qquad\qquad -H_2O$$
$$O\text{=}C(NH_2)_2 \quad \rightarrow \quad NH_2CN \rightarrow N(CNH_2)_3 \quad \text{melamine } (C_3H_6N_6) \qquad (10)$$

$$O\text{=}C(NH_2)_2 + HNCO \rightarrow O\text{=}C(NH_2)(NH\text{-}NC) + H_2O \quad \text{cyanourea } (C_2H_3N_3O) \quad (11)$$
$$O\text{=}C(NH_2)_2 + HNCO \rightarrow NH_2CONHCONH_2 \qquad \text{biuret } (C_2H_5N_3O_2) \qquad (12)$$
$$3\ HNCO \qquad \rightarrow O_3C_3(NH)_3 \qquad \text{cyanuric acid } (C_3H_3N_3O_3) \qquad (13)$$

melamine
cyanuric acid

The IR spectrum corresponding with the weight loss in the NU thermogram is shown in Figure 9. The location of the single weight-loss event for NU and the IR spectrum of its decomposition gases match those observed for urea (also Figure 9). The IR spectrum of urea decomposition gases match those predicted in eq. 5. The remaining solid residue was likely one of the products in eqs.

8-13. Not only is the TGA thermogram of UN more complex than that of NU, but the IR spectra of its decomposition gases also differed. Thus, urea nitrate decomposes via urea (eq. 7) and the decomposition route of urea (eqs. 8-13), while nitrourea decomposes via isocyanic acid and nitramide (eq. 4).

4 Conclusion

UN and NU can be distinguished by a number of their physical properties (Table 1). As expected UN behaves like an ionic compound and decomposes to urea and nitric acid. A difficulty in differentiating between UN and NU has been that they are both white solids with similar melting points.

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	UN	NU
melting point °C	157-159	153-155
density g/cm^3	1.67$\pm$0.011	1.73$\pm$0.026
DSC 20°/min dec °C	~160, ~380	~140
DSC J/g	~500, small	1000
TGA dec at °C, % wt loss	160°C, 40% 250°C, 40%	160°C, 100%
IR cm^{-1}	3500, 3200, 2410 broad 1704, 1568, 1426, 1298	3400-2700 mult peaks 1605, 1305
^{1}H NMR d^6-acetone ppm	8	7, 12
^{13}C NMR d^6-DMSO ppm	163	151
MS negative	nitrate	NU-H$^+$
MS negative with CCl4	urea + Cl$^-$ or 2 urea + Cl$^-$	NU + Cl$^-$
MS postive	urea + H$^+$	methyl carbonate+NH$_4^+$ cyanic acid+NH$_4^+$
solubility mg/mL:		
Water	167.2$\pm$0.5	20$\pm$2
Ethanol	14.2$\pm$0.1	17.2$\pm$0.6
Methanol	54.8$\pm$0.9	43$\pm$8
Acetone	10.4$\pm$0.2	41$\pm$5

Table 1. Comparison of UN and NU Physical Properties

Solvent & Additive	Size	Nitrourea		Urea Nitrate	
		negative	positive	negative	positive
Liquid Chromatography					
methanol/water CCl$_4$	large	NU-H$^+$	isocyanic acid+NH$_4$$^+$	urea+Cl$^-$	urea+H$^+$ 2(urea)+H$^+$
	M-S	NU+Cl$^-$ dicyanic acid-H$^+$ nitramide+Cl$^-$	methyl carbamate+NH$_4$$^+$ methyl carbamate+H$^+$	2(urea)+Cl$^-$ biuret+H$^+$ methylol urea+Cl$^-$	3(urea)+H$^+$ methylol urea+H$^+$ urea+NH$_4$$^+$
methanol CCl$_4$	large	NU-H$^+$	isocyanic acid+NH$_4$$^+$	urea+Cl$^-$	urea+H$^+$ 2(urea)+H$^+$
	M-S	NU+Cl$^-$ dicyanic acid-H$^+$ nitramide+Cl$^-$	methyl carbamate+NH$_4$$^+$	2(urea)+Cl$^-$ biuret+H$^+$ methylol urea+Cl$^-$	3(urea)+H$^+$ methylol urea+H$^+$ urea+NH$_4$$^+$
Direct Inject					
methanol/water CCl$_4$	large	NU-H$^+$	N/A	NO$_3$$^-$	2(urea)+H$^+$
	M-S	NU+Cl$^-$ nitramide+Cl$^-$ NO$_3$$^-$		HNO$_3$+NO$_3$$^-$	urea+H$^+$ 3(urea)+H$^+$ methylol urea+H$^+$
methanol/water NH$_4$ acetate	large	NO$_3$$^-$ NU-H$^+$	isocyanic acid+NH$_4$$^+$	NO$_3$$^-$	urea+H$^+$
	M-S	nitramide-H$^+$			
no additive	large	urea-H$^+$	isocyanic acid+NH$_4$$^+$	NO$_3$$^-$ urea-H$^+$	N/A
	M-S	dicyanic acid-H$^+$ NO$_3$$^-$	urea+NH$_4$$^+$ methyl carbamate+NH$_4$$^+$	Biuret-H$^+$	

