CONFINED RAPID THERMOLYSIS/FTIR/TOF STUDIES OF ENERGETIC IONIC LIQUIDS

A Dissertation in
Mechanical Engineering

by
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ABSTRACT

Current research is focused on the identification of the initiation and secondary reactions occurring during the thermal decomposition of energetic ionic liquids (EILs). The synergistic diagnostic tools, rapidscan Fourier transform infrared (FTIR) spectroscopy and time-of-flight mass spectrometry (ToFMS), were utilized in conjunction with confined rapid thermolysis. The thermal decomposition involved sub-milligram quantities of each compound subjected to heating rates of 2,000K/s and temperatures to 435°C in an ambient inert gas at one atm.

The objective of this research is to gain a thorough understanding of the reaction pathways and their corresponding rate parameters that govern the pre-ignition thermal decomposition of EILs. Although particular focus is laid on isolation of the initial reaction pathways, a detailed understanding of the effects of ring structure and the type and location of substituent groups on the secondary reactions are also of interest.

The imidazolium salts comprised of 1-ethyl-3-methyl-imidazolium as the cation, and NO$_3^-$, Cl$^-$, and Br$^-$ as the anions, and are found to be thermally most stable among the three families of salts. Examination of the evolution of gas-phase species reveal that the most probable sites for nucleophilic transfer and subsequent secondary reactions are primarily the methyl group and secondarily the ethyl group. The triazolium family is formed by pairing the 4-amino-1,2,4-triazolium cation with chloride (4ATCl), and nitrate (4ATN) anions, and rank second in thermal stability. Whereas a proton transfer from the N$_1$ position primarily initiates decomposition in 4ATCl, the amino group is found to primarily participate in the initiation reaction in case of 4ATN. The substituted triazolium
salts formed by pairing the 1-methyl-4-amino-1,2,4-triazolium and 1-methyl-4-amino-
1,2,3-triazolium cations with iodide and nitrate salts are also found to initiate
decomposition through the amino group.

The compounds studied from the tetrazolium family are 2-amino-4,5-dimethyl-
tetrazolium iodide (2AdMTZI) and nitrate (2AdMTZN), and 1-amino-4,5-dimethyl-
tetrazolium iodide (1AdMTZI) and nitrate (1AdMTZN). The major decomposition
pathway involves a nucleophilic transfer to the anion leading to the formation of methyl
iodide and methyl nitrate, from 2AdMTZI and 2AdMTZN, respectively. Unlike the
2AdMTZ salts, the 1AdMTZ salts are found to initiate decomposition through three
major pathways – formation of the corresponding methylated anion and 1-amino-5-
methyl-tetrazole, formation of ammonia by the amino group, and expulsion of nitrogen
from the tetrazole cation itself.

The Arrhenius-type reaction rate parameters for the initiation reactions governing
the thermal decomposition of several EILs are obtained by an evolutionary genetic
algorithm that compares the difference between the experimental and simulated species
evolution profiles from the decomposition process. The processes governing the
decomposition of these energetic compounds are found to be autocatalytic in nature, and
the autocatalytic agents are the strong acids generated by the initial decomposition step.
Additionally, the pre-ignition condensed phase chemistry during the hypergolic reaction
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Chapter 1

INTRODUCTION

1.1 Background

Ionic liquids (ILs) are a unique class of ionic compounds with melting points below the boiling point of water. Room temperature ionic liquids (RTILs) are a sub-category of ionic liquids with melting points below the ambient temperature. While the first room-temperature energetic ionic liquid, \([\text{CH}_3\text{CH}_2\text{NH}_3]^-\text{[NO}_3^-\), with a melting point of only 12°C was reported in 1914 by Walden [1], the modern era of ionic liquids started with the synthesis of 1-butylpyridinium chloride–aluminum(III) chloride mixture by Osteryoung et al. [2]. The reducible nature of \(N\)-alkyl-pyridinium cations in basic solutions led to a search for more stable cations. Wilkes [3] studied a wide range of heterocyclic cations with quaternary N-atoms and found the dialkyl-imidazolium cation to be the most suitable one. Further studies by Fannin et al. [4] revealed that the 1-ethyl-3-methyl-imidazolium (emim) cation was an excellent compromise between ease of synthesis and desirable properties. However, chloroaluminate ionic liquids, prepared by mixing aluminium chloride with dialkyl-imidazolium chlorides, were found to be hygroscopic. This led to the search for anions that would yield ionic liquids stable towards hydrolysis at room temperature, culminating in the discovery of tetrafluoroborate, hexafluorophosphate, nitrate, sulfate and acetate salts by Wilkes and Zaworotko [5]. The last decade has sparked a significant interest in synthesis and analysis
of new ionic liquids, with the focus being on imidazoles, triazoles, tetrazoles and other nitrogen-containing heterocyclic compounds and their salts.

The most significant characteristic of RTILs is their low melting points and extremely large liquidus range. The phase diagram of [emim]Cl-AlCl$_3$ shows that melting points below $-90^\circ$C are possible [4,6]. These properties can be attributed to absence of strong hydrogen bonding [5,7], highly asymmetric cations paired with bulky anions leading to poor packing efficiencies, charge delocalization on the cation, and addition of solvent-like tails [8-10]. They also display a remarkably low vapor pressure, related to their high cohesive energy density [11]. The above-mentioned properties make them environmentally benign replacements for noxious organic solvents [12,13]. High electrical conductivity, a wide electrochemical window as well as excellent thermal and chemical stability facilitate their use as electrolytic solvents for catalytic reactions [14-16] as well as the potential application to solar cells and fuel cells.

Besides their conventional application as solvents, the major motivation behind the current study of energetic ionic liquids (EILs) involve their application in propulsion systems, space-lift and aircraft propulsion [17], as well as gas generation for air bags. Advantageous properties of EILs include negligible vapor pressure, leading to minimal inhalation hazard; high density, leading to longer active life spans for satellites and longer travel distances for spacecrafts; reduced sensitivity to impact, friction and shock; and ease of synthesis. Among EILs, considerable promise has been shown by pairing nitrogen-containing heterocyclic rings as cations, such as imidazoles, triazole, and tetrazoles, with oxygen-rich anions, such as nitrate, perchlorate, dinitramide, and picrate. Though initial focus on energetic ionic liquids was concentrated on development of the
afore-mentioned monopropellants, it has been partially shifted to bipropellant systems with the recent discovery of the hypergolicity of a series of ionic compounds based on the anion dicyanamide. But before these fuels can be employed efficiently and safely in a practical setting, critical performance parameters must be calculated and optimized to match existing propellants. Hence, a detailed understanding about the temperature dependence and chemical kinetics of their thermal decomposition under high heating rates, as encountered during propulsion, is essential.

