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14. ABSTRACT The experimental work conducted under this program was designed to provide new insight into condensed-phase reactions leading to ignition of ionic liquids. The objectives of the work were: (1) to identify the initiation and secondary reactions in the condensed phase that lead to ignition and combustion, (2) to understand the effects of the structure of the cation on these reactions, and (3) to determine the effects of the type of ignition stimulus used. Two primary experimental approaches were applied: laser heating coupled with tandem mass spectrometry and rapid thermolysis coupled with FTIR and time-of-flight mass spectrometry. The compounds studied included: 1-Ethyl-3-Methyl-Imidazolium Nitrate, 4-Amino-1,2,4-Triazolium Nitrate, 1-Methyl, 4-Amino-1,2,4-Triazolium Nitrate, 2-Amino-4,5-Dimethyl Tetrazolium Nitrate and 1-Amino-4,5-Dimethyl Tetrazolium Nitrate.					
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1 EXPERIMENTAL METHODS

1.1 Laser-driven Decomposition

Testing of materials for which gram-quantities are available begins with a liquid or solid sample, typically 100 to 250 mg, placed in small quartz vial and seated in a sample holder that can be positioned precisely relative to the quartz microprobe or the molecular beam skimmer. The set-up for such a test using a quartz microprobe for sampling is illustrated in Figure 1. The CO₂ laser flux level is set by adjusting the position of a lens relative to the sample, and the flux is measured to ensure that the desired level has been achieved. The desired temporal flux profile is programmed using a PC interface; any flux profile can be programmed. Once the flux is verified and programmed, the test chamber is sealed and flushed with the desired ambient gas. The testing is triggered from a PC and data is collected using Extrel's Merlin data acquisition system. Data reduction is performed using calibration based on actual standards whenever possible, but approximate calibrations are estimated when necessary using a semi-empirical model.¹



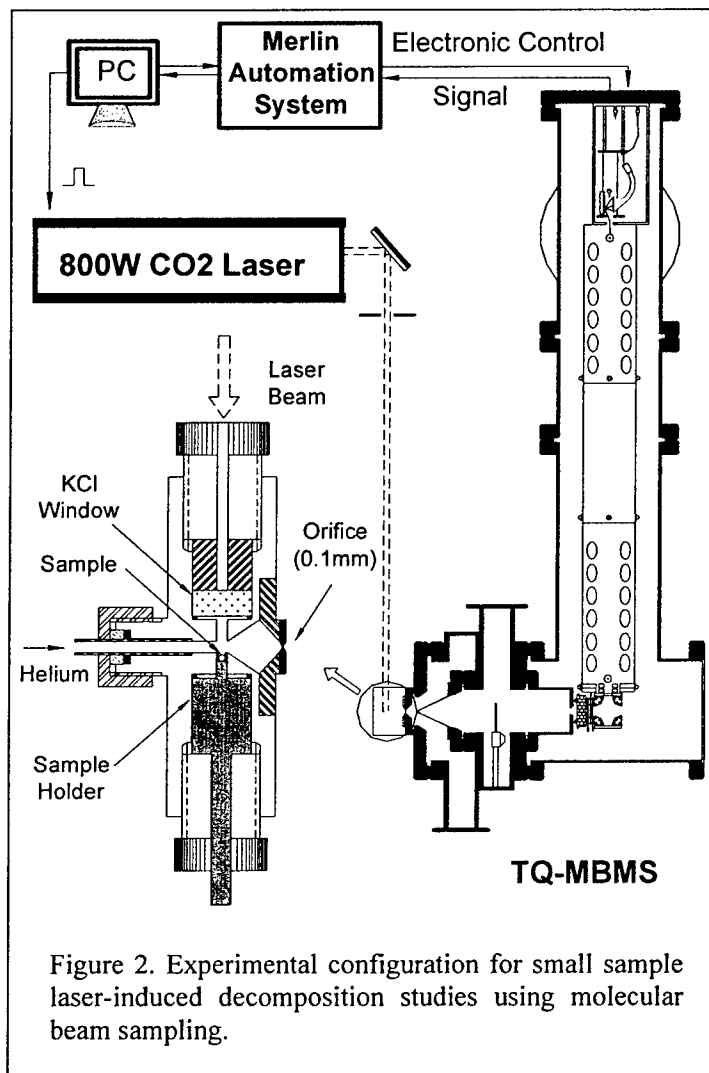
Figure 1. Experimental set-up for mass spectrometer studies showing a burning sample.

Due to the limited quantities of materials available for many of the ionic liquid samples, a new experimental approach was developed for testing milligram level samples. The overall set-up for these experiments is presented in Figure 2. A small sample, on the order of 1 milligram, is placed in the sample pedestal near the molecular beam sampling orifice. The IR-laser enters the test volume through a KCl window and impinges normally on the sample. Just prior to the firing of the laser, a slow flow of helium is started to carry the gas-phase products to the sampling orifice.

To identify species, the capabilities of the TQMS are utilized. Initial experiments are performed to identify the parent ions present in the system. Low electron energies (~22 eV) are used to reduce fragmentation of the parent ions. Once the parents have been identified, additional experiments are performed with MS/MS to determine the fragmentation patterns of the parent ion and to use those patterns to postulate its structure. MS/MS experiments are often done at two different collision energies to assist in the identification of the parent. Given that the test materials contain ions, some molecular beam sampling experiments are always conducted without electron impact to determine if any ions are reaching the gas-

phase. To date, none of these tests have identified ions in the gas-phase, most likely because of the relatively high pressures at which the tests are conducted.

Additional details on the experimental methods used in laser-driven decomposition studies are available in references 2 and 3.



1.2 Confined Rapid Thermolysis

In the confined rapid thermolysis (CRT)/FTIR/ToFMS studies, the thermal decomposition is limited to a volume confined between two heated, parallel surfaces. By using a small sample size compared to the volume, it is possible to study liquids that may otherwise largely boil off rather than decompose. The setup is composed of a constant pressure chamber, a Bruker IFS 66/S FTIR spectrometer and a commercially available ToF mass spectrometer. A three-dimensional view of the chamber, including a cut

that exposes the sample holder, is shown in Figure 3. The sample holder is designed to be lifted by the bottom heater to enclose the sample between the two heaters. Two ports are provided on the chamber, one serves as an inlet to the purge gas and the other exhausts decomposition products and the purge gas stream. The constant pressure chamber, resting on a rigid frame, has a height of 27.5 cm and an inner diameter of 5 cm approximately. The CRT/FTIR technique has been described in detail in a previous work.⁴

The rapid thermolysis is achieved by using two heaters: a stationary top heater and a mobile bottom heater. To achieve rapid thermolysis, defined as an event that occurs within 5 seconds, temperatures of above 400°C

are used. The gases evolved during the thermolysis are detected, identified and quantified using FTIR transmission spectroscopy. The spectra are acquired with a spectral resolution of 2 cm⁻¹ and a temporal resolution of 50 ms. A non-linear, least squares method is utilized to extract the species concentrations of the evolved gases by comparison with theoretical transmittance⁵. After completion of the iterations, the relative concentrations of various species, such as H₂O, N₂O, NO₂, NO, CO₂, and HNO₃ are obtained for each spectrum.