Table 2. Summary of HRMS fragmentation

Negative Mode

Additive	Mode	Solvent	Nitrourea				Urea Nitrate			
			Obs. Mass	Assignment	Calc. Mass	Size	Obs. Mass	Assignment	Calc. Mass	Size
CCl$_4$	LC	Fresh 50-50 MeOH-H$_2$O	85.0050	[Dicyanic acid - H$^+$]$^-$	85.0044	S	95.0008	[Urea + Cl$^-$]$^-$	95.0018	L
			96.9799	[Nitramide + Cl$^-$]$^-$	96.9810	T	96.9978	[Urea + ^{37}Cl$^-$]$^-$	96.9988	M
			104.0090	[Nitrourea - H$^+$]$^-$	104.0102	L	102.0299	[Biuret - H+]-	102.0309	T
			139.9858	[Nitrourea + Cl$^-$]$^-$	139.9868	M	127.0271	[Ammelide - H$^+$]$^-$	127.0262	S
							155.0334	[2xUrea + Cl$^-$]$^-$	155.0341	S
	LC	One Week Old 50-50 MeOH-H$_2$O	85.0050	[Dicyanic acid - H$^+$]$^-$	85.0044	L	Urea nitrate was not run with aged samples			
			96.9858	[Nitramide + Cl$^-$]$^-$	96.9810	S				
	Direct Inject	50-50 MeOH-H$_2$O	61.9871	[Nitrate$^-$]$^-$	61.9884	S	61.9878	[Nitrate$^-$]$^-$	61.9884	L
			96.9799	[Nitramide + Cl$^-$]$^-$	96.9810	S	124.9829	[Nitric acid + NO$_3^-$]$^-$	124.9840	T
			104.0090	[Nitrourea - H$^+$]$^-$	104.0102	L				
			139.9859	[Nitrourea + Cl$^-$]$^-$	139.9868	M				
NH$_4^+$ Acetate	Direct Inject	50-50 MeOH-H$_2$O	61.0032	[Nitramide - H$^+$]$^-$	61.0044	S	61.9872	[Nitrate$^-$]$^-$	61.9884	L
			61.9871	[Nitrate$^-$]$^-$	61.9884	L				
			104.0090	[Nitrourea - H$^+$]$^-$	104.0102	L				

Positive Mode

Additive	Mode	Solvent	Nitrourea				Urea Nitrate			
			Obs. Mass	Assignment	Calc. Mass	Size	Obs. Mass	Assignment	Calc. Mass	Size
CCl$_4$	LC	Fresh 50-50 MeOH-H$_2$O	61.0401	[Isocyanic acid + NH$_4^+$]$^+$	61.0396	L	61.0401	[Urea + H$^+$]$^+$	61.0396	L
			76.0395	[Methylcarbamate + H$^+$]$^+$	76.0393	S	78.0665	[Urea + NH$_4^+$]$^+$	78.0662	T
			93.0659	[Methylcarbamate + NH$_4^+$]$^+$	93.0659	M	93.0660	[Methylol urea + H$^+$]$^+$	93.0659	S
							121.0721	[2xUrea + H$^+$]$^+$	121.0720	L
							181.1045	[3xUrea + H$^+$]$^+$	181.1044	T
	LC	One Week Old 50-50 MeOH-H$_2$O	61.0401	[Isocyanic acid + NH$_4^+$]$^+$	61.0396	L	Urea nitrate was not run with aged samples			
			93.0658	[Methylcarbamate + NH$_4^+$]$^+$	93.0659	M				
	Direct Inject	50-50 MeOH-H$_2$O		N/A			61.0394	[Urea + H$^+$]$^+$	61.0396	M
							121.0724	[2xUrea + H$^+$]$^+$	121.0720	L
							130.0652	[Cyanuric acid + H$^+$]$^+$	130.0253	S
							181.1049	[3xUrea + H$^+$]$^+$	181.1044	S
NH$_4^+$ Acetate	Direct Inject	50-50 MeOH-H$_2$O	61.0401	[Isocyanic acid + NH$_4^+$]$^+$	61.0396	L	61.0408	[Urea + H$^+$]$^+$	61.0396	M
							62.0435	[Nitromethane + H$^+$]$^+$	62.0237	M
							93.0666	[Methylol urea + H$^+$]$^+$	93.0659	M

**Table 3.** Fragmentation patterns of NU and UN. Assignments with Cl$^-$ adduct were supported by additional mass peaks corresponding to the ^{37}Cl$^-$ adduct.

UN Ramp Rate (°C/min)	MP (°C)	Max. (°C)	Heat (J/g)	NU Ramp Rate (°C/min)	Max. (°C)	Heat (J/g)
20	163.74	175.79	304.5	20	163.11	1143
20	163.77	174.27	627.3	20	164.15	1077
20	161.15	174.26	415.3	20	161.92	1099
10	159.18	166.7	477.6	20	163.69	887.1
10	159.42	167.12	477.4	20	154.21	1054
10	160.73	167.09	424.9	20	158.71	1113
10	159.51	167.13	399.14	10	152.68	1105
10	158.75	166.55	433.5	10	148.74	1140
				10	148.19	1089
				10	143.67	1045

