

Decompositions of Urea and Guanidine Nitrates
Jimmie C. Oxley; James L. Smith; Sweta Naik; Jesse Moran
Chemistry Department, University of Rhode Island

Abstract

The decompositions of urea nitrate (UN) and guanidine nitrate (GN) are determined with isothermal heating followed by quantification of both remaining nitrate and remaining base. Activation energies determined for UN were 158 kJ/mol and 131 kJ/mol with the pre-exponential factors being $1.39 \times 10^{12} \text{ s}^{-1}$ and $2.66 \times 10^9 \text{ s}^{-1}$, for nitrate and urea, respectively. These pairs of Arrhenius constants predict decomposition rates less than a factor of two apart. For GN the activation energies were 199 kJ/mol and 191 kJ/mol with the pre-exponential factors being $1.94 \times 10^{15} \text{ s}^{-1}$ and $3.20 \times 10^{14} \text{ s}^{-1}$, for nitrate and guanidine, respectively. These pairs of Arrhenius constants predict identical decomposition rates (Table V). Literature values for ammonium nitrate decomposition indicate it should decompose somewhat slower than UN and faster than GN. DSC also indicates this ordering (Table III) but suggested UN is substantially less stable than was observed in the isothermal experiments. Decomposition products, both gaseous and condensed, are reported for UN and GN (Table VI), and decomposition routes are suggested. Experimental results indicate that NO_2^+ is generated during the decomposition mechanism. This mechanism appears to differ from that of the analogous nitro derivatives.

Introduction

This study examined the thermal stability of urea nitrate and guanidine nitrate. Both urea and nitrate salts find use as fertilizers. Annual United States production of urea is about 10 million tons, while imports are about 3 million tons. Most of that urea (85%) ends up as fertilizer, with a small percentage used for resins and plastics, and a tiny percentage, used in cattle feed.¹ For over a decade; urea nitrate has been used by terrorists to make improvised explosives. It was used in the bombing of the World Trade Center (February, 1993) and in many car bombings in Palestine.² In 1992, use of urea nitrate became so prevalent in bombings by the Shining Path (a South American terror cell), that sales of urea were outlawed in Peru. Guanidine nitrate (GN) is an explosive used by the military and commercial sectors, but has not seen use as a terrorist material. The purpose of this research was to determine the stability and detectability of urea nitrate and guanidine nitrate as compared to the well-known explosive, ammonium nitrate.

Urea may be used as a stabilizer in some commercial blasting agents.³ On the other hand, UN has poor stability in moist environments and is not considered useful as a blasting agent. Nevertheless, it is potentially a terrorist's tool due to availability of the precursor chemicals and ease of preparation in large quantities. Since counterterrorism efforts have been forced to face the threat of UN, it is important to address its stability. Herein the stability of UN is compared to a number of nitrate salts and specifically to guanidine nitrate and ammonium nitrate which have similar detonation velocities (Table I). Guanidine nitrate and its dehydration product, nitroguanidine, are also explosives⁶ that are sometimes used in ammonium nitrate explosive formulations and in various propellant applications including triple-base gun propellants.⁷ Urea nitrate and guanidine nitrate are in some ways analogous. Urea nitrate and guanidine nitrate share common decomposition products such as melamine, and the precursor materials, urea and guanidine, are both found in urine.

Experimental Section

Reagents: Urea nitrate was synthesized as follows. Nitric acid (15.9 M, 5.75 mL, 0.0916 mol, 1.1 eq) was added dropwise with stirring over 5 minutes to a cold (10°C) urea solution (10.86 g, 0.083 mol, 46 % w/w urea). The addition raised the reaction mixture temperature 25°C and resulted in precipitation of copious amounts of white crystals, hampering stirring. The solution was allowed to stir 15 minutes at room temperature, vacuum filtered, and washed with water (2 mL, 0°C). The filter cake was dried under vacuum in a desiccator overnight to yield urea nitrate (9.2 g, 90 % with m.p. 160°C).^{8,9} Urea nitrate was also purchased from TCI America. The dry urea nitrate was a white powder; it was stored under vacuum to avoid moisture. Guanidine nitrate (98%) was purchased from Fluka; methanesulfonic acid (99%) and perchloric acid, from Acros Organics; sodium dihydrogen phosphate (99.9%) from Fisher; and lithium hydroxide (99%) from Sigma Aldrich. Arenes were purchased from Fisher Scientific or Sigma Aldrich.

Determination of Isothermal Rate Constants: The decomposition rate constants were determined for at least five temperatures. At each temperature, the extent of decomposition was quantified and the analyses were run in triplicate. At the completion of the heating interval, sample ampules were cooled to room temperature, opened, and extracted with 5 mL de-ionized water. Aqueous samples were analyzed by liquid chromatography (LC). Quantification of remaining reactants, urea nitrate (UN) and guanidine nitrate (GN) was accomplished using a LC (Agilent Model 1100 LC) equipped with a photodiode array detector (PDA). Conditions for separation of GN¹⁰ and UN¹¹ are given in Table II. The natural logarithm of the fraction remaining was plotted versus time to construct the first-order plots (Fig. 1).