A low-pressure chamber with identical heater configurations is utilized for acquiring the ToF mass information at a high temporal resolution. The ToF MS system (Model D-677 from R. M. Jordan) is equipped with a 1m flight tube and a 44 mm microchannel plate (MCP) detector. Here, the recharging of the MCP detector limits the temporal resolution to about 1 ms. Molecular beam sampling from atmospheric pressure gases is performed using a 100 μm orifice plate attached to the first stage, a 1mm diameter Ni skimmer (manufactured in-house by electroplating) attached to the second stage and a vertically translatable 0.5×12mm² slit attached to the entrance of the third stage. A schematic is shown in Figure 4. Electron impact ionization is set at 70eV, resulting fragmentation of molecules, but allowing comparison with mass spectral and related data bases⁶. Time-to-mass scaling is determined using the expressions $m=a(t-t_0)^2$, where the two constants for each mass spectrum are obtained from known positions of helium and argon.

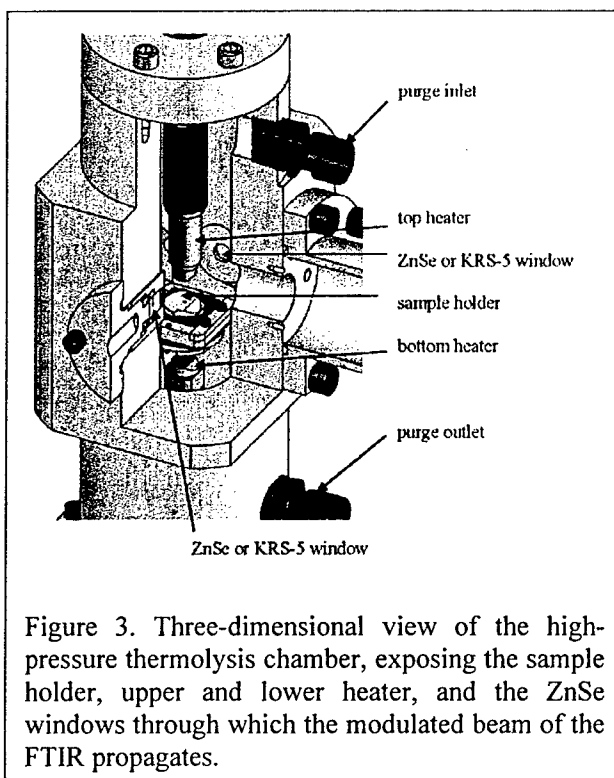
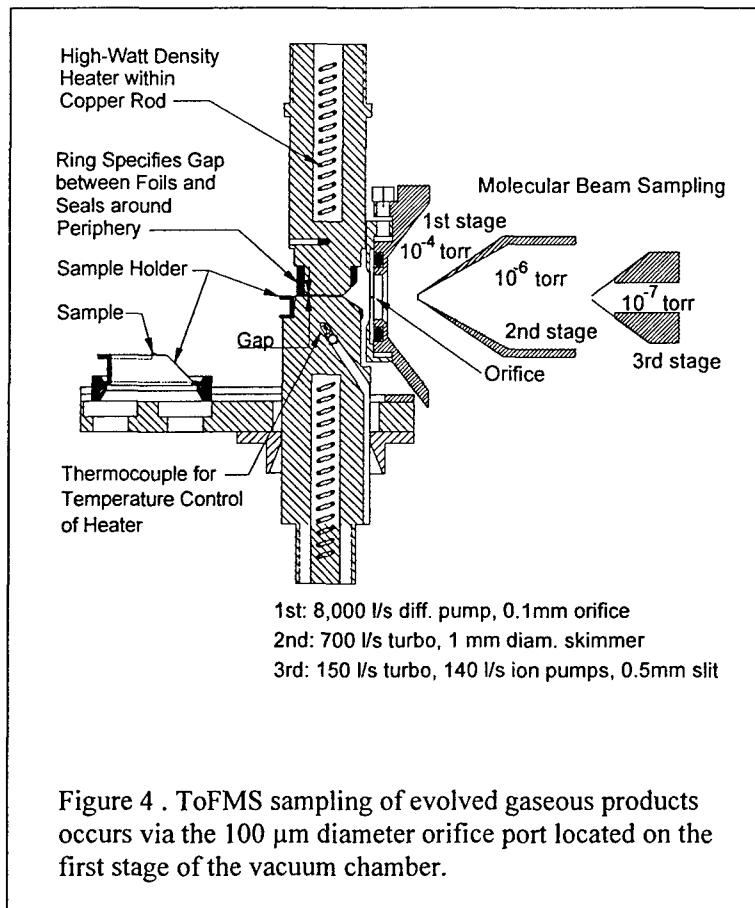
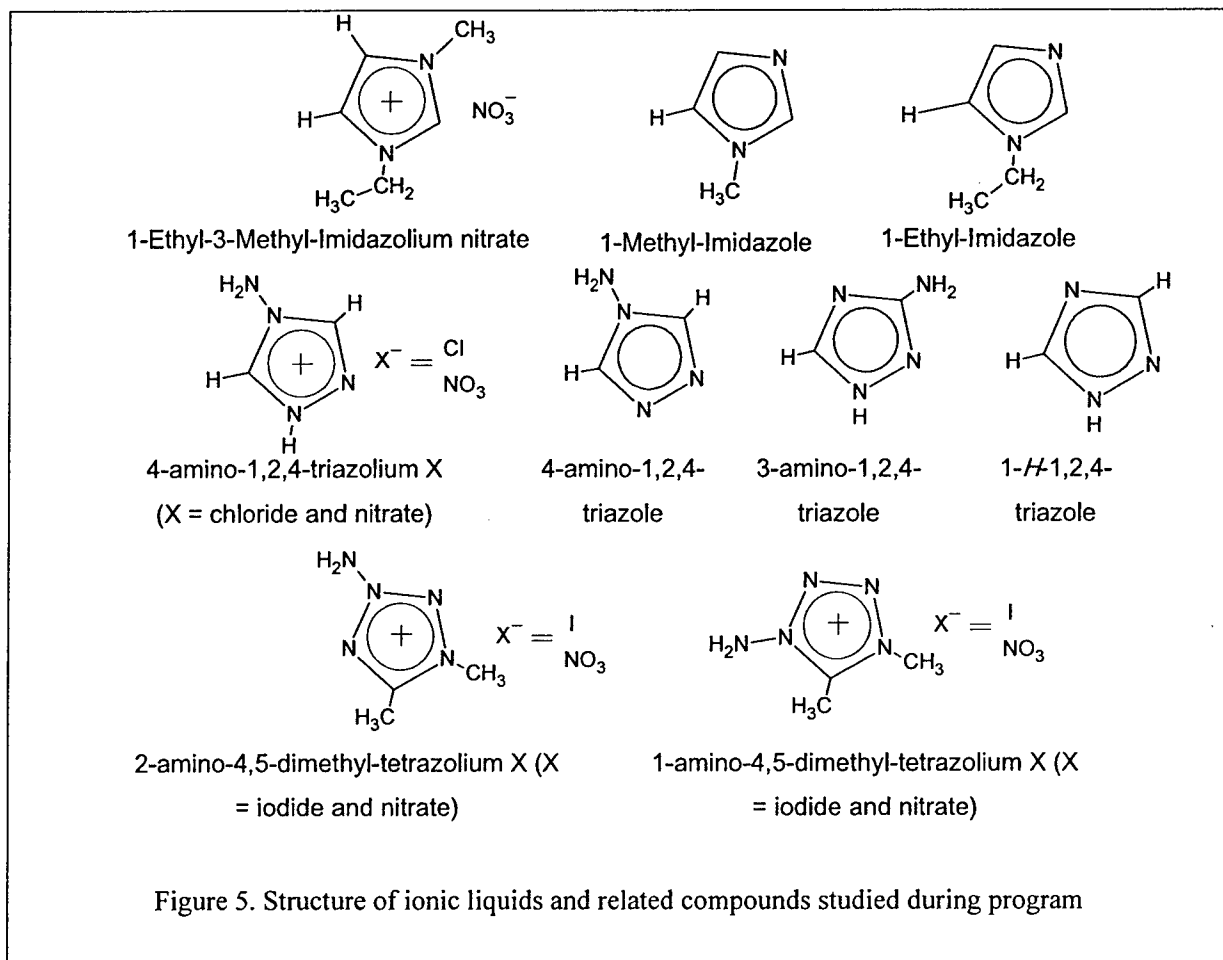