Table 4. DSC Summary of Urea Nitrate & Nitrourea
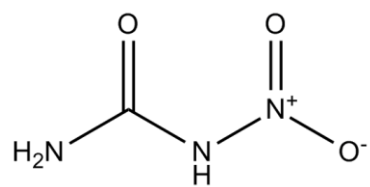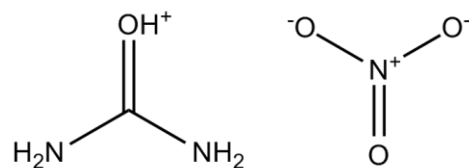
Figure 1. Chemical Structures of Nitrourea (NU) and Urea Nitrate (UN)
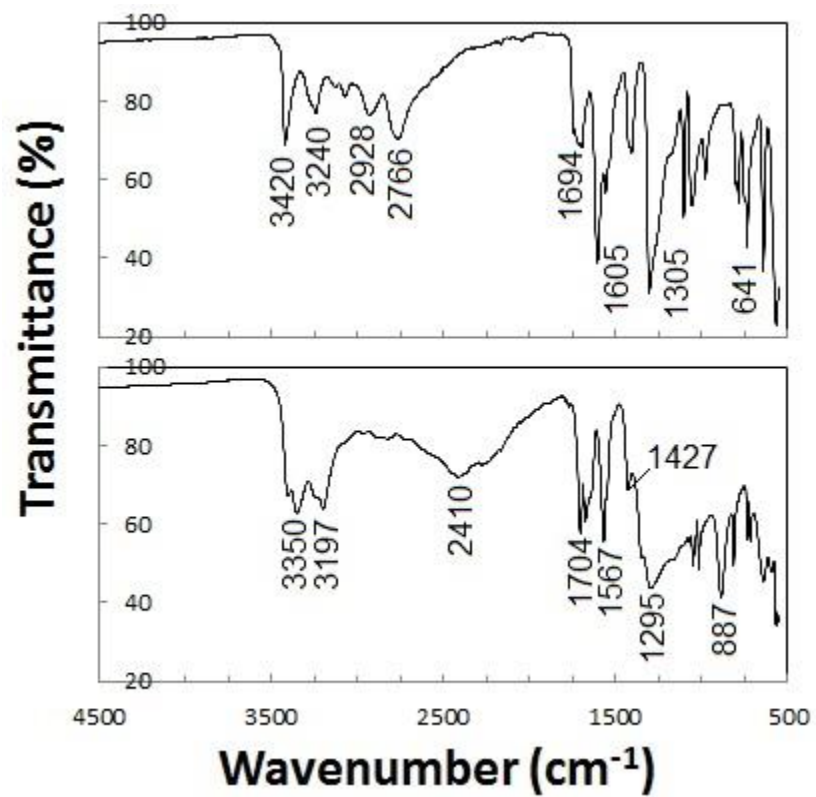