Differential Scanning Calorimetry: Differential scanning calorimetric (DSC) analyses were performed on a TA Instruments model Q-100 DSC. Exemplary scans are shown in Figure 2. Samples were run under nitrogen flow (50 mL/min), and the system was calibrated against indium (m.p. 156.60°C, H_f 28.71 J/g), tin (m.p. 231.93°C, H_f 60.6 J/g), lead (m.p. 327.50°C, H_f 23.1 J/g), and zinc (m.p. 419.53°C, H_f 108 J/g). Sample amounts ranged from 0.2- 0.5 mg and were sealed in glass capillary tubes (1.5 mm O.D., 0.28 mm wall thickness, and 8 mm length).¹² The sealed capillaries were held in aluminum holders during the scans from 50°C to 450°C at different scan rates.

A DSC method, established by the American Society for Testing and Materials (ASTM), was used to determine Arrhenius activation energies and pre-exponential factors.¹³ Data was collected at five or more heating rates ($\beta = 1, 3, 5, 7, 10, 13, 15, \text{ or } 20^\circ\text{C}/\text{min}$). Plots were constructed of $\log_{10}\beta$ versus $1/T$, where T was the exothermic peak maximum temperature in Kelvin. The slopes $[d(\text{Log}_{10}\beta)/d(1/T)]$ were used to calculate activation energies using the equation:

$$E_a = -2.19R [d(\text{Log}_{10}\beta)/d(1/T)]$$
$$R = \text{gas constant } 8.314 \text{ J K}^{-1}\text{mol}^{-1}$$

The Arrhenius pre-exponential factor (A) was calculated: $A = \beta E_a e^{E_a/RT}$

Product Identification: Condensed-phase UN decomposition products were identified by matching retention times on an LC with those of authentic samples. UN was heated at 200°C for 60 minutes to affect partial decomposition. At the completion of heating, samples were handled as described above for determination of remaining starting material. Conditions used on the Agilent 1100 LC are listed in Table II.

To identify decomposition gases of UN and GN, samples were heated at 200°C for 60 minutes for UN and 250°C for 60 minutes for GN. Capillary tubes were broken in a sampling loop directly linked via a 6-port valve to the injection port of an HP model 5890 GC equipped with an electronic pressure control system and a model 5971 electron-impact quadrupole MS.¹⁴ Manual tuning of the MS with perfluorotributylamine (PFTBA) was used to adjust relative abundance for m/z 69, m/z 100, and m/z 131 to 100, 15, and 45% +/- 1, respectively. The MS was run in scan mode (m/z range 10-300) with a threshold of 100 and a sampling of 4 (2.2 scans/s). UHP helium passed through moisture, hydrocarbon, and oxygen traps and was used as the carrier gas. The injector temperature was 100°C and the detector-transfer line temperature was 180°C. Liquid N₂ was used to cool the GC oven to -80°C. After 5 min, the oven was ramped to 150°C at 15°C/min. Initial flow was 14 mL/min. Injector pressure 0.2 psi. Septum purge was measured as 2.5 mL/min. Column flow was 1.2 mL/min at -80°C. Purge valve was initially off and turned on after 0.5min. The split ratio was approximately 15:1. A calibration gas mixture from Scott Specialty Gases, composed of N₂, CO, CO₂, and N₂O, was used to determine the peak identities by retention time matching.

Nitration: A melting point capillary was used to encapsulate a mixture of an arene and nitrate salt. A short length of capillary tube (~40mm), sealed at one end, was loaded with dry nitrate salt [about 3-7 mg of UN, nitrourea (NU), GN, nitroguanidine (NQ), or AN] and a liquid aromatic (toluene or nitrobenzene). The other end of the tube was sealed to form a closed capillary which could maintain the mixture at temperatures above the decomposition temperatures of the nitrate salts. The capillaries were heated in an oven at 250°C for several hours. The nitrate salts were somewhat soluble at temperature but did not form homogenous solutions during workup. To remove the solution for analysis, the liquid inside was shaken to one end of the tube, the liquid was frozen in liquid nitrogen, and the tube cracked open near the top. As the solution warmed, the liquid was quickly extracted via a microsyringe and put into a GC vial fitted with a 250uL glass insert. Sufficient dichloromethane was added to fill the insert to volume. Analysis of the solution was performed on an Agilent 6890N gas chromatograph (GC) with an electron impact (EI) source with a 5973inert mass spectrometer (MS) detector. The chromatograph was equipped with a HP-5MS fused-silica capillary column (6m length × 0.25mm internal diameter and 0.25µm film thickness). The chromatographic elution was temperature programmed as follows: initial temperature 50°C was ramped to 280°C at a rate of 10°C/min with an isothermal hold at 280°C for 2 min for a total run time of 25 min. The carrier gas was helium with a constant flow of 3 mL/min. The injector temperature was 250°C and split 2:1 with a split flow of 6 mL/min. The auxiliary (transfer line) temperature was set at 300°C. The chromatographic peaks were identified by comparison with a reference mass spectral library (US National Institute of Standards and Technology, NIST) and retention time matching with known compounds. Analysis was for the production of a specific nitroaromatics and not specific yield, no quantitative workup was attempted. Resulting spectra were analyzed for the indication of nitration products; 2, 3, or 4 nitrotoluene in the case of toluene reactions, or dinitrobenzene isomers in the case of nitrobenzene reactions.