Figure 3. Three-dimensional view of the high-pressure thermolysis chamber, exposing the sample holder, upper and lower heater, and the ZnSe windows through which the modulated beam of the FTIR propagates.



2 SUMMARY OF RESULTS FROM CURRENT PROGRAM

The compounds studied during the program included: 1-Ethyl-3-Methyl-Imidazolium Nitrate, 4-Amino-1,2,4-Triazolium Nitrate, 1-Methyl, 4-Amino-1,2,4-Triazolium Nitrate, 2-Amino-4,5-Dimethyl Tetrazolium Nitrate and 1-Amino-4,5-Dimethyl Tetrazolium Nitrate. Structures of these compounds and related salts that were studied are presented in Figure 5.



2.1 1-ethyl-3-methyl imidazolium nitrate

The work began with a study of 1-ethyl-3-methyl imidazolium nitrate (EmimNO_3) based on discussions with the Ionic Liquids Group at Edwards. Several compounds with simpler anions were studied to isolate the effects of the nitrate group; these compounds included the bromide and chloride salts. In addition, the decomposition of key intermediates was studied including methyl-imidazole and ethyl-imidazole. More details on the EmimNO_3 results can be found in References 7 and 8.

Figure 6 presents a typical FTIR spectrum obtained during the confined rapid thermolysis of EmimNO₃. The compounds corresponding to the major bands in the spectrum included N₂O, CO, CO₂, and water. The spectrum shows no indication of the presence of nitric acid, so proton transfer is apparently not a major initiation pathway. The methanol present in the spectrum is probably formed from methoxy. Figure 7 presents a mass spectrum from the confined rapid thermolysis of EmimNO₃. It shows the presence of ethyl and methyl imidazole as well as a peak at $m/z=126$ corresponding to ethyl, methoxy imidazole. Results from the laser-driven decomposition of EmimNO₃ show similar species in the mass spectrum, except for the $m/z=126$ product.

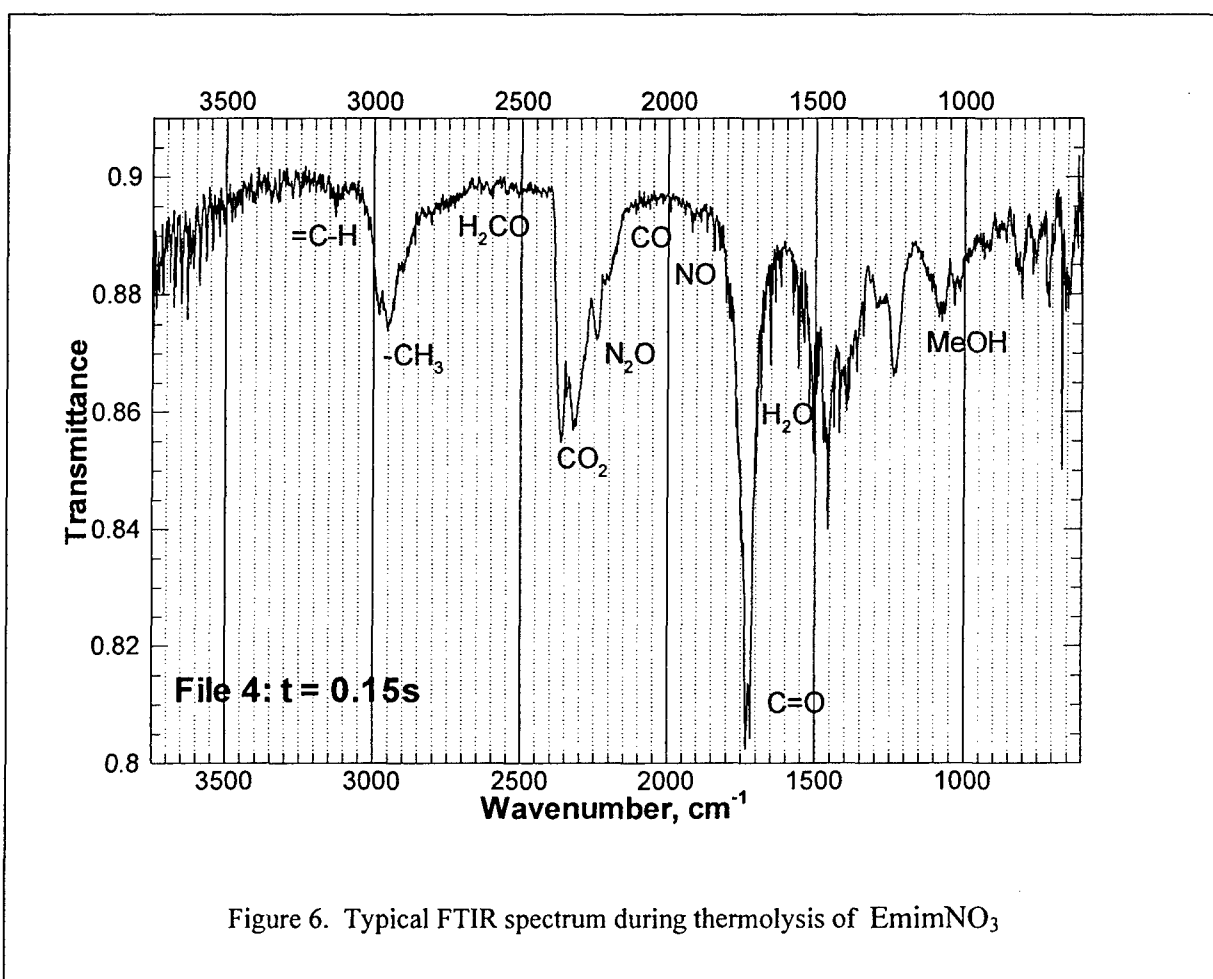
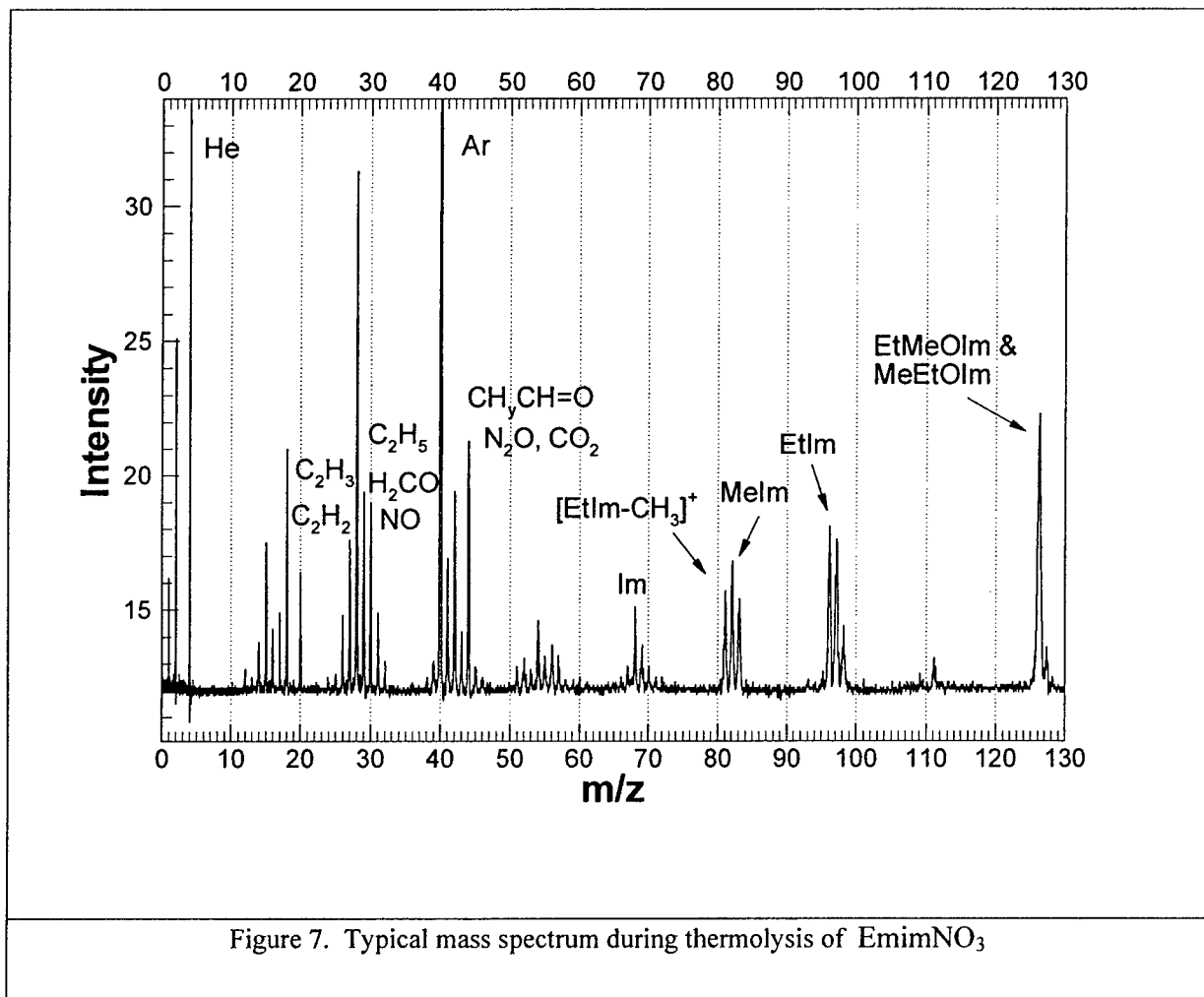