Figure 2. Stacked transmission mode IR spectra of recrystallized Nitrourea (Top) and Urea Nitrate (Bottom)
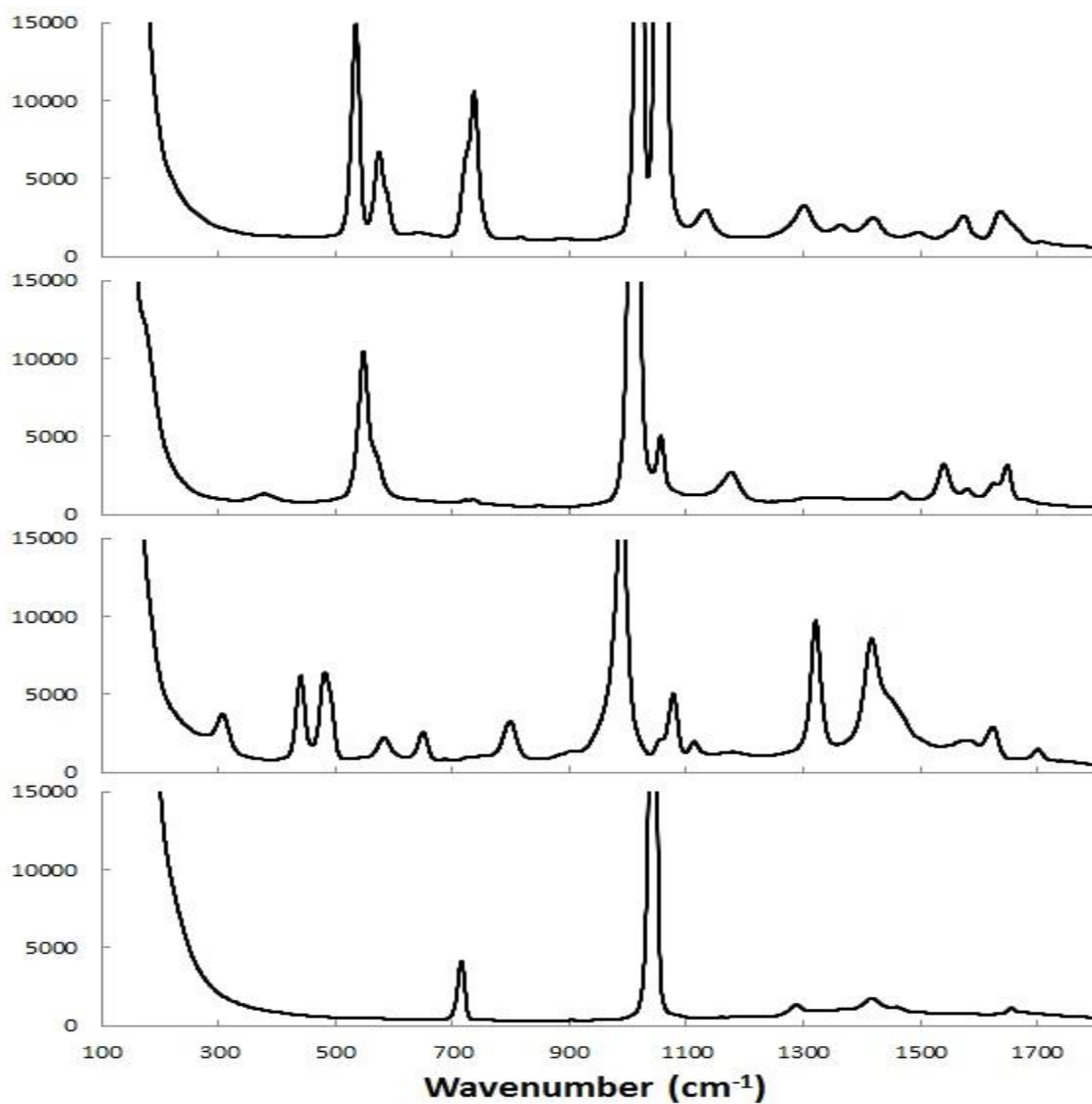
Figure 3. Raman Spectrum, from top, of UN, Urea, NU, Ammonium Nitrate, respectively. Ammonium nitrate exhibited additional small peak at ~2900cm^{1-}.