Results and Discussion

Kinetics of Decomposition

Initial screening of the nitrates was performed using DSC. Table III shows the average response at a scan rate of 20°C per minute. Potassium and sodium nitrates, lacking a fuel source, exhibited no exotherms. Nitrates with cations containing hydrogen or carbon were energetic, and, indeed, are known explosives. The early DSC exotherm of urea nitrate suggested it was the least stable. It exhibited two exothermic regions, but the sum of the heat released was still less than that released by guanidine nitrate (Table III). Guanidine nitrate exhibited the highest temperature exotherm, but also the most heat release. Ammonium nitrate produced the least heat; more would be produced if it were sufficiently fueled. (It should be noted that heat of thermal decomposition is less; about half that of detonation.)

An attempt was made to determine Arrhenius parameters using the ASTM DSC method,¹³ but it was unsuccessful. First-order isothermal rate constants were determined and evaluated in Arrhenius fashion to obtain activation parameters (Tables IV and V). They were obtained for UN and GN by following the loss of the nitrate and the associated cations by separate chromatographic analyses. Isothermal decomposition rates for AN have been previously reported by this group; they were determined by both nitrate loss¹⁶ and by product (N₂O) formation.¹⁷

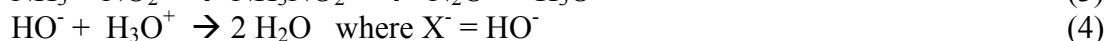
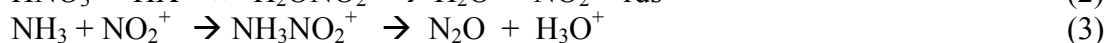
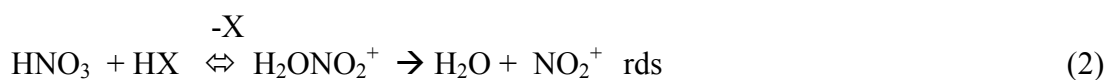
Activation parameters, reported for AN, are numerous, but few are reported for urea nitrate or guanidine nitrate. Borham has reported activation energies for urea nitrate, but these are not useful without the pre-exponential factors.^{18,19} Arrhenius plots (Figure 3) of the isothermal rate constants for the three salts suggest that, in contrast to the wide differences in DSC exotherms, the rates of decomposition of all these salts are similar.

Mechanisms of Decomposition

Thermal decomposition of AN has been extensively studied, and its decomposition products are gaseous.¹⁷ UN^{9,18,22,23} and GN^{20,21} also produce primarily gases, but condensed-phase residue has also been reported (Table VI). For AN two mechanisms of decomposition have been proposed.¹⁷ The dominance of one route over the other depends on temperature, but the initial step is dissociation of ammonium nitrate to ammonia and nitric acid:



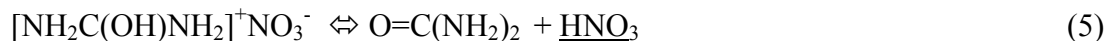
The next step is decomposition of nitric acid to form NO₂ (at high temperature) or NO₂⁺ (below 270°C). This was considered to be the rate-determining step (rds) by the observations that AN decomposition was slowed in the presence of base and accelerated in the presence of acid. Subsequent attack of NO₂ or NO₂⁺ species on ammonia leads to nitrous oxide and water.



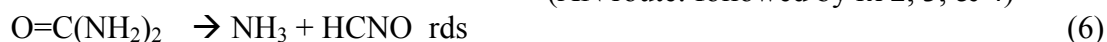
Scheme 1: AN Dissociation

If the decompositions of guanidine and urea nitrates are analogous to that of AN, then their decomposition rates should be sensitive to the acidity of the reaction mixture. To consider this possibility, samples of GN and UN were heated at 250°C with water, ammonium hydroxide, as

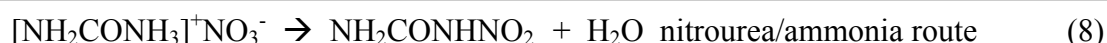
well as sulfuric and hydrochloric acid solutions. Like AN, the decomposition of both nitrate salts was dramatically accelerated in acidic media; and like AN, the UN decomposition rate was slowed by water and by ammonium hydroxide, but the decomposition of GN was accelerated (Table VII). Since the reactivity of the urea nitrate melt parallels AN, a similar decomposition scheme is postulated. The decomposition of UN via dissociation (reactions 5 to 7) would produce urea and nitric acid and result in the formation of the elements of AN. Another possible route is the dehydration of UN to nitrourea (8) with subsequent decomposition into gaseous products (8 to 9).^{23,25,26}



(AN route: followed by rx 2, 3, & 4)