Figure 6. Typical FTIR spectrum during thermolysis of EmimNO₃

The results from the two sets of experiments indicate that proton transfer is not the primary initiation reaction for EmimNO₃. The presence of methyl imidazole and ethyl imidazole in the products indicates that transfer of an alkyl group to form alkyl nitrate is the major initiation pathway. Methyl nitrate will decompose to form methoxy, which most likely accounts for the methanol found in the FTIR and mass

spectra. Thus it appears that methyl transfer is the more important path under the conditions of these studies.



2.2 4-Amino-1,2,4-Triazolium Nitrate

4-Amino-1,2,4-Triazolium Nitrate (ATANO₃) was available in gram quantities which allowed studies of its ignition and combustion behavior. In air at atmospheric pressure, ATANO₃ starts to melt and decompose at a laser heat flux about 35 W/cm². Ignition is not achieved until the heat flux is increased to 150 W/cm² and occurs after a ~ 4 second delay during which significant “smoking” is observed. In an inert environment, e.g. helium, ignition occurs at a higher heat flux around 200 W/cm². Figure 8 presents a

few images showing the “smoke” and flame at a heat flux of 200 W/cm² in one atm air. Prior to a luminous flame (5th image from left), the solid sample (1st image) melts (2nd image) and vaporizes (3rd and 4th images) into gaseous

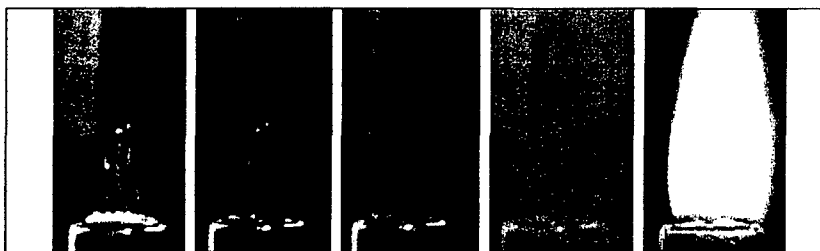
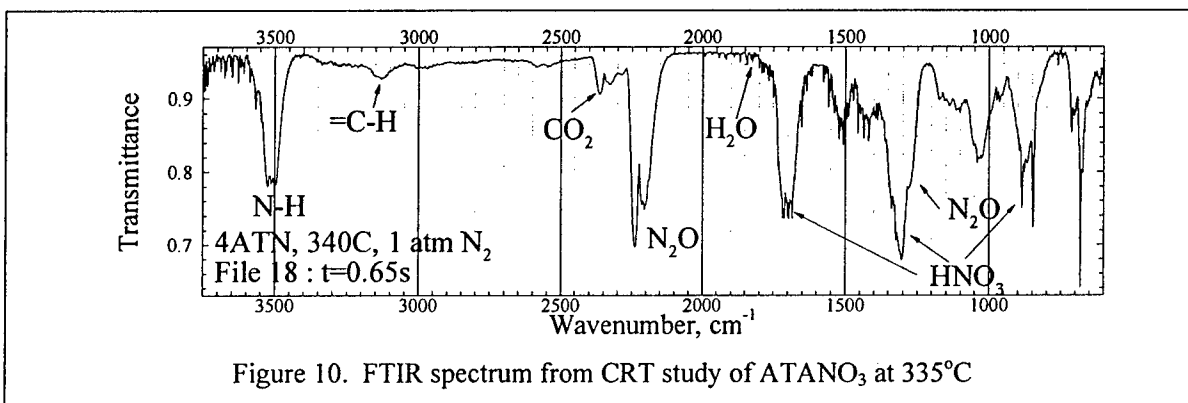
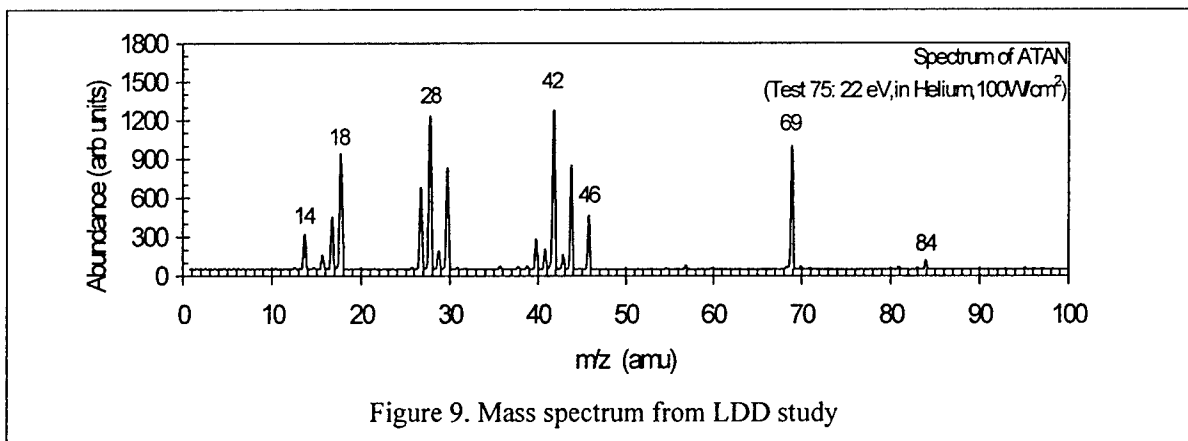