Based on the concluded discussion, the objectives of this dissertation are as follows – identification of the initiation and secondary reactions in the condensed phase that lead to ignition and combustion; a detailed understanding of the effects of ring structure and the type and location of substituent groups on the afore-mentioned reactions; and, determination of the rates of decomposition and the corresponding kinetic parameters for these reactions over a range of temperatures relevant to potential applications. As verification of the primary and secondary reactions and related kinetic parameters were extremely difficult due to the lack of relevant publications in the literature, two synergistic diagnostic tools, Fourier transform infrared spectroscopy and time-of-flight mass spectrometry, have been utilized to afford better probabilities of identifying the decomposition products and thus, accurately determining the reaction pathways.
1.2 References


2.1 Thermal Decomposition of Energetic Imidazoles and Salts

For efficient use and safety concerns, an understanding is needed about the temperature dependence and chemical kinetics of their thermal decomposition under high heating rates. Information available on the kinetics of the thermal decomposition of imidazoles and their salts is relatively sparse in the literature. However, studies on solubilities, vapor-liquid equilibria, molar volumes and specific heat are available for some imidazolium salts [1-3]. No chemical kinetics on thermal decomposition appear to be available on the energetic imidazolium compounds, such as [emim]-X, with X as NO$_3^-$, ClO$_4^-$, N(NO$_2$)$_2^-$, and others. Except one, most studies on decomposition have been carried out using thermogravimetric techniques [4,5-10].

Pyrolysis of a wide range of 1,3-disubstituted imidazolium salts, $R_1R_2$Imidazolium X ($R_1$, $R_2$ = methyl, ethyl, propyl, isopropyl, butyl, benzyl, vinyl, phenyl, and allyl; X = Cl$^-$, Br$^-$, I$^-$, Ph$_4$B$^-$, and ClO$_4^-$) was carried out by Chan et al. [11]. Barring the Ph$_4$B$^-$ and ClO$_4^-$ salts, all the other [emim]-X compounds, when subjected to a temperature of 220 – 260ºC for 0.5 – 1.5 hours under vacuum, formed 1-substituted imidazoles. Quantitative analysis of the products was carried out by n.m.r spectroscopy and gas chromatography. 1-ethylimidazolate was found to dominate the products over 1-methylimidazolate, and no traces of HX were detected. Similar studies on [emim]-X salts
(X = bis-(methanesulfonyl)amide, bis-(trifluoromethanesulfonyl)amide) by Baranyai et al. [12] yielded 1-ethylimidazole as the major degradation product and 1-methylimidazole as the minor one. Again, no acids corresponding to the anions were detected. The predominance of 1-ethylimidazole during decomposition was attributed to an $S_N2$ process.

Bônhote et al. [10] examined the thermal stability of a wide variety of 1,3-dialkylimidazolium cations and hydrophobic anions, which included trifluoromethanesulfonates (TFO$^-$), bis((trifluoromethanesulfonyl)amides (Tf$_2$N$^-$), and trifluoroacetates (TA$^-$). The melting points of many of these salts were as low as -30 to -50°C but their correlation to chemical composition was difficult. For heating rates of 10°C/min, the [emim]TfO and [emim]Tf$_2$N were stable up to 400°C, but decomposed rapidly between 440 and 480°C. However, [emim]TA initiated its decomposition at 150°C and continued until reaching 250°C, when nearly all the material was converted to gaseous products. The same results were obtained with either air or N$_2$. Correlation of mass loss with evolved species was not discussed.

Ngo et al. [5] used TGA/SDTA and DSC to study the thermal stability of a wide variety of imidazolium cations as well as organic and inorganic anions at heating and cooling rates of 10°C/min. The thermal decomposition behavior varied considerably with salt structure, as well as pan composition. The aluminum pan catalyzed the decomposition, requiring the use of alumina pans. Nonetheless, many interesting findings were obtained. The thermal stability was enhanced with increased substitution on the imidazolium cation; i.e. replacing the ring hydrogens with methyl or $N$-propyl groups enhanced stability. The effect on stability was observed when the C(2) hydrogen was
removed due to the acidity of the proton. Additionally, [emim] halides (Cl\(^-\), Br\(^-\), and I\(^-\)) exhibited the lowest temperature for the onset of decomposition. (280-310°C), and the salts showed similar thermal behavior in O\(_2\) or N\(_2\) environments.

Egashira et al. [8] examined the thermal stability of three different [emim] salts with either individual anions, such as CF\(_3\)SO\(_3\)^- or BF\(_4\)^-, or mixture of different anions, such as CF\(_3\)SO\(_3\)^- or BF\(_4\)^- with bis(tetrafluoromethanesulfonylimide)imide (TFSI\(^-\)). A heating rate of 5°C/min in an Ar environment was employed. The thermogravimetric data for [emim](BF\(_4\))\(_{0.5}\)(TFSI)\(_{0.5}\) were essentially the arithmetic average of the data from for [emim]BF\(_4\) and [emim]TFSI. However, the data for [emim](CF\(_3\)SO\(_3\))\(_{0.5}\)(TFSI)\(_{0.5}\) was more similar to [emim]CF\(_3\)SO\(_3\) than to [emim]TFSI.

Bhattacharjee and Choudhury [9] studied several imidazole complexes of Cu(II). For the (H\(_2\)Im)\(_4\)[CuF\(_6\)] salt, thermogravimetric studies revealed 66% weight loss over the temperature range from 250 to 350°C by a release of (3HIm+3HF+F\(_2\)) in an endothermic process. From 400°C to 700°C, (H\(_2\)ImF) was released also in an endothermic process; a Cu\(_2\)O residue remained. The thermogravimetric data on imidazole complexes revealed similar processes occurring in either two or three endothermic stages.