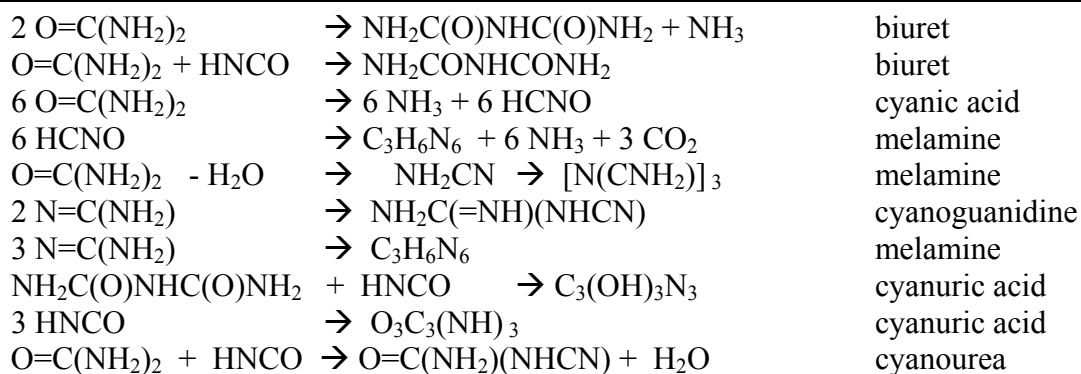


Scheme 2: UN Dissociation



Scheme 3: UN Dehydration

Brill *et. al.* reported the heat of reaction for the UN dissociation scheme to be +29 kcal/mol, and that of the dehydration scheme is -8.8 kcal/mol.²³ Thus, the route proceeding through AN (5 to 7) only becomes exothermic when completely decomposed through reactions 2, 3, and 4 achieving the final gaseous products. It is this route which would be accelerated by the presence of acid. Underlined species have been observed in the decomposition gases (Table VI and reference 23). Nitrourea was not observed among the condensed-phase urea nitrate decomposition products (Table VI), but other species have been reported as products of urea thermolysis.¹¹ We confirmed their presence in the UN thermolysis mixture by comparison of chromatographic retention times with authentic samples: cyanuric acid, biuret, urea, and melamine (Table VI). Possible routes to them are shown in Scheme 4.

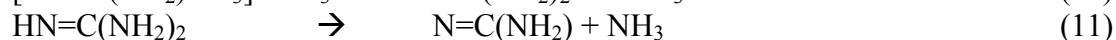
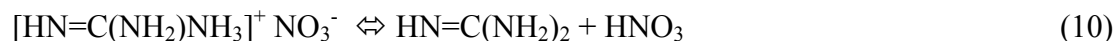


Scheme 4: UN Decomposition Products form Observed Condensed-Phase Species

For both GN and UN, the decomposition gases CO₂ and N₂O were observed by GC (Table VI). Between the peaks of those gases, there was another peak also with m/e 44; we interpret this to be H₂NCO⁺. Although ammonia gas could be smelled when the thermolyzed samples of GN and UN were opened, it was not observed by GC.

For guanidine nitrate several possible decomposition routes can be envisioned. A decomposition pathway for GN proceeding via dissociation to nitric acid (10) would be analogous to that proposed for AN and UN. This is essentially the reverse reaction for GN synthesis.²⁴ Reaction (10) and subsequent decomposition of nitric acid and reaction with ammonia (reactions 2, 3, and 4) would explain the observed acceleration by the presence of acid (Table VII). Cyanamide fate is shown in Scheme 4, but reaction (12) is also possible.

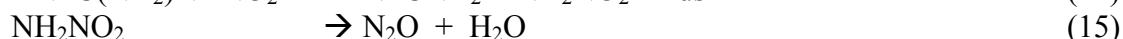
Unlike AN and UN, GN decomposition is accelerated by basic species as well as acids. Reaction pathways involving H^+ loss, such as reaction 12, would explain such sensitivity.



Scheme 5: GN Dissociation



Nitroguanidine may also be formed by the dehydration of GN (13). Its decomposition also produces ammeline and melamine.²⁷ Subsequent reaction would give cyanamide and nitramine which rapidly undergo further decomposition (14, 15, 12 and Scheme 4).

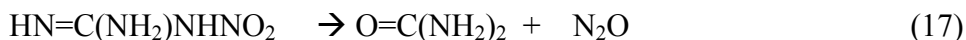


Scheme 6: GN Dehydration

Alternatively, ammonium nitrate could be an intermediate in GN decomposition (16). AN would decompose to nitrous oxide and water via steps (2), (3), and (4); and cyanamide would dimerize or trimerize (Scheme 4).



All three routes of GN decomposition are reasonable. Ruled out was a decomposition route via urea (17), because neither urea nor its decomposition products, cyanuric acid and biuret, were observed (Table VI).



In an effort to probe the decomposition mechanisms, several of the compounds were thermally decomposed in the presence of simple arenes. It is well-known that NO_2^+ is the active nitrating agent in the formation of nitroaromatics. Under acid conditions, rapid ionization of a nitrate to NO_2^+ affects nitration of aromatics. Furthermore, nitro-organic compounds have also been used as “dry acids” under acidic conditions.²⁸⁻³⁰ If the nitro-organic or organic nitrate compounds decompose via a NO_2^+ -generating route, then they should also nitrate susceptible aromatics under decomposition, but not necessarily acid, conditions. A trapping experiment was devised to test for the production of NO_2^+ *in situ*, using 1) urea nitrate and nitrourea and 2) guanidine nitrate and nitroguanidine. Under thermal decomposition conditions, where no additional acid was present, the nitrate salts reacted in the presence of arenes to yield the nitroarene. However, the nitro derivatives of the same nitrate compounds did not nitrate (Table VIII). As a comparison,

ammonium nitrate was tested for its effectiveness. Its low solubility in the arene solvents, coupled with its high decomposition temperature reduced its overall reactivity under our experimental conditions. Nevertheless, its decomposition through release of NO_2^+ was confirmed; nitroaromatic products were detected. The results confirm the importance of Schemes 2 and 5 in the decomposition of urea nitrate and guanidine nitrate, respectively.