Figure 8. Images from combustion of ATANO₃ in 1 atm of air with an IR laser heat flux of 200 W/cm²

species. Bubbles were observed to develop during melting. The onset of ignition is about 3.2 seconds after triggering of the laser.

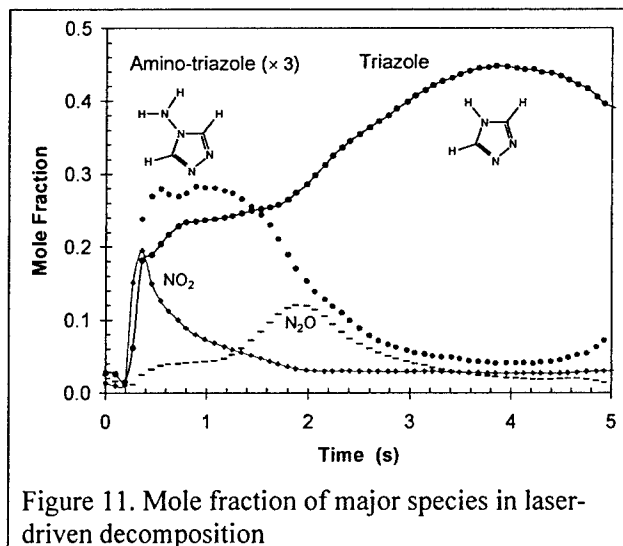
Several tests were run to obtain the spatial species profile through the smoking region starting from the sample surface up to 6 mm above the sample surface. The profiles revealed consistency in species detected across this region; an indication that early decomposition occurs in the condensed phase. Dessiaterik et al.⁹, who used IR lasers to ablate imidazolium salts, suggested decomposition would occur in the gas phase, since the laser heating usually gives such high heating rates that the vaporization rate is higher than decomposition rate. However, Dessiaterik et al. conducted their experiments under vacuum conditions that would have increased the probability that the reaction would have occurred in the gas-phase, whereas the present experiments were conducted at atmospheric pressure.

A representative mass spectrum from the laser-driven decomposition (LDD) experiments with ATANO₃ is presented in Figure 9. The peaks at 84 and 69 m/z correspond to amino-triazole and triazole, products formed respectively by the transfer of a proton and the amino group from the cation. Transfer of the proton should produce nitric acid, 63 m/z, which is not present in the mass spectrum; the ToFMS measurements during Confined Rapid Thermolysis experiments do not show it either. However, the FTIR shows large amounts to nitric acid as illustrated in Figure 10. Measurements in the triple quadrupole mass spectrometer (TQMS) with vaporizing nitric acid determined that it is fragmented by electron impact,



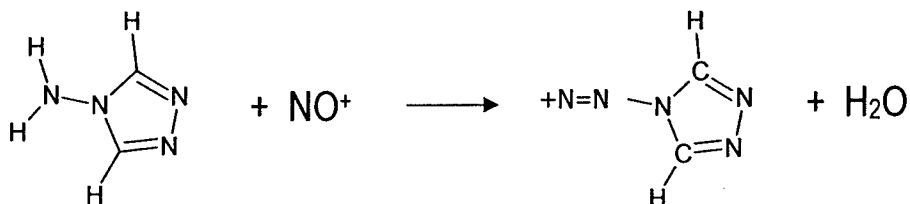
even at 22 eV, and forms products at 30 and 46 m/z, both of which are present in the mass spectrum. Thus it appears that nitric acid is formed in both the LDD and the CRT experiments. MS/MS analysis of the species at 30 m/z indicates that it contains both NO and HNNH. Other species present include nitrogen (28), HCN (27), and water. 42 m/z corresponds to HCNNH, which could have a linear or ring structure.

Plots of the temporal evolution of the mole fractions of selected species in the LDD and CRT experiments are presented in Figures 11 and 12; note that in Figure 11 the mole fraction of amino-triazole has been multiplied by a factor of 3 to enhance legibility of the data. Similar patterns for the nitric acid (indicated by the NO₂ in the LDD data) and N₂O are present in the two experiments and suggest a two stage reaction process. The FTIR results show that HCN follows the trend of the N₂O data; the LDD