Minier et al. [13] studied the solid-phase thermal decomposition of 2,4-dinitro- imidazole (DNI) using thermogravimetric and mass spectrometric techniques. The first stage of decomposition was found to be related to the presence of water and impurities in the DNI. As this “early decomposition” was ending, an induction period began with the evolution of CO\(_2\) and NO. This stage was followed by an auto-acceleratory stage where the major products included CO\(_2\), CO, NO, N\(_2\), HNCO, and H\(_2\)O. Finally, the residue from this stage decomposed. It was also postulated that the decomposition of DNI
involved multiple pathways including a nitro-nitrite rearrangement, followed by bond scission to form NO, and then an N-C bond scission, which opened the ring. Intra- and inter-molecular hydrogen abstraction was also believed to be one of the initiation steps.

The temperatures defining onset of the thermal decomposition of a broad range of energetic ionic liquids have recently been established by thermogravimetric methods [14-16]. Nitrates and perchlorates of azido and nitro derivatives of imidazole, 1,2,4-triazole, and substituted derivatives of tetrazoles were synthesized and their decomposition points recorded under a heating rate of 10°C/min. Nitrate salts of substituted imidazoles, triazoles and tetrazoles were found to have a lower thermal stability than the perchlorate salts in general. Decomposition temperatures of substituted imidazoles were found to decrease with increased substitution of ring hydrogens. As a result, 1,3-dimethyl-5-nitroimidazolium nitrate (174°C) was found to be more stable than 1,3,5-trimethyl-5-nitroimidazolium nitrate (166°C), which in turn was found to be more stable than 1-ethyl-2,3-dimethyl-5-nitroimidazolium nitrate (146°C). However, such a relationship was lacking among the perchlorate salts of the same category, where 1,3,5-trimethyl-5-nitroimidazolium perchlorate (307°C) was found to be the most stable salt. Similar trends were observed among the triazole and tetrazole salts.

Recently, the slow thermal decomposition characteristics of several energetic ionic liquids were examined using thermogravimetric analysis and differential scanning calorimetry, coupled with IR spectroscopy and mass spectrometry [17]. Decomposition of the 1,5-diamino-4-methyl-1H-tetrazolium nitrate involved methyl group transfer to form MeONO₂, rather than proton transfer to form HNO₃. At heating rates of 10°C/min,
this ionic liquid began to decompose at 181°C, and showed a peak heat release rate at 200°C.

Finally, IR laser ablation of 1, 3-disubstituted imidazolium salts, \(R_1R_2\text{Imidazolium }X\) (\(R_1\) = methyl, \(R_2\) = methyl, ethyl, butyl, and hexyl; \(X = \text{Cl}^-, \text{NO}_3^-, \text{and } \text{CH}_3\text{SO}_4^-\)) was studied using time-of-flight mass spectrometry by Baer et al. [18]. Unlike previous studies, the heating rates employed were \(10^8 - 10^{13}\) K/s. The internal temperature of the ablated vapor plume was measured to be 450 to 500°C by an ethylene glycol thermometer. Vacuum photoionization was utilized to detect the neutral species. Approximately 100 mg of the ionic liquids studied was ablated and 99% of the sample was found to be vaporized to form nano- or micro-droplets. The remaining 1% was comprised mainly of stable di-substituted imidazoles, formed by expulsion of HCl from the imidazolium salt. About 0.1% was found to be the gas-phase parent molecules, \(R_1R_2\text{Imidazolium }X\).

### 2.2 Thermal Decomposition of Energetic Triazoles and Salts

Numerous synthesis, characterization and decomposition studies have been conducted on energetic salts containing the heterocyclic triazolium cation. Early, the focus was on the metalized salts involving the 5-nitro-2,4-dihydro-1,2,4-triazole-3-one (NTO) [19-24], and a complex between trinitromethane and 4-amino-1,2,4-triazole (4AT) [25]. Recently, significant strides in developing salts based on various derivatives of 1,2,4-triazole (1TA) or 1,2,3-triazole as cations and nitrates, perchlorates, and dinitramides as anions have been made by Shreeve et al. [26-33] and Drake et al. [34,
Since the hydrogen atoms on these azoles can be substituted easily by energetic functional groups, the family of the triazole salts has been expanded to include azido, amino, nitro, and nitramino azolium salts. The oxygen-rich substitute groups improve oxygen-balance of the cations and result in higher exothermicity during combustion. However, most of the thermal decomposition studies have been carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under slow heating rates without any particular emphasis on the chemical kinetics of these decomposition reactions. Though these studies were carried out under low heating rates, the underlying trends provide valuable insights into the thermal stability of these compounds, the effects of various groups substituting the protons on the triazole ring, and their decomposition behavior under elevated heating rates. Some molecular modeling work has also been carried out to determine various macromolecular properties, such as melting point, heats of formation, etc. [36-41].

Nitrate, perchlorate and dinitramide salts of 1,2,3-triazole, 1TA, and 4AT were prepared and characterized by Drake et al. [26]. Phase change and decomposition onset temperatures ($T_d$) were recorded using DSC, and mass-loss studies were also conducted by TGA. The dinitramide salts of all three cations were found to be the least stable, followed by the nitrates and the perchlorates. Shifting the ring nitrogen from the $N_3$ position to the $N_4$ position increased the $T_d$ of 1,2,3-triazolium perchlorate from 200°C to 285°C, the probable reason being a decrease in the ease of ring-fracture through evolution of dinitrogen. Similar effects were observed with the nitrates and dinitramides. While the introduction of the amino group at the $N_4$ position lowered the thermal stability of the
dinitramide salt, it increased the $T_d$ of the perchlorate salt and had no effect on the nitrate salt. Nitrate, perchlorate and dinitramide salts of 3,4,5-triamino-1,2,4-triazole were also synthesized [27]. The order of thermal stability of these salts was found to be unaltered. Replacement of two ring H atoms with amino groups had no effect on $T_d$ of the dinitramide salt, but the perchlorate and the nitrate salts showed an increased thermal stability. Theoretical calculations carried out to ascertain the geometry of the salts showed excellent agreement with X-ray diffraction studies.