Conclusions

Ammonium nitrate (AN), guanidine nitrate (GN) and urea nitrate (UN) decompose in the 200 to 300°C temperature range with rate constants within an order of magnitude of each other. GN is notably slower, but the decomposition rates of UN and AN are comparable by isothermal analyses. This is surprising since the first DSC exotherm of UN decomposition (172°C) appears at substantially lower temperature than for the AN exotherm (327°C). One decomposition route common for all three salts is dissociation into nitric acid and the corresponding base. This is an endothermic step which substantially cools the nitrate salts. Subsequent reaction of the produced nitric acid provides the exothermicity to the overall decomposition and explains the reason acidic media speed the decompositions of these salts. Analysis of the decomposition mechanism showed that under thermal decomposition, the nitrate salts produce a species able to nitrate arenes (assumed to be NO_2^+) while their dehydrated derivatives (nitroguanidine and nitrourea) do not.

References

1. Jackson, M. D.; Venkatesh, S.; Scott, F., *Supplying Urea for the On-Road Vehicle Market*. 7th Diesel Engine Emissions Reduction (DEER) Workshop Fuels and Lubricants Section. 2001.
2. Almog, J.; Klein, A.; Tamiri, T.; Shloosh, Y.; Abramovich-Bar, S., "Field Diagnostic Test for the Improvised Explosive Urea Nitrate." *J. Forensic Sci.* **2005**, 50(3), 582-586.
3. Medard L., "Explosive Properties of Urea Nitrate, Nitrourea, and Guanidine Nitrate" *Memorial des Poudres* **1951**, 33 113 -123.
4. Encyclopedia of Explosives and Related Items Vol 10; Ed Kaye, S.M. U.S. Army Armament Research and Development Command; 1983; pp U 102-105.
5. Encyclopedia of Explosives and Related Items Vol 10; Ed Kaye, S.M. U.S. Army Armament Research and Development Command; 1960; pp A 321.
6. Urbanski, T. Chemistry and Technology of Explosives II; Pergamon, NY, 1965; 467-470.
7. Ulas, A.; Risha, G. A.; Kuo, K. K., "Ballistic Properties and Burning Behaviour of an Ammonium Perchlorate /Guanidine Nitrate/ Sodium Nitrate Airbag Solid Propellant." *Fuel* **2006**, 85, 1979-1986.
8. Kutty, T. R. N.; Murthy, A. R. N., "Physico-chemical Properties of Urea Nitrate: Part I- Preparation & Characterization." *Indian J. Technol.* **1972**, 10, 305-308.
9. Udapa, M. R., "Thermal Behaviour of Urea Nitrate." *Thermochim Acta.* **1982**, 55, 359-362.

10. Qiu, J.; Lee, H.; Zhou, C., "Analysis of Guanidine in High Salt and Protein Matrices by Cation- Exchange Chromatography and UV Detection." *J. Chrom. A.* **2005**, 263-267.
11. Koebel, M.; Elsener, M., "Determination of Urea and its Thermal Decomposition Products by High-performance Liquid Chromatography." *J. Chromatogr. A.* **1995**, 689, 164-169.
12. Whiting, L.F., Labean, M.S.; Eadie, S.S., "Evaluation of a Capillary Tube Sample Container for Differential Scanning Calorimetry," *Thermochem. Acta* **1988**, 136, 231-245.
13. ASTM E698-05 "Standard Test Method for Arrhenius Kinetics Constants for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method." from Annual ATSM Standards E 698-79, reapproved 1993 2005.
14. Zheng, W.; Dong, X.; Rogers, E.; Oxley, J.C.; Smith, J.L., "Improvements in the Determination of Decomposition Gases from 1,2,2,-Trinitroazetidine and 5-Nitro-2,3-dihydro-3H-1,2,4-triazol-3-one Using Capillary Gas Chromatography-Mass Spectrometry" *J. Chrom. Sci.* **1997**, 35, 478-482.
15. Almog, J.; Klein, A.; Sokol, A.; Sasson, Y.; Sonenfeld, D.; Tamiri, T., Urea nitrate and nitrourea: powerful and regioselective aromatic nitration agents. *Tetrahedron Letters* **2006**, 47, 8651-8652.
16. Oxley, J.C.; Smith, J.L.; Wang, W. "Compatibility of Ammonium Nitrate with Monomolecular Explosives, Part I" *J.Phys.Chem.* 1994, 98, 3893-3900.
Oxley, J.C.; Smith, J.L.; Wang, W. "Compatibility of Ammonium Nitrate with Monomolecular Explosives, Part II: Nitroarenes" *J.Phys.Chem.* 1994, 98, 3901-3907.
17. Brower, K.R.; Oxley, J.C.; Tewari, M.P. "Homolytic Decomposition of Ammonium Nitrate at High Temperature" *J. Phy. Chem.* 1989, 93, 4029-4033
18. Borham, B. M.; Olson, F. A., "Isothermal Decomposition of Urea Nitrate." *Thermochim Acta.* **1973**, 6, 353-360.
19. Borham, B.M.; Olson, F. A., "Measurement of Reaction Kinetics by a Pressure Rise Method." *J. Thermal Anal.* **1980**, 19, 3-9.
20. Shoppelrei, J. W.; Kieke, M. L.; Wang, X.; Klein, M. T.; Brill, T.B. Spectroscopy of Hydrothermal Reactions. 4. Kinetics of Urea and Guanidium Nitrate at 200-300°C in a Diamond Cell, Infrared Spectroscopy Flow Reactor. *J. Phys. Chem.* 1996. 100 (34), 14343-143451.
21. Udapa, M. R., "Thermal Decomposition of Guanidinium Nitrate" *Thermochim Acta.* **1982**, 53(3), 383-385.
22. Kutty, T. R. N.; Murthy, A. R. V. "Physio-chemical Properties of Urea Nitrate: Part II – Thermal Behaviour" *Indian J. Technol.* **1972**, 10, 309-312.