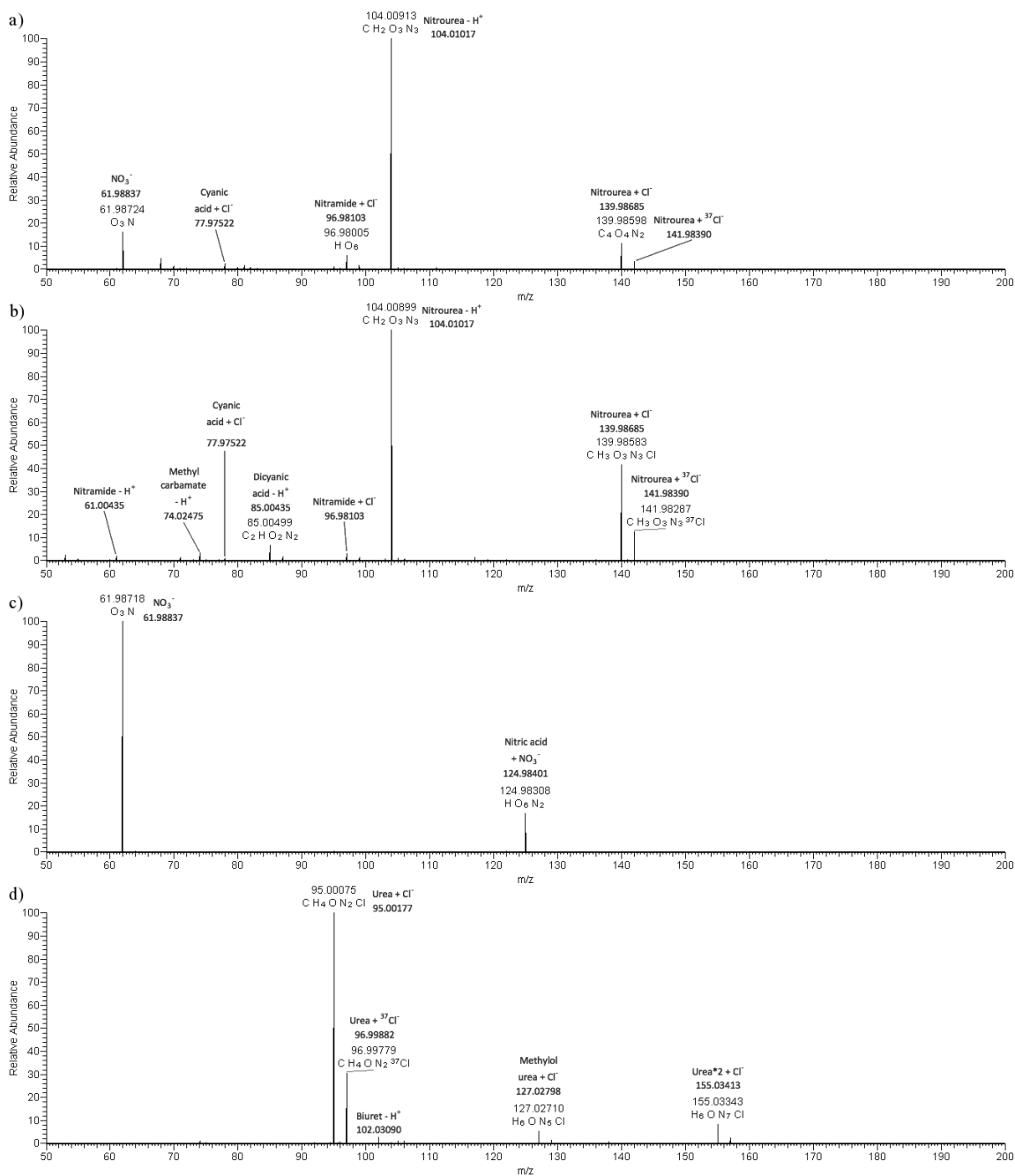
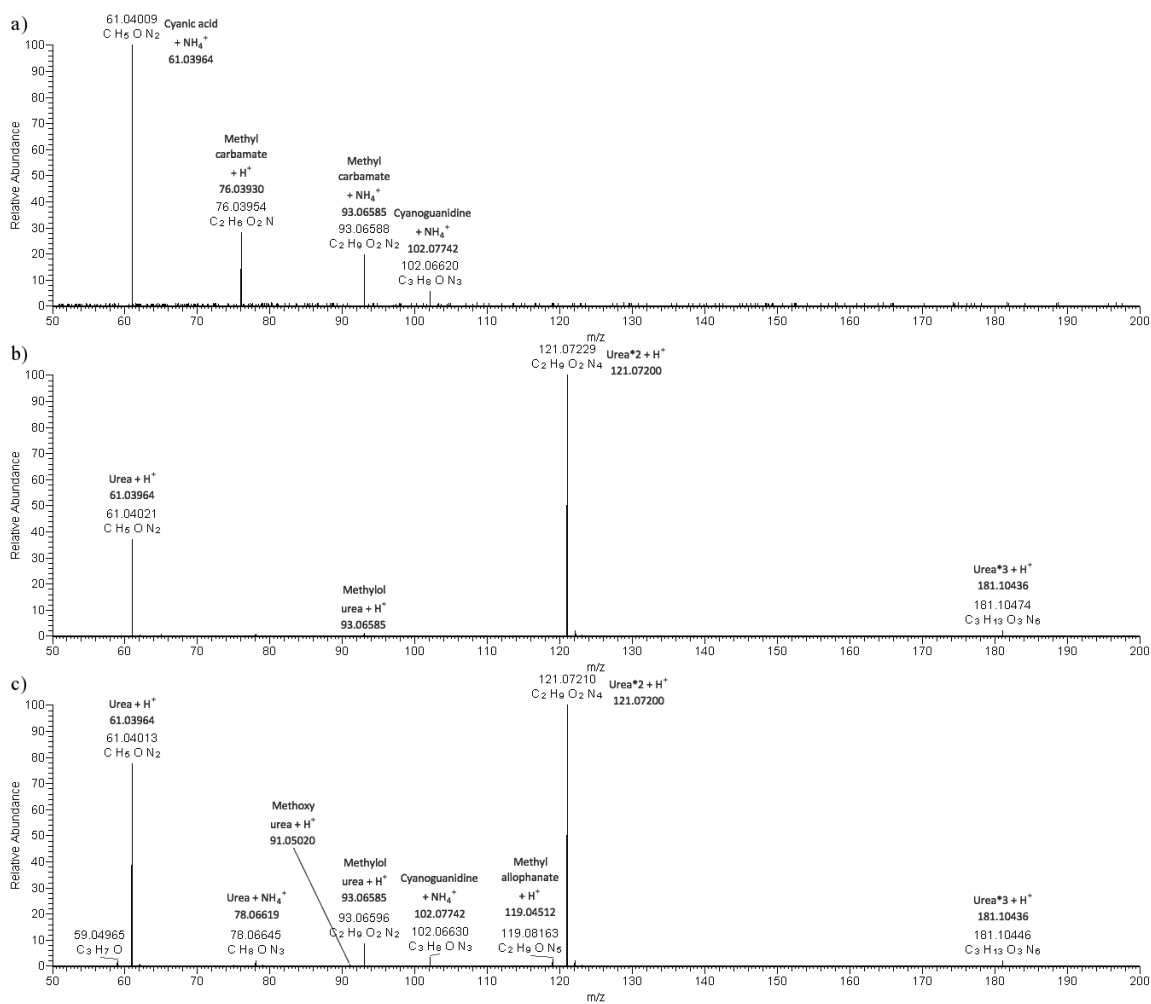**Figure 4.** Negative mode mass spectra of NU and UN in 50-50 MeOH-H₂O with CCl₄. a) direct inject NU, b) LC NU, c) direct inject UN, d) LC UN.