Temperatures defining onset of thermal decomposition of a broad range of energetic ionic liquids have recently been established using thermogravimetric methods by Shreeve et al. [18-25]. Nitrates and perchlorate salts of amino and alkyl derivatives of 1TA were synthesized and their decomposition onset temperatures were recorded under a heating rate of 10°C/min [21]. The results reiterate the increased stability of the perchlorate salts over the nitrate salts, as established by Drake et al. [26]. It is speculated that the hydrogen bonding between the amino group and the nitrate anion is reduced when the amino group is attached to N₄, as opposed to N₁. Though this causes a decrease in the melting point, $T_d$ increased from 149°C for 1-amino-1,2,4-triazolium nitrate to 181°C for 4-amino-1,2,4-triazolium nitrate.

Novel energetic ionic liquids, with substituted 1,2,4-triazolium cations and azolate anions, such as 4,5-dinitroimidazolate and 5-nitrotetrazolate were prepared by Shreeve et al. [22]. The compounds with 5-nitrotetrazolate as the anion exhibited greater thermal stability and higher molar enthalpies of formation than the corresponding 4,5-dinitroimidazolate salts. 4-amino-1,2,4-triazolium 4,5-dinitroimidazolate had the greatest
Heats of formation showed an increased positive value due to the azido group on the ring.

Li and Litzinger [42] studied the thermal decomposition of 4ATN, driven by a CO₂ laser with a heat flux of 100 W/cm² in a helium environment at 1 atmosphere. The gaseous products from the decomposition of the sample material in the condensed phase were analyzed by a triple quadrupole mass spectrometer. Though the temperatures of decomposition were not stated, under the extremely high heating rates applied, a proton transfer involving the N₁ position was identified as the initiation reaction. The resultant neutral species, HNO₃ and 4AT were found to react subsequently to produce mainly H₂O and N₂O through an ionic route analogous to the low-temperature decomposition of NH₄NO₃. The significant amount of 1TA detected among the products was attributed to the displacement of the amino group on 4AT by a hydrogen radical.

Schmidt et al. [29] employed ab initio quantum chemistry calculations of a gas-phase anion-cation pair to predict heats of formation and charge delocalization in energetic ionic liquids formed by the 1,2,4-triazolium cation family. Suitability of several groups, such as F, OH, NH₂, CH₃, CN, N₃, NF₂, NO₂, C₂H₃, and OCH₃ was tested as substituents on the 1,2,4-triazolium cation, while dinitramide was selected as the anion. Charge delocalization studies, integral to the prediction of lower melting points, suggested that only CN and the NF₂ groups degraded the resonance structures to a small extent, without hampering the ability of the cations to form ionic liquids. However, these two groups provide the maximum molar heats of formation, though CN is preferable, as N₃ involves forming a ring exo NN bond. Deprotonation studies with the parent cation
and 4AT by geometry optimization indicate that deprotonation from the N$_1$ position is the possible first step during thermal decomposition. The factors responsible for deprotonation were small energy barriers and spontaneous proton-transfer from ionic dimers to form neutral pairs.

Several attempts have been made to predict melting points and other physical properties of the mono- or di-substituted 1,2,4-triazolium class of ionic liquids by molecular dynamics simulations or by Quantitative Structure-Property Relations (QSPRs). Factors affecting the melting points of ionic liquids include arrangements of atoms in the crystal lattice, interactions among ion-pairs, molecular symmetry, and conformational degrees of freedom. Thompson et al. [28] used molecular dynamics simulations, based on a force field modeled after the one developed by Lopes et al. [43]. The method of void-induced melting predicted the melting point of 1-$n$-propyl-4-amino-1,2,4-triazolium bromide at 360K, whereas the experimental melting point is 333K. The velocity autocorrelation function indicated strong degrees of ion-counterion interactions common among systems with cage effects. Trohalaki et al. [30, 31] derived QSPRs for melting points of 1-substituted-4-amino-1,2,4-triazolium bromide, nitrate, and nitrocyanamamide salts from molecular orbital, electrostatic, and thermodynamic descriptors. The optimal molecular geometries of the cations were calculated using ab initio quantum chemical methods.
2.3 Thermal Decomposition of Energetic Tetrazoles and Salts

The higher nitrogen content of the heterocyclic tetrazole compounds has prompted numerous studies on the compounds themselves and their derivatives. Experimental and numerical studies have been conducted on the thermal decomposition and combustion of tetrazole [44-47], amino-tetrazoles [48-51], nitramino-tetrazoles [52, 53], nitro-tetrazoles [54-56], and even polymeric forms of tetrazoles [57, 58]. Ab initio calculations on decomposition of substituted tetrazoles [59, 60] indicate that ring-opening is initialized by N–N bond cleavage, instead of C–N bond scission.

The high heats of formation of nitrate, dinitramide, azide, and perchlorate salts of substituted tetrazoles, and production of high quantities of dinitrogen during decomposition has generated considerable interest in them as gas generators, propellants and explosives. However, limited knowledge is available in the literature on these energetic salts of tetrazoles. Shreeve et al. [61] synthesized nitrate and perchlorate salts of 2,4,5-trimethyltetrazolium and 4,5-dimethyl-1-aminotetrazolium cations. As observed with the triazole salts, the perchlorate salts were thermally more stable than the nitrate salts. Replacing a methyl group with an amino group lowers the onset of decomposition for both salts. Similar salts of 2-amino-4,5-dimethyltetrazolium cations [62] showed analogous decomposition trends.

Weigand et al. [63] prepared 1,5-diaminotetrazolium nitrate and perchlorate, and 1,5-diamino-4-methyl-tetrazolium nitrate, dinitramide, and azide salts. The salts were characterized by vibrational and NMR spectroscopy, mass spectrometry, X-ray crystallography and elemental analysis. The azide salt was found to be the least thermally
stable, and provided the maximum molar enthalpy of formation. 1,5-diaminotetrazolium perchlorate was also synthesized and studied by Drake et al. [64]. Diaminotetrazolium nitrate exhibited detonation velocities and pressures comparable to high explosives, such as HMX, RDX or PETN [65].