23. Hiyoshi, R. I.; Brill, T. B.; Kohno, Y.; Takahashi, O.; Saito, K. "Experimental and Computational Study of the Thermal Decomposition of Uronium Nitrate (Urea Nitrate)" 12th *Int. Detonation Symp.* **2002**, Aug 11-16, San Diego, CA.
24. Hill, W.H.; Swain, R.C.; Paden, J. H. "Production of Guanidine Nitrate" US Patent 2,252,400 awarded American Cyanamid Co.; Aug 12, 1941
25. Kohno, Y.; Takahashi, O.; Hiyoshi, R. I.; Nakamura, J.; Saito, K. Theoretical Study of the Initial decomposition Process of the Energetic Material Urea Nitrate. *J. Phys. Chem. A.* **2003**, 107(33), 6444-6450.
26. Tokmakov, I. V.; Alavi, S.; Thompson, D. L. *Urea and Urea Nitrate Decomposition Pathways: A Quantum Chemistry Study. J. Phys. Chem. A.* **2006**, 110, 2759-2770.
27. Volk, F. Determination of Gaseous and Solid Decomposition Products of Nitroguanidine *Propellants, Explosives, Pyrotechnics*, **2004**, 10 (5), 139-146.
28. Ramana, M. M. V.; Malik, S. S.; Parihar, J. A., Guanidinium nitrate: a novel reagent for aryl nitrations. *Tetrahedron Letters* **2004**, 45, 8681-8683.
29. Tsang, S. M.; Paul, A. P.; DiGiaino, M. P., The Nitration of Toluene with Alkyl Nitrates and Polyphosphoric Acid. *Journal of the American Chemical Society* **1964**, 29, 3387-3390.
30. Almog, J.; Klein, A.; Sokol, A.; Sasson, Y.; Sonenfeld, D.; Tamiri, T., Urea nitrate and nitrourea: powerful and regioselective aromatic nitration agents. *Tetrahedron Letters* **2006**, 47, 8651-8652.
31. <http://www.chem.wisc.edu/areas/reich/pkatable/index.htm> accessed Jan. 23, 2008
J Am Chem Soc. 1991, 113, 8398 and J Org Chem. 1991, 56, 4218.

List of Figures

Figure 1: Exemplary First-order Plot	10
Figure 2: Exemplary DSC Scans	10
Figure 3: Arrhenius Plot for nitrate in AN (◆), UN (▲), GN (■) Decomposition	10

List of Tables

Table I: Detonation Velocities of Nitrate Explosives	14
Table II: LC Conditions to Quantify & Identify GN & UN Decomposition Products	15
Table III: DSC Summary of Various Nitrate Salts (20°/min scan rate).....	16
Table IV: Isothermal Rate Constants for Nitrate Salts	174
Table V: Activation Parameters for Nitrate Salts	18
Table VI: Thermal Decomposition Products of AN, GN, UN	19
Table VII: Effect of Catalytic Amounts of Acid or Base	20
Table VIII: Attempted Use of Nitrates and Nitro Organics for Nitration at 250°C	18

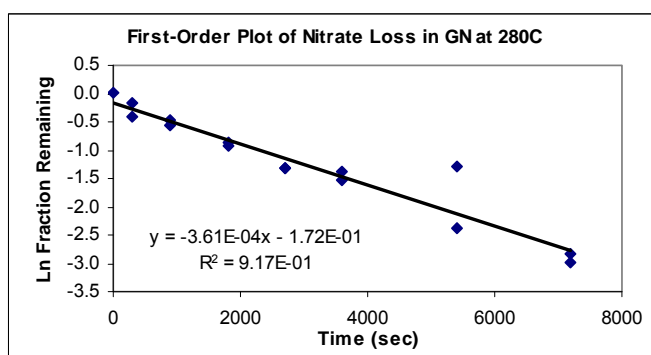
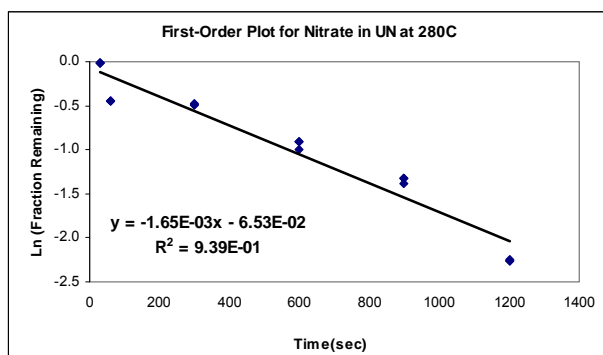
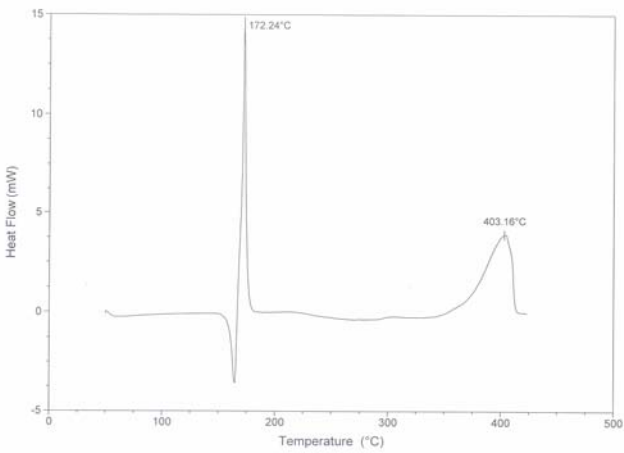