Figure 5. Positive mode mass spectra of NU and UN in 50-50 MeOH-H_2O with CCl_4. a) LC NU, b) direct inject UN, c) LC UN.
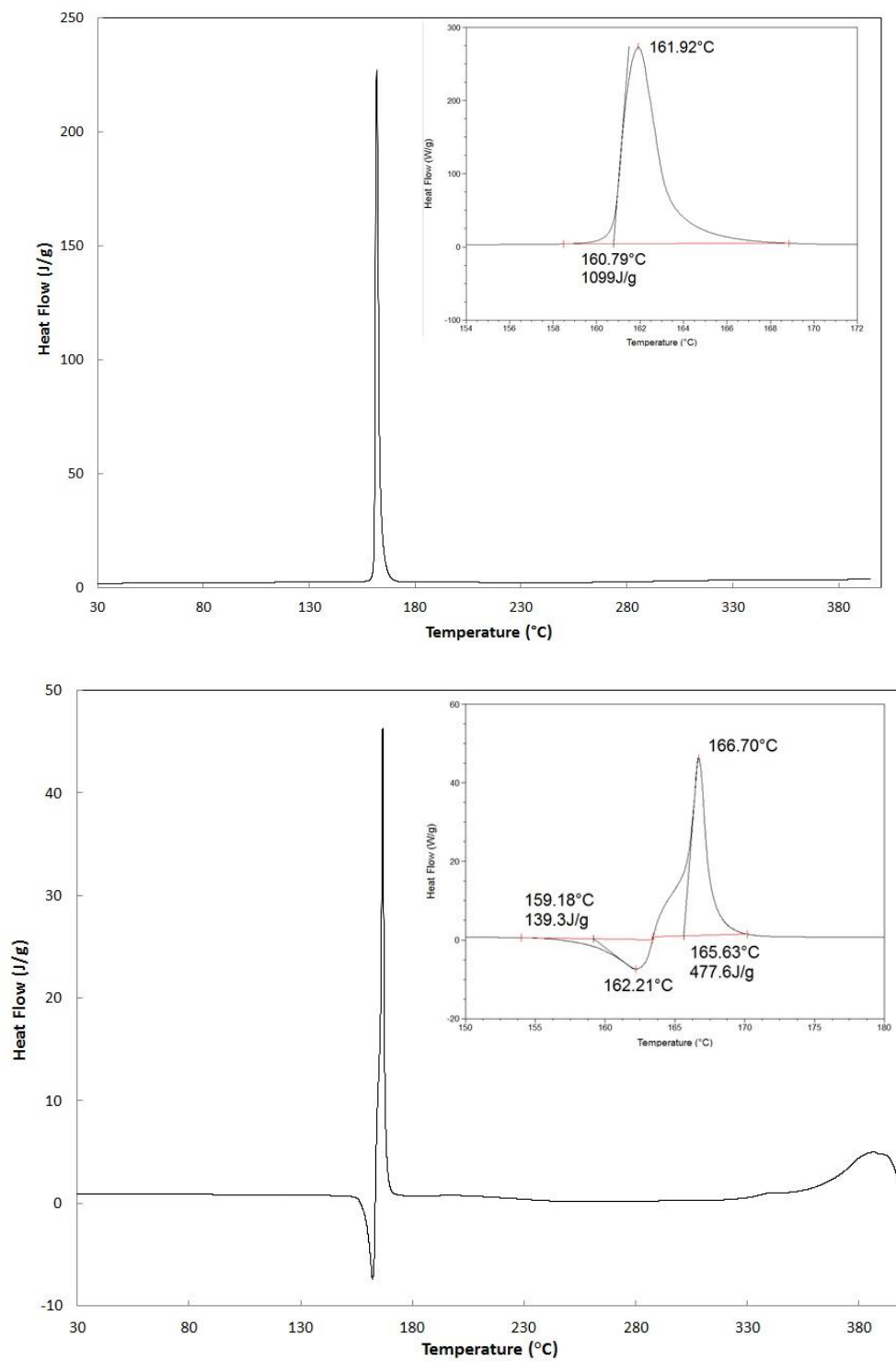
Figure 6. DSC thermograms of nitrourea (top) & urea nitrate (bottom) scanned at 10 °C/minute