The slow thermal decomposition characteristics of derivatives of 1,5-diaminotetrazole were examined using thermogravimetric analysis and differential scanning calorimetry [66]. The gaseous products were identified by IR spectroscopy and mass spectrometry. Decomposition of the 1,5-diamino-4-methyl-1H-tetrazolium nitrate involved methyl group transfer to form MeONO₂, rather than proton transfer to form HNO₃. At heating rates of 10°C/min, this ionic liquid began to decompose at 181°C, and showed a peak heat release rate at 200°C. The resultant 1,5-diaminotetrazole (DAT) readily produced nitrogen and an unstable nitrone, which subsequently produced ammonia and HCN. The azide salt decomposed through deprotonation to form 1-amino-4-methyl-5-imino-tetrazole and the corresponding acid HN₃. The decomposition temperatures were high enough to cause ring fracture of the tetrazole formed during the initiation step and led to the formation of smaller fragments, including methyl azide and aminocyanamide. The dinitramide salt also followed a similar deprotonation reaction to form 1-amino-4-methyl-5-imino-tetrazole and HN(NO₂)₂. HN(NO₂)₂ decomposes to N₂O and HNO₃, and HNO₃ promptly reacts with 1-amino-4-methyl-5-imino-tetrazole producing its nitrate salt, which decomposes in a manner discussed earlier.

Flash pyrolysis of 5-amino-1H-tetrazolium halides (chloride, bromide and iodide) was carried out by Brill and Ramanathan [48], and the products were identified by FTIR spectroscopy under temperatures ranging from 350°C to 450°C. The products indicated
the presence of two different reaction pathways, the first being the dissociation of the salts to form molecular nitrogen. The remaining species decomposed spontaneously to form mainly HCN and the corresponding protonated anion (HCl, HBr, or HI). The second pathway involved deprotonation of the ring hydrogen and subsequent dissociation of 5-amino-tetrazole (5ATZ) into HN$_3$ and NH$_2$CN. The first channel of reaction is favored over the second in the order of $\Gamma^->\text{Br}^->\text{Cl}^-$, which is the same order as the basicities of these anions. The burning rates of the salts were found to be dependent on the extent of decomposition of 5ATZ molecule, rather than that of the 5ATZH$^+$ ion.

In another pertinent work, Brill et al. [67] studied the different decomposition pathways occurring due to the presence of an amino group on the ring carbon (5-amino-tetrazole, 5ATZ) instead of a ring nitrogen (1-aminotetrazole, 1ATZ). Rapid thermolysis of 1ATZ above 200ºC proceeded with the expulsion of HCN and N$_2$ from the ring leaving N$_2$H$_2$ to produce NH$_3$ and N$_2$. But the shift of the amino group prompts the scission of two weak ring N-N bonds to form HN$_3$ and NH$_2$CN as the principal products. As the temperatures were increased, NH$_2$CN trimerized to form the cyclic azine, melamine. The decomposition of two other compounds, 1,5-diamino-tetrazole and 2,5-diamino-tetrazole occurred through competitive reaction pathways, the first yielded HCN, whereas the second produced NH$_2$CN as the primary product. Both channels produced N$_2$ and NH$_3$ as the common species.
2.4 Kinetics of Decomposition of Energetic Ionic Liquids

Although considerable efforts have been expended so far on studying procedures of synthesis, characterization of various properties, as well as decomposition mechanisms of these EILs, data regarding their reaction kinetics is not readily available in the literature. In our publications, the decomposition pathways under high heating rates of several imidazolium-based [68], triazolium-based [69], and tetrazolium-based [70] energetic ionic liquids were covered. Since the primary decomposition pathways of the triazolium-based salts as well as the hydrazine-based salt, the primary targets of this study, was determined to be deprotonation of the cations, several ionic compounds with similar decomposition patterns were identified and the kinetic parameters governing the initiation of their decomposition were procured. The compounds of interest can be roughly subdivided into salts of the ammonium family, namely ammonium nitrate (AN) and ammonium dinitramide (ADN), and salts of the hydrazinium family, namely hydrazinium nitrate, hydrazinium chloride, and hydrazinium azide. It is of significant importance at this juncture to note that autocatalytic processes are integral to the decomposition of explosives in the condensed phase [71] and are primarily of the acid-base nature.

The thermal decomposition of AN has been subjected to in-depth studies, and the kinetics of its decomposition to nitrous oxide and water have been probed [72–75]. Especially, most of the complexities surrounding the decomposition were discussed by Rosser et al. [73] and Brower et al. [74]. Particularly, the autocatalytic reaction dominating the initial step, which occurs by AN dissociating into HNO₃ and NH₃, has
been studied by Rubtsov et al. [75] by confining samples of AN within sealed and temperature-controlled glass ampoules. The kinetics of ADN, studied separately by manometric methods by Pavlov et al. [76], and by Oxley et al. [77] by sealed glass ampoules in constant temperature baths, yielded reasonably similar values of the activation energies for the initiation step. The kinetic parameters associated with autocatalytic behavior, though present during decomposition of ADN through the presence of products like HNO₃ and H₂O, was not presented in the literature. Thermal decomposition of the hydrazinium family of salts was studied in the condensed phase by Rubtsov et al. [78–80]. The decomposition of all three salts proceeds through their dissociation into hydrazine and the corresponding acid. For both hydrazinium chloride [79] and nitrate [78], the kinetic parameters for the primary step as well as the autocatalytic step were found to be remarkably similar, whereas the significant variation of the parameters for hydrazinium azide [80] was attributed to the considerably lower acidity of hydrazoic acid, compared to nitric and hydrochloric acids. The decomposition mechanisms and their associated Arrhenius-type rate parameters for the compounds discussed above are provided in Table 2.1.
Singh and his coworkers have investigated a series of compounds for which thermal decomposition was initiated by proton transfer [81]. The kinetic parameters of decomposition were determined mainly by TG / DTG / DTA / DSC methods, and cover a wide range of values. Fox et al. [82] studied the kinetics of decomposition of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate by TGA and extracted the apparent activation energy and pre-exponential factor for a global kinetic model. Aside from these experimental efforts, Schmidt et al. [83] attempted to calculate the deprotonation energies for 1-H,4-H or 1-H,2-H substituted triazolium cations by employing ab initio methods. It

Table 2.1: Arrhenius-type parameters of decomposition.