Fig. 1 First-Order Plot of UN & GN Decomposition at 280°C following Nitrate Loss

Sample: UN3 20C/min 50-450
Size: 0.3600 mg



Sample: GN2 20 082606
Size: 0.3360 mg
Method: Custom
Comment: GN2 20C/min 50 - 450C

DSC

File C:\Sweta\GN20C\GN2 20 082606.002
Operator: Sweta
Run Date: 26-Aug-2006 22:47
Instrument: DSC Q100 V3.5 Build 175

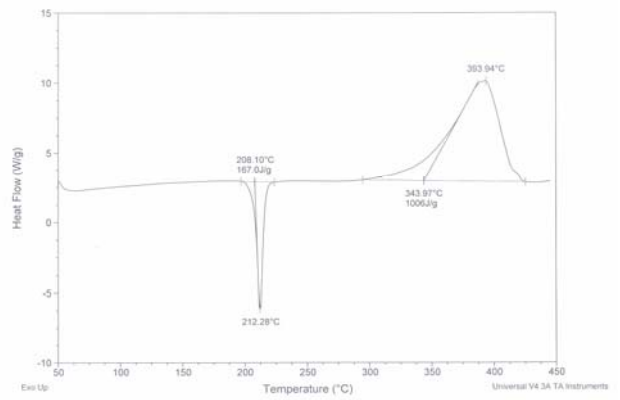


Fig. 2 DSC Scans at 20°C/min of UN (left) & GN (right) Decomposition

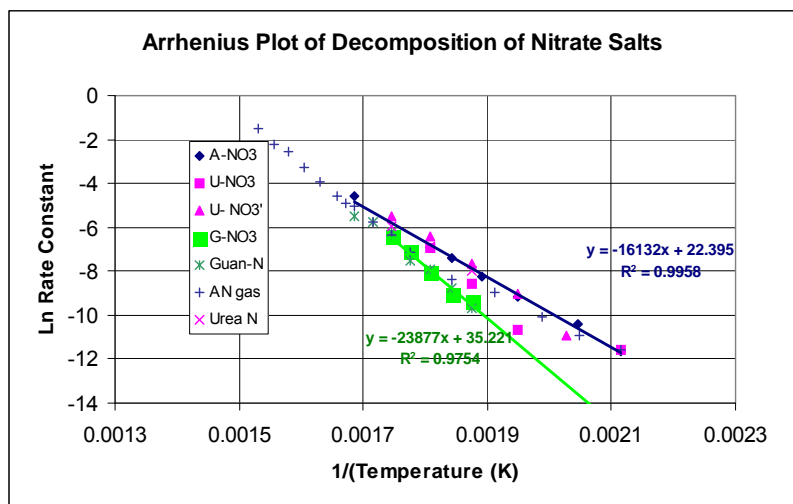


Fig. 3: Arrhenius Plots for nitrate in AN (◆), UN (▲), GN (■) Decomposition

Table I: Detonation Velocities of Nitrate Explosives

Nitrate	Density	Container/ mm diameter	Detonation velocity m/s	Reference
UN	0.85	paper tube/ 30	3400	4
UN	1.2	steel tube/ 30	4700	3
GN	1	steel tube/ 36	3700	4
AN	0.98	steel tube/ 80	2700	5

Table II: LC Conditions for Quantifying GN & UN and Identifying UN Decomposition Products

	Column	Column Dimension	Guard column	Guard Column Dimension	Eluent	Eluent (Conc)	Eluent (pH)	Flow Rate mL/min	Intensity (nm)
Guanidine Nitrate									
Guanidine	Dionex Ion Pac CS14 Cation	4X250mm	Dionex Ion Pac CG14	4X50mm	Methyl Sulfonic Acid	3mM	-	1	195
Nitrate	Waters IC-Pak Anion HC	4.6X150mm	Waters Guard-Pak Anion	Inserts	Phosphate Buffer	5mM	7	1.5	210
Urea Nitrate									
Urea	YMC Pak C18 Polymer	4.6X150mm	YMC Polymer C18	4.0X20mm (6 μ)	Perchloric acid	0.40%	1.3		200
Nitrate	Waters IC-Pak Anion HC	4.6X150mm	Waters Guard-Pak Anion	Inserts	Phosphate Buffer	5mM	7	1.5	200
Decomposition products	Waters IC-Pak Anion HC	4.6X150mm	Waters Guard-Pak Anion	Inserts	Phosphate Buffer	5mM	7	1.5	200