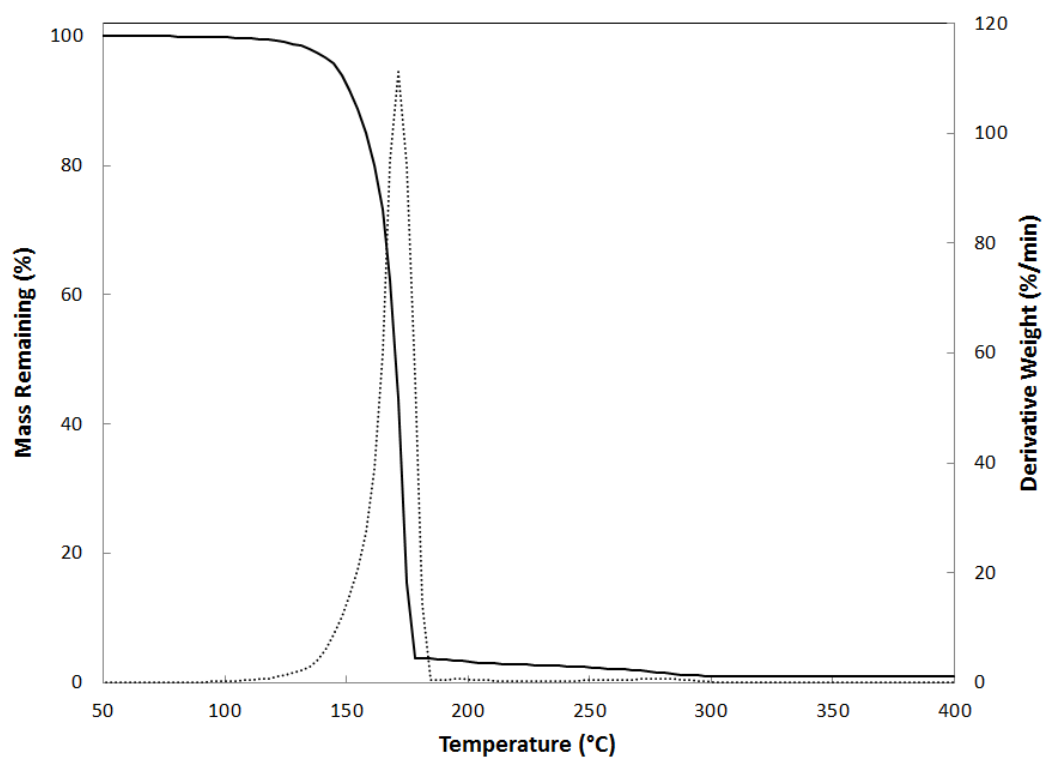
Figure 7. TGA trace of nitrourea
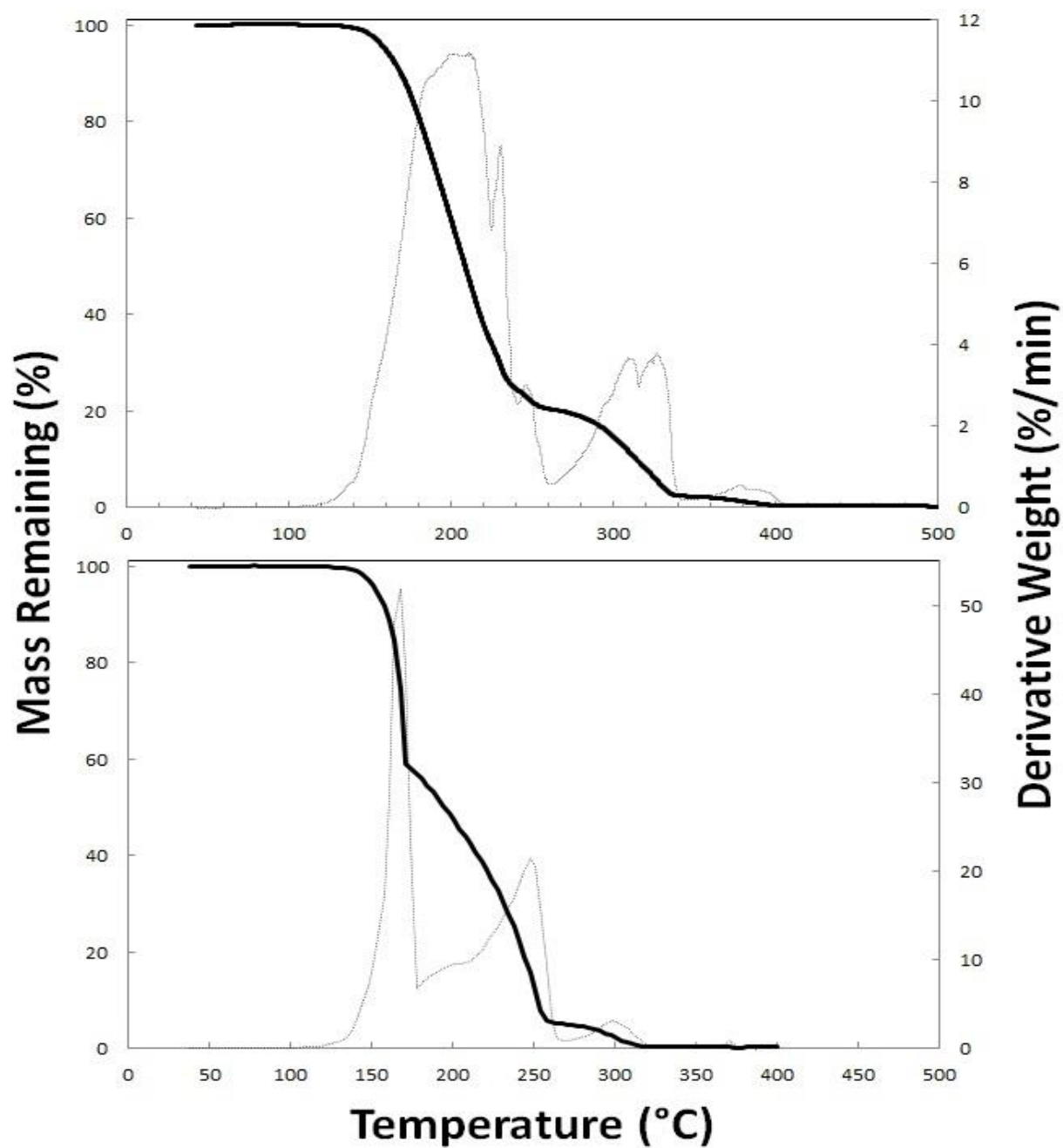
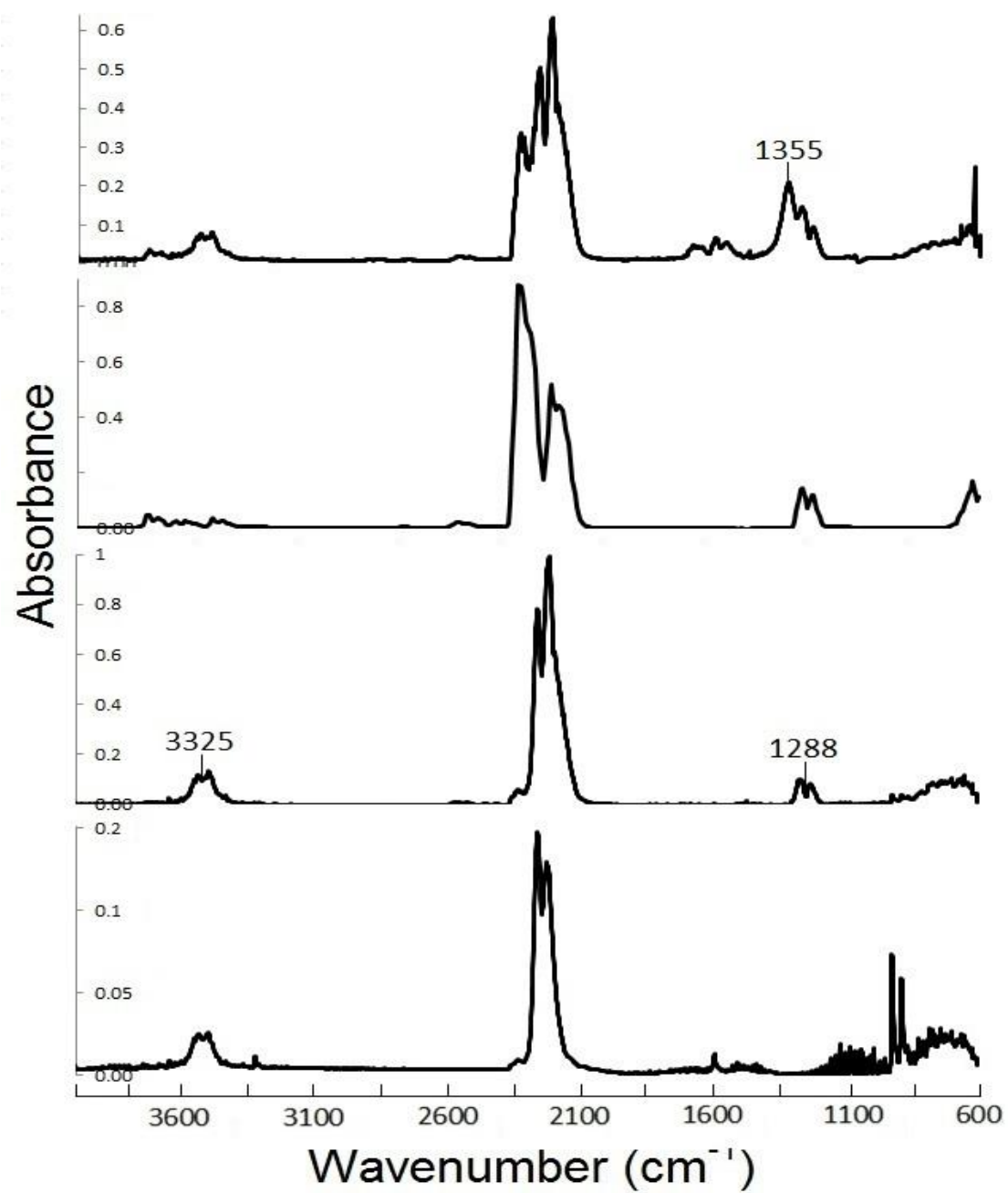**Figure 8.** Stacked TGA Trace of urea (top) and recrystallized Urea Nitrate (bottom).