<table>
<thead>
<tr>
<th>Reaction Mechanism</th>
<th>Activation energy (kcal/mol)</th>
<th>Preexponential factora</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃ → NH₃ + HNO₃</td>
<td>47.2</td>
<td>2.5 × 10^{14}</td>
<td>[75]</td>
</tr>
<tr>
<td>NH₄NO₃ + HNO₃ → NH₃ + HNO₃ + HNO₃</td>
<td>24.0</td>
<td>2 × 10^{7}</td>
<td>[75]</td>
</tr>
<tr>
<td>NH₄N(NO₂)₂ → NH₃ + HN(NO₂)₂</td>
<td>35.5</td>
<td>2.5 × 10^{14}</td>
<td>[76]</td>
</tr>
<tr>
<td>NH₄N(NO₂)₂ → NH₃ + HN(NO₂)₂</td>
<td>39.9</td>
<td>8.8 × 10^{16}</td>
<td>[77]</td>
</tr>
<tr>
<td>N₂H₅NO₃ → N₂H₄ + HNO₃</td>
<td>38.0</td>
<td>1.6 × 10^{12}</td>
<td>[78]</td>
</tr>
<tr>
<td>N₂H₅NO₃ + HNO₃ → N₂H₄ + HNO₃ + HNO₃</td>
<td>26.5</td>
<td>6.3 × 10^{7}</td>
<td>[78]</td>
</tr>
<tr>
<td>N₂H₅Cl → N₂H₄ + HCl</td>
<td>40.0</td>
<td>1.6 × 10^{13}</td>
<td>[79]</td>
</tr>
<tr>
<td>N₂H₅Cl + HCl → N₂H₄ + HCl + HCl</td>
<td>26.0</td>
<td>5 × 10^{7}</td>
<td>[79]</td>
</tr>
<tr>
<td>N₂H₅N₃ → N₂H₄ + HN₃</td>
<td>24.0</td>
<td>10^{8}</td>
<td>[80]</td>
</tr>
<tr>
<td>N₂H₅N₃ + HN₃ → N₂H₄ + HN₃ + HN₃</td>
<td>16.0</td>
<td>10^{4}</td>
<td>[80]</td>
</tr>
</tbody>
</table>

aUnits are s, cm³, mol
was observed that 224 kcal/mol was required for deprotonation from the N$_1$ position in 1-H-4-NH$_2$-1,2,4-triazolium cation, compared to 220.7 kcal/mol for 1-H-4-H-1,2,4-triazolium cation. Although the decomposition mechanism was through methyl group transfers instead of proton transfers, the quantum chemical studies by Kroon et al. [84] on various imidazolium-based ionic salts showed that the activation energy barrier for the ionic liquid 1-butyl-3-methyl-imidazolium chloride was 30.2 kcal/mol, whereas that for the dicyanamide anion was 38.1 kcal/mol.

### 2.5 References


Chapter 3

EXPERIMENTAL AND COMPUTATIONAL METHODS

3.1 Experimental Approach

3.1.1 Experimental Setup

The technique utilized to study the products formed under rapid decomposition of a material is referred to as confined rapid thermolysis (CRT)/FTIR/ToFMS. Using this technique, 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 3.1. 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 [1].
The rapid thermolysis is achieved by using two heaters: a stationary top heater and a mobile bottom heater. In both heaters, isothermal conditions are established by using high-watt density cartridge heaters (Omega CIR-1014/120V) and controlled by proportional-integral-derivative (PID) controllers (Omega CN8500). Both heaters are sheathed in copper rods, 53 mm in height and 15.6 mm in diameter. There are two auxiliary systems, a pneumatic piston-cylinder (Motion Controls) for lifting the bottom heater and a purge gas system. The purging system using an inert gas serves a dual purpose. One, it purges the chamber of the decomposition products and prevents

Figure 3.1: 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.
recirculation of products into the path of the modulated FTIR beam, and two, it prevents oxidation of the copper rods at elevated temperatures. The temperature of the cartridge heaters is monitored and controlled by two 75 \( \mu \text{m} \) K-type thermocouples embedded in the copper sheaths of the heaters.

To achieve rapid thermolysis, defined as an event that occurs within 5 seconds, high temperatures are used. The experimental procedure is as follows: the heaters are brought up to the pre-set temperature. Approximately 0.5 mg of the ionic liquid is placed on the sample holder. As shown in Fig. 3.1, the sample holder is a hollow cylindrical ring with a thin foil attached on top. Though it is possible to utilize different types of foils, an 11 \( \mu \text{m} \) thick aluminum foil is used to minimize conductive heat transfer resistance. The sample holder is then placed over the guiding tube for the bottom heater and the bottom heater is raised by the pneumatic piston-cylinder. The sample holder is brought in contact with the ring retaining an aluminum foil over the top heater. This ring also defines and seals a gap of approximately 300 \( \mu \text{m} \) between the two heaters. The final position of the sample holder and the two heaters is shown in Figure 3.2. A rectangular slit, 8.25 mm by 300 \( \mu \text{m} \), is left open in the gap for gases generated during decomposition of the sample to gain access to the FTIR beam or to the orifice port on the vacuum chamber.
3.1.2 FTIR Spectrometer

The gaseous products evolve into the FTIR beam passing through two ZnSe (or KRS-5) windows, which are offset by 0.313 inches from the center of the chamber, offering a spectral coverage of 500-10,000 cm$^{-1}$. This wide range is truncated using a germanium coated KBr beamsplitter and a mercury-cadmium-telluride detector to the mid-IR range of 600-5,000 cm$^{-1}$. 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.

Figure 3.2: Cross-sectional view when the two isothermal heaters are in contact, as well as initial sample holder position.
3.1.3 ToF Mass Spectrometer

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, www.rmjordan.com) 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. The vacuum system is differentially pumped using a Leybold DIP8000 diffusion pump in the first stage, a Leybold TW700 turbomolecular pump in the second stage, and a Leybold TMP151 turbomolecular pump as well as two Varian Starcell 75 ion pumps in the third stage; four backing pumps are also used. Typical pressures are $10^{-4}$ torr in the first stage, $10^{-6}$ torr in the second stage and $10^{-7}$ torr in the third stage. 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 $0.5\times12\text{mm}^2$ slit attached to the entrance of the third stage. A schematic is shown in Figure 3.3. The distance between the orifice plate and the electron beam in the flight tube is 0.279m. Electron impact ionization is set at 70eV, resulting fragmentation of molecules, but allowing comparison with mass spectral and related data bases [2]. The electron beam interacts with the molecular beam during a period of 3 µs, after which extraction of positive ions occurs as a 250V voltage difference is applied between the grid plates; the overall potential is normally set at 2.5kV. Data acquisition at 1GHz is PC-based using the 8-bit PDA1000 PCI-board (www.Signatec.com), which has 256MB of on-board memory and a 3-dB bandwidth of
0.5GHz. The MCP output signal is inverted and amplified 3.5× using a THS3201 amplifier from Texas Instruments. Time-to-mass scaling is sufficient 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.