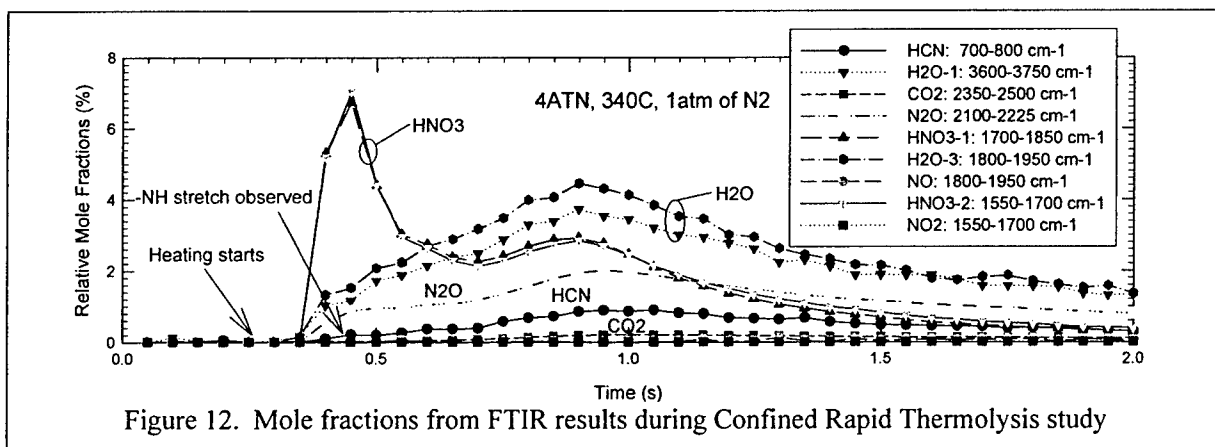


results show this as well. Thus the two stages appear to involve initiation during which amino-triazole, triazole, N_2 , and HNNH form, followed by reactions that form N_2O and HCN. The FTIR results also show that the ratio of water to N_2O is approximately 2:1. This ratio has been used in studies of ammonium nitrate decomposition as an indicator as to which pathway, ionic or non-ionic, was dominant during AN decomposition; for AN the ratio of 2:1 was an indication that the ionic route to N_2O was dominant.¹⁰

The presence of nitric acid in the CRT-FTIR results and the amino-triazole in the LDD-MS/MS results are consistent with proton transfer as an initiation reaction. However, the mole fraction of triazole is even larger than that of amino-triazole indicating that the formation of triazole is significant. Furthermore the appearance of triazole and amino-triazole is nearly simultaneous during the LDD experiments indicating the triazole may be forming directly via transfer of the amino group. Recent work at AFRL in which amino-triazolium salts were reacted with N_2O_4 in an attempt to synthesize nitrate salts showed that the amino group was removed during the nitration process.¹¹ There is also work in German literature showing that HONO will readily deaminate amino-triazole.¹² The reaction pathway for deamination involves the NO^+ ion, which could be formed once nitric acid is present:



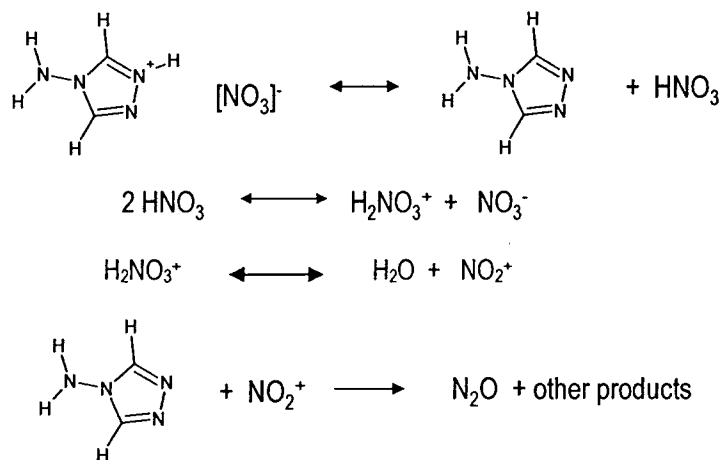
Deamination leads to the formation of N_2 , which would explain some of the early N_2 formation observed in the LDD experiments. Collectively, these results indicate that the amino group is susceptible to removal in the presence of a strong oxidizer; therefore, secondary reactions involving the amino-group may account for the triazole formation.



Reactions that open the five-membered ring can be hypothesized based on the experimental data. In the LDD experiments, N_2 is observed essentially simultaneously with the appearance of the triazole. In

experiments with 1,2,4-triazole, N_2 was observed supporting direct elimination of N_2 from the ring. For 4-amino-1,2,4-triazole, elimination of the amino-nitrogen bonded to N_4 could also lead to N_2 . In the LDD experiments, HNNH is observed for both 1-H-4-amino-1,2,4-triazolium nitrate and for 4-amino-1,2,4-triazole. HNNH is not observed in the decomposition of 1,2,4-triazole, which indicates that its formation is related to the presence of the amino group and that it does not involve reaction with the nitrate ion.

The reaction chemistry of ammonium nitrate provides the closest analogy that can be used to conjecture possible reactions for $ATANO_3$. AN reacts via two different routes: a low temperature ionic route and a high temperature radical driven route. Both routes are initiated by proton transfer to form nitric acid. The high temperature route is driven by OH formed by dissociation of nitric acid to NO_2 and OH whereas the low temperature route does not involve NO_2 , but rather NO_2^+ . The FTIR results in the CRT experiments show no evidence of NO_2 which indicates that $ATANO_3$ is not reacting via a radical driven chain. This is additional evidence beyond the ratio of water to N_2O that ionic reactions may be dominant. Based on analogies to the ionic AN chemistry, the reactions leading to N_2O formation for $ATANO_3$ would be:



2.3 1-Methyl, 4-Amino-1,2,4-Triazolium Nitrate

1-Methyl, 4-Amino-1,2,4-Triazolium Nitrate (MeATAN) was also provided by the Ionic Liquids Group at Edwards. Its structure is the same as 1-H, 4-Amino-1,2,4-Triazolium Nitrate ($ATANO_3$) except that the proton in the 1-position is replaced with a methyl group, which is expected to reduce the importance of proton transfer as an initiation reaction. Figure 13 presents a typical FTIR spectrum for MeATAN during confined rapid thermolysis. The products observed are similar to those for $ATANO_3$; however, the nitric acid bands are less intense for MeATAN. Thus proton transfer appears to be occurring even though the most readily transferred proton in the 1-position of $ATANO_3$ is not present in MeATAN.

Figure 14 presents a typical mass spectrum for the early times of a laser-driven decomposition test of MeATAN. The high molecular weight products, methyl-amino triazole, amino-triazole, and methyl triazole, indicate the parallel initiation pathways are present. Methyltriazole is by far the largest peak; ToF mass spectra taken during confined rapid thermolysis show only the methyltriazole peak.

The methyl-amino triazole would be formed by proton transfer to the anion to produce the nitric acid observed in the FTIR spectra. Once nitric acid is formed, secondary reactions, such as the deamination reactions involving NO^+ , could lead to removal of the amino-group to form methyltriazole. The presence of the aminotriazole in the laser-driven decomposition experiments suggests that the methyl is also reacting. It is not clear at this time what reactions are removing the methyl group.