Table III: DSC Summary of Various Nitrate Salts (20°C/min scan rate)

	Endotherm			Exotherm			Exotherm		
	Onset (°C)	Peak (°C)	Heat (J/g)	Onset (°C)	Peak (°C)	Heat (J/g)	Onset (°C)	Peak (°C)	Heat (J/g)
Potassium nitrate	137	145	43		none to 450°C				
Sodium nitrate	307	311	31		none to 450°C				
Urea nitrate	161	166	90	169	172	564	378	409	634
Ammonium nitrate	162	166	34	300	327	316			
Guanidinium nitrate	213	217	186	354	401	1979			

Table IV: Isothermal Rate Constants for Nitrate Salts

				re-run			
°C	AN N ₂ O ¹⁷	AN NO ₃ ⁻¹⁶	UN NO ₃ ⁻	UN NO ₃ ⁻	GN NO ₃ ⁻	UN urea	GN guanidine
200	9.26E-06	8.57E-06	9.07E-06				
215	1.80E-05						
216		3.00E-05					
220				1.84E-05			
230	4.21E-05						
240		1.06E-04	2.32E-05	1.20E-04			
250	1.30E-04						
256		2.60E-04					
260		1.95E-04	1.88E-04	4.71E-04	8.67E-05	3.32E-04	6.19E-05
270	2.37E-04	6.25E-04			1.20E-04		1.60E-04
280		1.00E-03	9.81E-04	1.66E-03	3.16E-04	1.03E-03	3.74E-04
290	7.79E-04				8.56E-04		5.55E-04
300	1.75E-03		1.72E-03	4.08E-03	1.63E-03	2.64E-03	2.02E-03
310	3.13E-03						3.17E-03
320	6.69E-03	1.02E-02					4.08E-03
325	7.50E-03						
330	1.00E-02						
340	1.94E-02						
350	3.73E-02						
360	8.00E-02						
370	1.05E-01						
380	2.22E-01						

Table V: Activation Parameters for Nitrate Salts

Nitrate Loss						
	Ea kJ/mol	Ea kcal/mol	A	R ²	Calculated Rate 280°C	Temperatures °C
UN	158	37.8	1.39E+12	0.996	1.65E-03	220,240, 260, 280,300
AN	134	32.1	5.32E+09	0.996	1.17E-03	320,280,270,256,240,216,200
GN	199	47.5	1.94E+15	0.975	3.23E-04	300,290, 280,270, 260
Cation Loss (AN - N ₂ O formation)						
UN	131	31.4	2.66E+09	0.9	1.02E-03	300, 280,260
AN	147	35.1	6.63E+10	0.970	8.63E-04	every 10° 380-290 & 270,260,250,230,200
GN	190.5	45.5	3.20E+14	0.980	3.24E-04	320,310,300,290, 280,270, 260

Table VI: Thermal Decomposition Products of AN, GN, UN

	Compound	Decomposition gases	Residue	References
AN	NH_4NO_3	N_2O , N_2 , H_2O		16
GN	$\text{HN}=\text{C}(\text{NH}_2)(\text{NH}_3)^+$ NO_3^-	N_2O , N_2 , H_2O , NH_3 , CO_2	cyanamide, cyanoguanidine, melamine, cyanuric acid*	19, 20 *this work
UN	$\text{HO}=\text{C}(\text{NH}_2)(\text{NH}_2)^+$ NO_3^-	N_2O , HCNO , CO_2 , H_2O , NH_3	urea, AN, biuret, cyanuric acid, melamine	9, 17, 21, 22

Table VII: Effect of Catalytic Amounts of Acid or Base

	fraction nitrate remaining at 250°C		
	GN 2 hr	UN 10 min	AN 10 min
pKa free organic (DMSO) ³¹	28.5	26.9	10.5
alone	0.81	0.53	0.97 ¹⁷
+ H ₂ O	0.60	0.71	slows
+ NH ₄ OH	0.38	1.04	slows
+ H ₂ SO ₄	0	0	increases
+ HCl	0.31	0	increases
25 uL additive; acid is concentrated; values are average of 3 or 4 tests			

Table VIII: Attempted Use of Nitrates and Nitro Organics for Nitration at 250°C

Arene Substrate	Nitration Agent	Result	Products
Toluene	Urea Nitrate	Nitration	2,3, & 4-Nitrotoluene
	Nitrourea	No Rxn	
	Guanidine Nitrate	Nitration	2,3, & 4-Nitrotoluene
	Nitroguanidine	No Rxn	
	Ammonium Nitrate	Nitration	Trace nitrotoluenes
Nitro Benzene	Urea Nitrate	Nitration	1,3-Dinitrobenzene
	Nitrourea	No Rxn	
	Guanidine Nitrate	Nitration	1,3-Dinitrobenzene
	Nitroguanidine	No Rxn	
	Ammonium Nitrate	Nitration	Trace dinitrobenzene