![High-Watt Density Heater within Copper Rod](image)

Figure 3.3: Sampling of evolved gaseous products occurs via the 100 µm diameter orifice port located on the first stage of the vacuum chamber.

### 3.1.4 Data Reduction in FTIR Spectroscopy

A non-linear, least-squares method is utilized to extract the species concentrations of the evolved gases by comparison with theoretical transmittance [3]. The radiative properties, such as partition function, half-width of spectral lines, and its temperature exponent, are determined from the HITRAN data base [4]. The measured gas-phase temperature serves as an input to the data-reduction technique. The computational procedure involves specifying the total pressure, measured gas-temperature profile, and
assumed path length. The algorithm computes the partial pressures, and coefficients for linear base-line shifts. Iterations are continued till a change in the sum of the errors between successive guesses is less than 0.01%. After completion of the iterations, the relative concentrations of various species, such as $\text{H}_2\text{O}$, $\text{N}_2\text{O}$, $\text{NO}_2$, $\text{NO}$, $\text{CO}$, $\text{CO}_2$, $\text{HCl}$, $\text{NH}_3$ and $\text{HNO}_3$ are obtained for each spectrum.

### 3.2 Computational Approach

#### 3.2.1 Molecular Modeling of Tetrazolium Salts

The predicted reaction enthalpies and free energies of tetrazolium-based EILs were calculated using the Gaussian 03 suite of programs [5]. All geometrical structures were fully optimized using Density Functional Theory (DFT) with the B3LYP exchange correlation functional and 6-31++G** basis set, with the exception of iodine, for which 6-311G* [6], with extra diffuse functions [7], was used. Vibrational frequencies were calculated to confirm identification of the local minima and obtain thermodynamic properties. Enthalpies and free energies were calculated at 298K and 1 atm pressure. In this study, calculations were carried out to identify the possible initiation steps during the decomposition of the tetrazolium family of EILs. A detailed study of the extensive set of secondary reactions as well as estimation of kinetic rate parameters using ab initio methods is the subject of future studies.
3.2.2 Chemical Kinetic Model

A chemical kinetic model was constructed in order to emulate the physicochemical processes occurring in the condensed and gas phases during the decomposition of the EILs, and provide inputs to the optimization module. The model was developed by generating two sets of conservation equations for the condensed-phase and the gas-phase regions by treating them with a lumped parameter analysis. A schematic view of the control volumes in the condensed and gas phases is shown in Figure 3.4. The principal assumptions of the model are as follows. The decomposition of the compound is assumed to occur only in the condensed phase, and gas-phase reactions are not considered; products of the condensed-phase reactions are treated as gases dissolved in liquid; pressure is assumed to be constant in the gas phase due to exposure of the gas phase to purge gases at atmospheric pressure; the concentration gradients in the condensed phase are ignored due to the small volume of the samples; and lastly, radicals generated in the condensed phase are assumed to react immediately prior to desorption into the gas phase.

Mass loss in the condensed phase occurs only due to conversion of product species from liquid to gas phase. Therefore, the sample mass conservation in the condensed phase is governed by the following equation

$$\frac{d}{dt}(m_{c,cv}) = -\sum_{i=1}^{N} m_{i-g,i}$$  \hspace{1cm} (3.1)
where \( m_{c,cv} \) is the mass in the condensed phase, and \( \dot{m}_{l-g,j} \) is the mass conversion rate from liquid to gas of the \( i \)th species, and \( N \) is the total number of species in the condensed phase.

![Figure 3.4: Schematic of condensed-phase and gas phase regions and related components.](image)

The rates of conversion from liquid to gas for individual species is given by

\[
\dot{m}_{l-g,i} = (k_{l-g,i}) m_{c,i} = (k_{l-g,i})(V_c W_i C_i)
\]

(3.2)

where \( k_{l-g,i} \) is the conversion rate from liquid to gas of the \( i \)th species, \( m_{c,i} \), \( C_i \), and \( W_i \) are the mass, concentration, and the molecular weight of the \( i \)th species, respectively, and \( V_c \) is the volume of the condensed phase. The parent compounds, such as hydroxy-ethyl-hydrazine, and the larger molecular weight species, such as 4-amino-triazole were assumed to be confined to the condensed phase as they remained undetected in the gas phase by both diagnostic tools. The smaller molecular weight species, such as HNO_3,
HCl, NH₃, H₂O, N₂O, CO₂, and N₂ were allowed to emerge into the gas phase. The conversion rate from liquid to gas of the \( i \)th species can be stated as

\[
k_{l-g} = A_{l-g} \exp \left( -\frac{E_{a,l-g}}{R_u T} \right)
\]

(3.3)

where \( A_{l-g} \) and \( E_{a,l-g} \) are the rate constants for the liquid-to-gas conversion process, \( R_u \) is the universal gas constant, and \( T \) is the sample temperature at that particular instant. Although enough data was not found in the literature describing the conversion rates from liquid to gas at comparable temperatures, the integrated Clausius-Clapeyron equation was used to model the phenomenon as an evaporative process [8]. Thus, the activation energy for the process \( (E_{a,l-g}) \) was assumed to be related to the heat of vaporization of HCl, HNO₃, and H₂O. For the rest of the gases with small molecular weights, and low boiling points, their low solubility in the condensed phase dictated an immediate release into the gas phase after generation.

The conservation of mass for the individual species in the condensed phase yields the following expressions

\[
\frac{d}{dt} \left( m_{c,i} \right) = \dot{\omega}_{c,i} V_c W_i \omega_{l-g} - \dot{m}_{l-g,i}
\]

(3.4)

\[
\dot{\omega}_{c,i} = \sum_{j=1}^{M} v_{ji} k_j \prod_{j=1}^{N} C_j^{v_{ji}}
\]

(3.5)

where \( \dot{\omega}_{c,i} \) is the net production rate of the \( i \)th species, \( M \) is the total number of reactions in the condensed phase, \( N \) is the total number of species in the condensed phase, \( v_{ji} \) is the stoichiometric coefficient of the reactants in the \( i \)th reaction for the \( j \)th species, and \( k_j \) is
the rate coefficient of the $i$th reaction. The rate constant of the $i$th reaction can be expressed as

$$k_i = A_i \exp\left(-\frac{E_{a,i}}{R_a T}\right)$$  \hspace{1cm} (3.6)

where $A_i$ and $E_{a,i}$ are the pre-exponential factor and activation energy, respectively, for the $i$th reaction.