Figure 9. Stacked IR spectra of urea nitrate, CO_2 and N_2O mixture, nitrourea, and urea from top to bottom, respectively. Selected wavenumbers are shown.
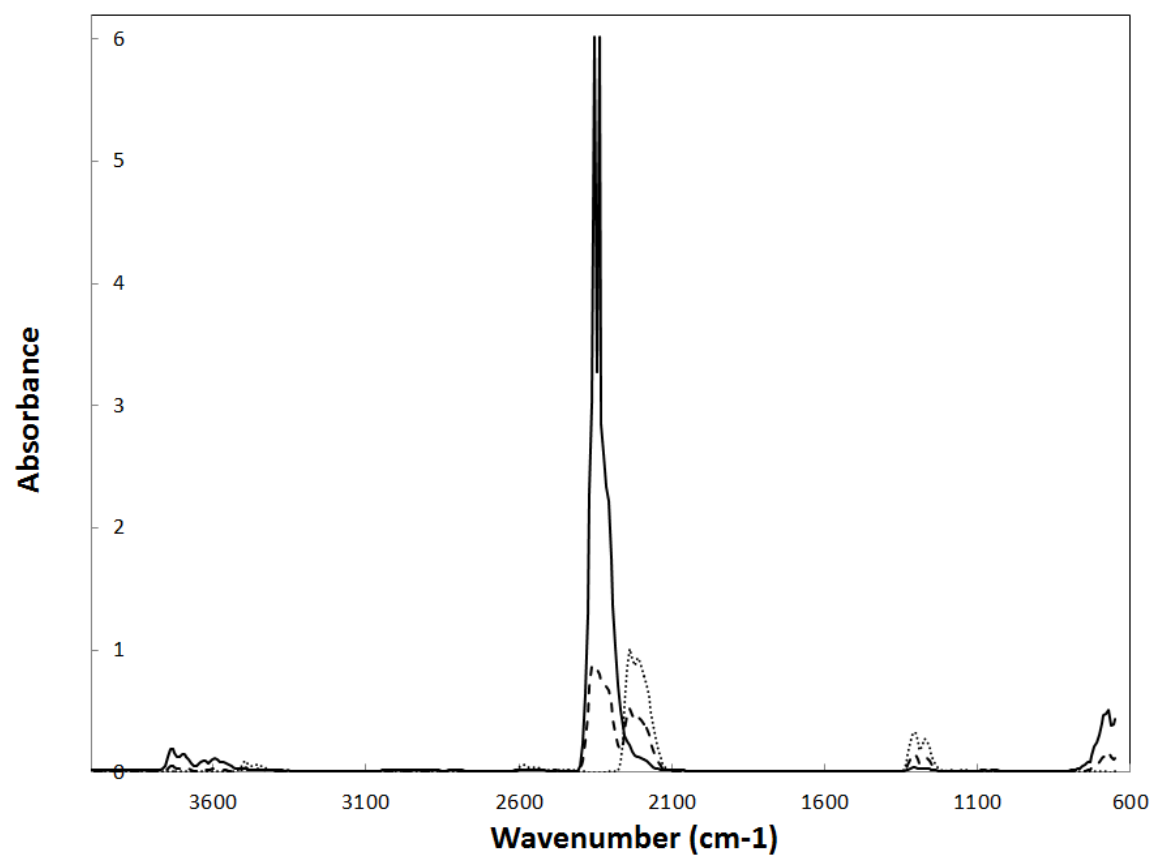
Figure 10. Overlap spectra of CO_2 (—), N_2O ($\cdots$), and a mixture of both (---).
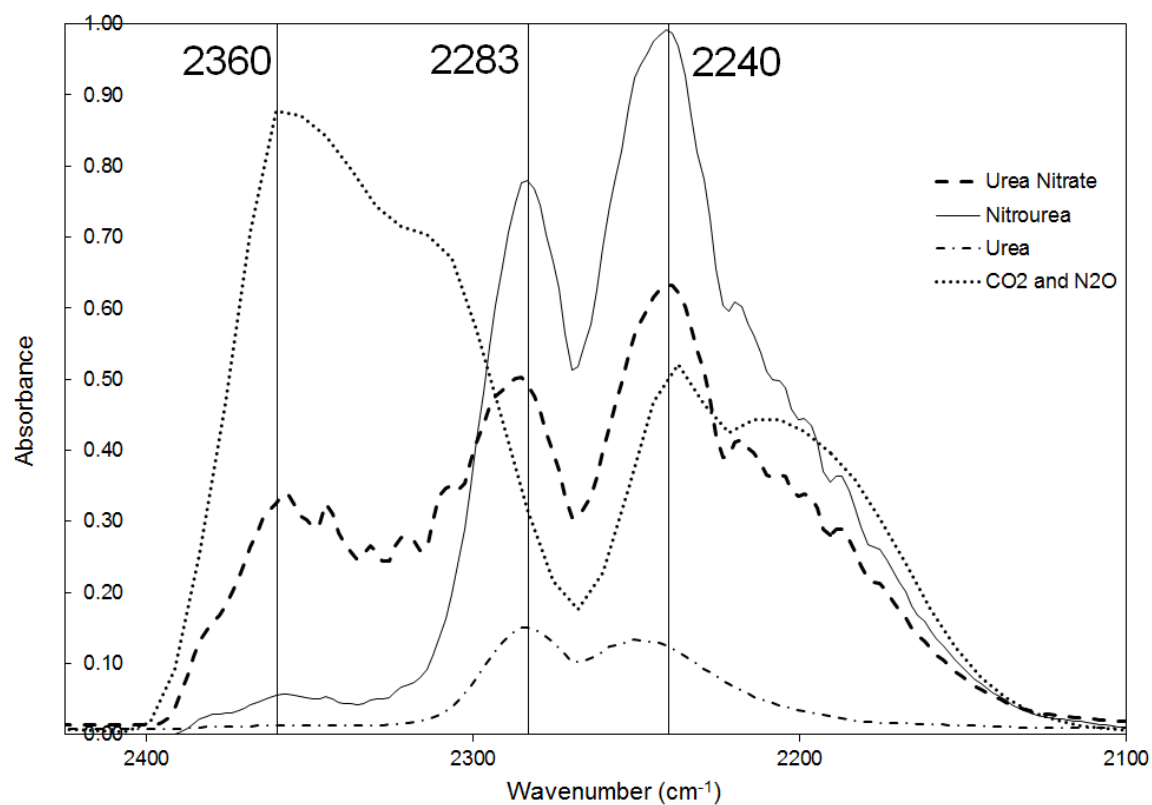
Figure 11. Overlap magnified IR spectra of urea nitrate, nitrourea, urea, and a mixture of CO_2 and N_2O.