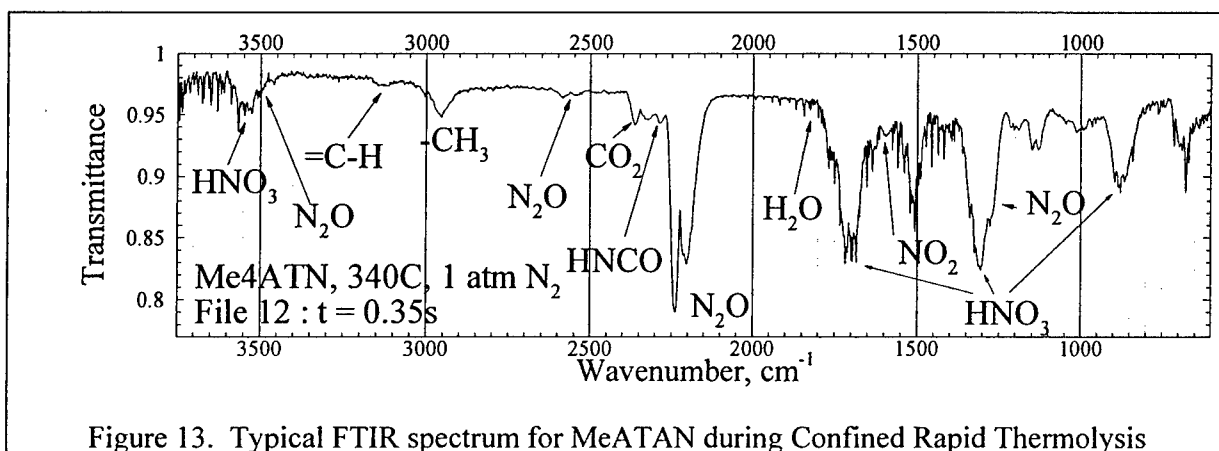


Figure 13. Typical FTIR spectrum for MeATAN during Confined Rapid Thermolysis

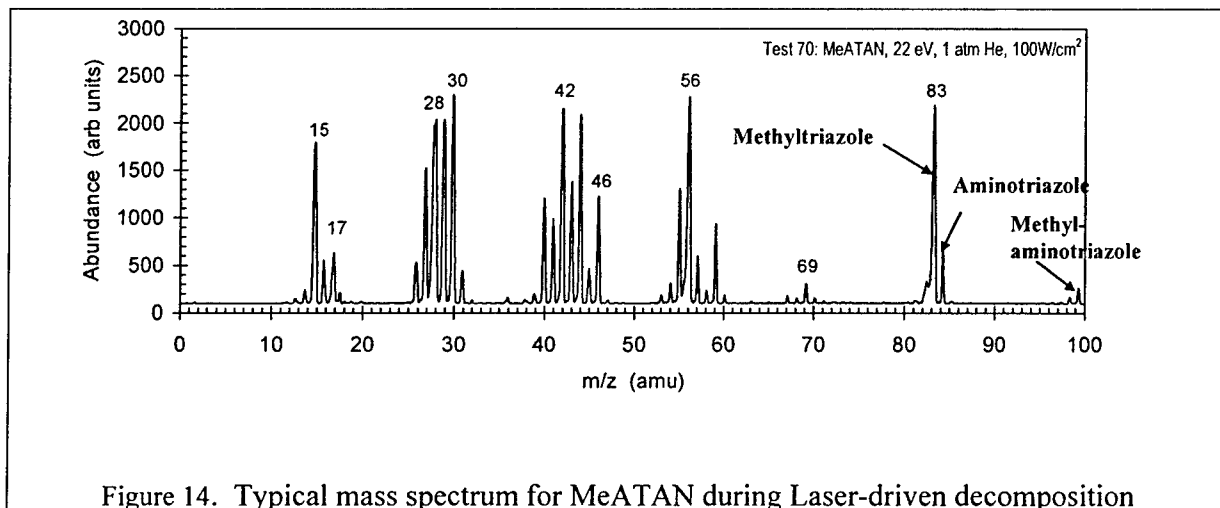
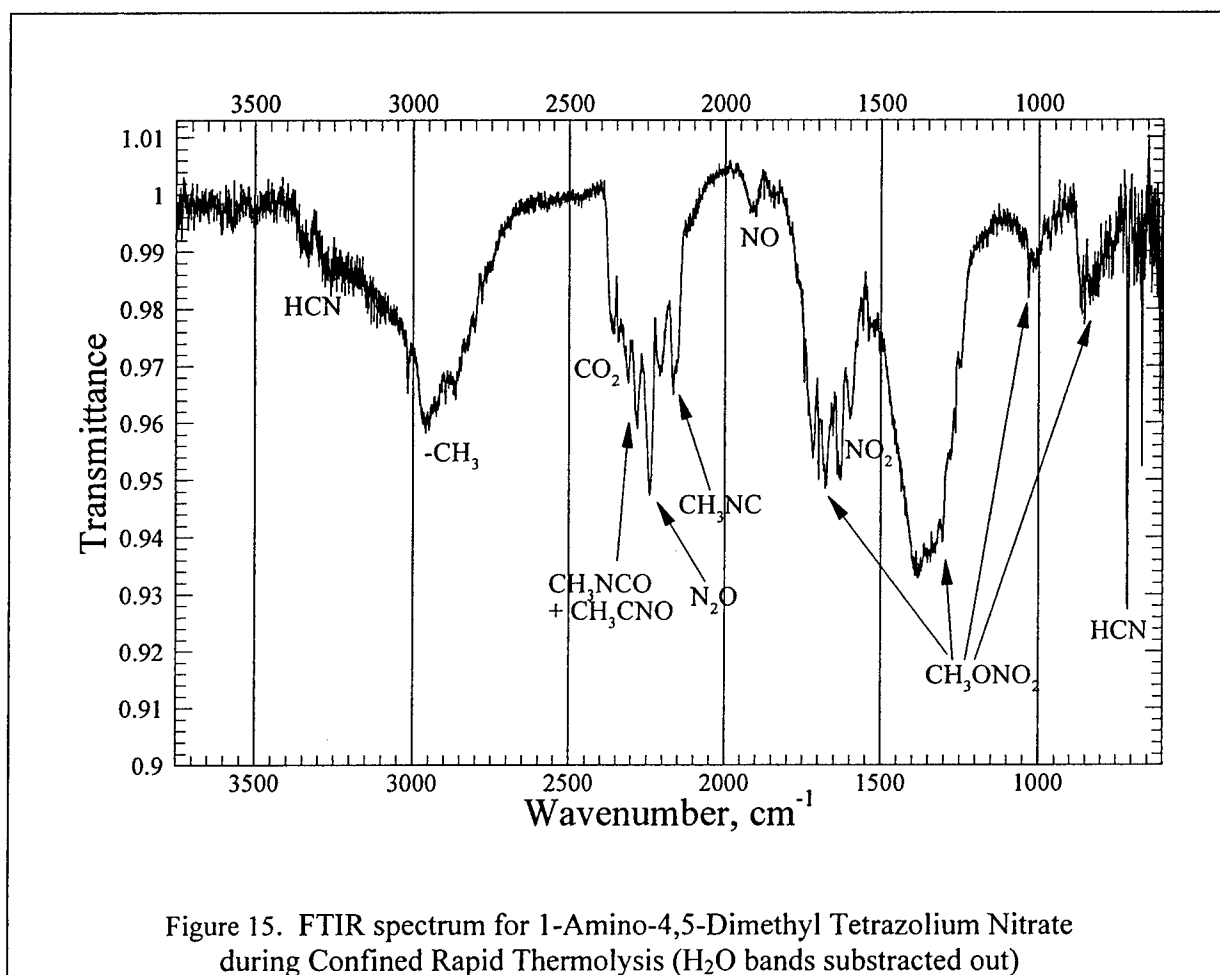
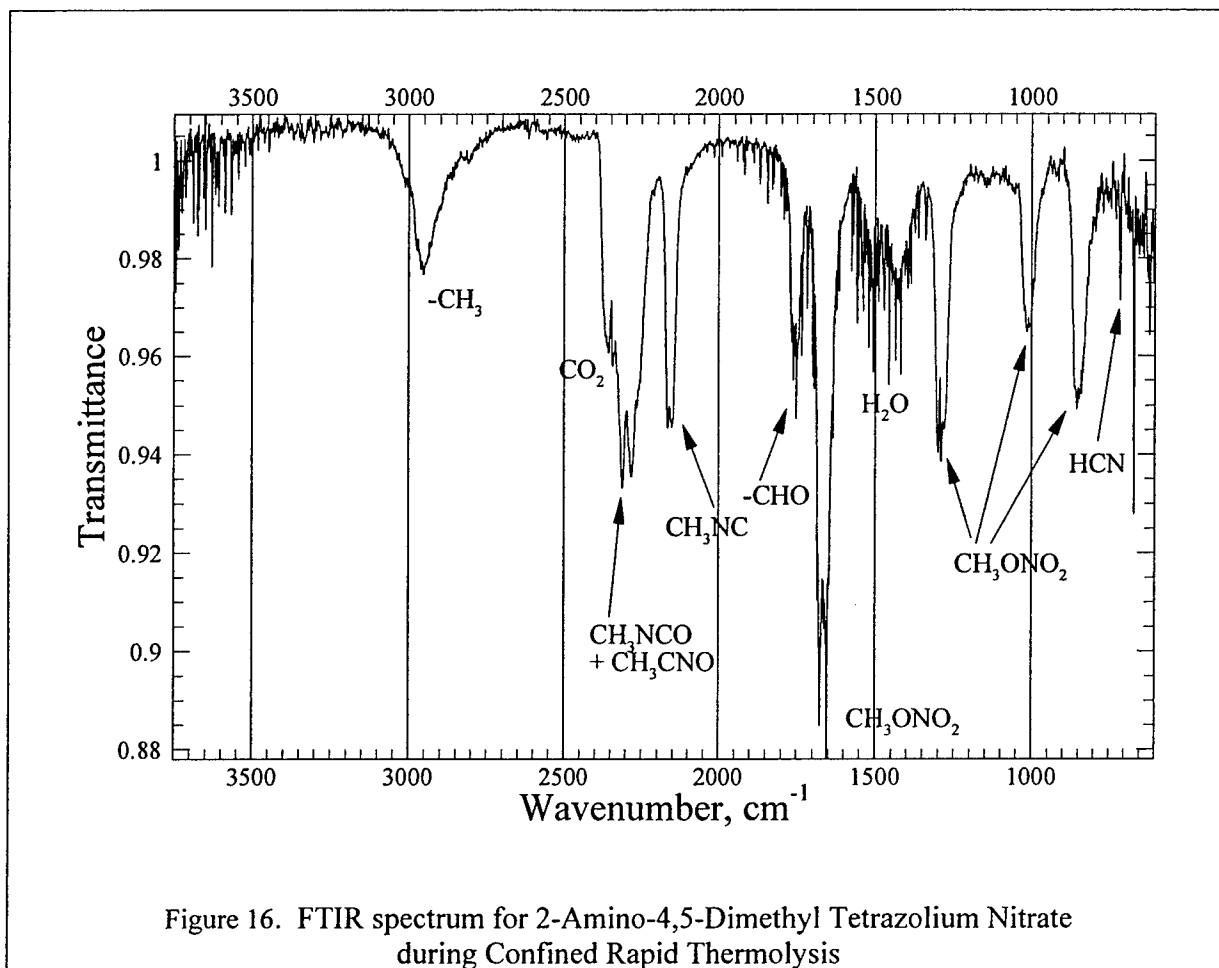


Figure 14. Typical mass spectrum for MeATAN during Laser-driven decomposition

2.4 Dimethyl Tetrazolium Nitrates

Dr. Jean'ne Shreeve provided several tetrazolium compounds for study during the program. Typical FTIR spectra obtained during confined rapid thermolysis of two of them are presented in Figure 15 Figure 16. Both compounds show bands corresponding to methyl nitrate and neither shows nitric acid. In combination these two observations indicate that methyl transfer is dominant, just as it was for the EmimNO₃.





2.5 Effect of Cation Structure

The results of the project provide substantial insight into the initiation reactions of three classes of ionic liquids: imidazoles, 1,2,4-triazoles, and tetrazoles. Evidence suggests that proton transfer and alkyl transfer to form nitric acid and alkyl nitrates, respectively, are both significant initiation reactions. There is also evidence that reactions are occurring at the amino-group for the triazole compounds. It is not clear, however, whether these reactions of initiation or secondary reactions. The most intriguing trend observed when comparing results across the classes of compounds is that proton transfer appears to be important only the 1,2,4-triazoles whereas for the imidazoles and tetrazoles alkyl transfer appears to be dominant. Explaining this trend will require molecular modeling of the initiation reaction pathways.

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Personnel Supported over duration of grant

Faculty: Tom Litzinger, Stefan Thynell
Research Technician: Larry Horner
Undergraduate students: Mike Garbinski, Rich Heibel
Graduate Students: Arin Chowdhury, Jianquan Li
Post-doctoral Scholars: Jianquan Li, Suresh Iyer

Publications over duration of grant

Archival:

Li, J. and T.A. Litzinger, "Thermal decomposition of 4-amino-1,2,4-triazolium nitrate under infrared laser heating," *Thermochimica Acta*, Volume 454, Issue 2, 15 March 2007, Pages 116-127

Chowdhury, A., and S. T. Thynell, "Confined rapid thermolysis/FTIR/ToF studies of imidazolium-based ionic liquids," *Thermochimica Acta*, Vol. 443, No. 2, 2006, pp. 159-172

Meeting Proceedings:

Chowdhury, A., and S. T. Thynell, "Confined rapid thermolysis/FTIR/ToF studies of imidazolium -based ionic liquids," *Proceedings 2005 Technical Meeting of the Eastern States Section of the Combustion Institute*, pp. 108-111

Chowdhury, A., and S. T. Thynell, "Confined rapid thermolysis/FTIR/ToF studies of triazolium -based ionic liquids," *Proceedings 2005 Technical Meeting of the Eastern States Section of the Combustion Institute*, pp. 112-115

Li, J. and T.A. Litzinger, "Laser-driven Decomposition and Combustion of 4-Amino-1,2,4-triazolium Nitrate," *Proceedings 2005 Technical Meeting of the Eastern States Section of the Combustion Institute*, pp. 116-119

Interactions/Transitions over Course of the Grant

We had continuing interactions the ionic liquids group of AFRL at Edwards including transfer of materials to our labs for testing. We also made a visit to Edwards in 2005 to present our work and to learn more about the on-going efforts at Edwards.

We had substantive interactions with Mark Gordon and Mike Schmidt of Iowa State regarding molecular modeling of the reactions of ionic liquid. Mike was able to predict the proton transfer reactions of the EmimNO₃ compound.

Jean'ne Shreeve provided a series of tetrazolium compounds for our project.

New Discoveries/Inventions/Patent Disclosures

None to report

Honors and Awards

Lifetime achievement awards: Stefan Thynell is a Fellow of ASME.