As the products evolve into the gas phase, thorough mixing with the purge gas $N_2$ ensures that concentration gradients are absent in the control volume. Hence, the following set of governing equations govern mass and species conservation in the gas phase

$$\frac{d}{dt}(m_{g, cv}) = \sum_{i=1}^{N} \dot{m}_{l-g,i}$$  \hspace{1cm} (3.7)

$$\frac{d}{dt}(m_{g, i}) = \dot{m}_{l-g,i}$$  \hspace{1cm} (3.8)

where $m_{g, cv}$ is the mass in the gas phase, $m_{g, i}$ is the mass of the $i$th species in the gas phase, and $\dot{m}_{l-g,i}$ is the mass conversion rate from liquid to gas of the $i$th species. The concentrations in the condensed phase and the masses of the species in the gas phase were recovered by solving the set of ordinary differential equations 3.1–3.8 by utilizing LSODE [9]. The masses of products in the gas phase were converted to normalized mole fractions, the normalization being done with respect to the initial sample mass in the condensed phase, for ease of comparison with experimental data in the optimization module.
3.2.3 Optimization Scheme

The selection of a suitable method for determination of optimal reaction rate parameters for a reaction mechanism involves an objective function is generally highly structured, with multiple peaks and valleys. A significant drawback of the traditional gradient-based algorithms [10] remains in their tendency to converge to the next available local optima of the objective function, which poses a serious threat to cases where the objective function is a complex landscape. The results obtained by optimization are also largely dependant on the initial guess of the solution. Alternately, genetic algorithms (GA) are particularly suited for optimizing objective functions with the above-mentioned characteristics [11], as they are able to depart from the local optima due to their inherent randomness.

GAs typically start with a randomly initialized population chosen from the parameter space and implement a probabilistic search using domain-independent genetic operators to produce a new population of solutions, which ‘evolve’ through reproduction between relatively ‘good’ solutions. The ‘bad’ solutions die off after every iteration. An objective fitness function serves the role of natural environment during this selection process. These evolutionary algorithms have been successfully implemented in the recent past [12,13] to extract optimum chemical kinetic rate constants for various combustion mechanisms. A public domain GA-based function optimization package, PIKAIA [14], was utilized for optimizing the reaction rate parameters in this study. Instead of the generic binary-coding used in most GAs, the encoding within PIKAIA is based on a decimal alphabet made of the 10 integers, 0 through 9. The input parameters for the GA,
namely the population-size, number of generations, crossover mode and probability, mutation rates, and elitism modes are enlisted in Table 3.1. The sole change implemented in the PIKAIA module was the introduction of a non-uniform mutation operator. The fitness function governing the evolutionary process in the GA was defined as the inverse of the objective function, $\chi^2$, given by

$$\chi^2 = \sum_{i=1}^{N} \sum_{j=1}^{M} \left[ \frac{X_{ex}(T_i,t_j) - X_{theo}(T_i,t_j)}{\sigma_{i,j}} \right]^2$$

(3.9)

where $T_i$ denotes the $N$ set temperatures at which the experiments were conducted for that particular compound, $t_j$ denotes the time of acquiring the $i$th data point, the total number being $M$ at each temperature, $X_{ex}$ and $X_{theo}$ represent the experimental and theoretical normalized mole fractions of the major species in the gas phase, namely HNO$_3$ for AN and 4ATN, HCl for 4ATCl, and H$_2$O for HEHN, and $\sigma_{i,j}$ denotes the standard deviation in the experimental data.

Table 3.1: Governing parameters for the GA module.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Population size</td>
<td>200</td>
</tr>
<tr>
<td>Generation number</td>
<td>500</td>
</tr>
<tr>
<td>Probability of crossover</td>
<td>0.85</td>
</tr>
<tr>
<td>Initial mutation rate</td>
<td>0.05</td>
</tr>
<tr>
<td>Minimum mutation rate</td>
<td>0.0005</td>
</tr>
<tr>
<td>Maximum mutation rate</td>
<td>0.25</td>
</tr>
<tr>
<td>Reproduction plan</td>
<td>1 (full generational replacement)</td>
</tr>
<tr>
<td>Elitism parameter</td>
<td>0 (off)</td>
</tr>
</tbody>
</table>

The computational procedure leading to the retrieval of the optimal kinetic rate parameters for a particular compound is as follows. The experimentally derived normalized species mole fractions at pre-set temperatures, and the parameter bounds for
the activation energies and the pre-exponential factors for the primary reaction mechanism are provided as inputs to the optimization module. The PIKAIA module randomly constructs a population within the provided parameter space. Thereafter, the normalized species mole fractions for parameters corresponding to each member of the population are theoretically generated by solving Eqs. 3.1–3.8. The fitness function defined by Eq. 3.9 is then used to calculate the fitness of the entire population, and a new set of offspring are produced from this parent population through the application of crossover and mutation operators. The parent and the offspring populations are ultimately merged to construct the next generation based on selected sampling techniques. The evolutionary process continues until the preset number of generations is reached. Typically, the use of 500 generations, in conjunction with non-uniform mutation operator has been found to yield satisfactory results for the targeted parameters starting with a wide parameter range. The use of a larger number of generations does not provide a justifiable increment in the fitness of the population in exchange of the entailed computational cost.

3.3 References


Chapter 4

IMIDAZOLIUM SALTS

Rapidscan FTIR spectroscopy and time-of-flight mass spectrometry were utilized to study thermal decomposition of three imidazolium-based ionic liquids, with 1-ethyl-3-methyl-imidazolium (emim) as the cation, and NO$_3^-$, Cl$^-$, and Br$^-$ as the anions, as depicted in Fig. 4.1.

![Structures of 1-Ethyl-3-Methyl-Imidazolium nitrate, 1-Methyl-Imidazole and 1-Ethyl-Imidazole](image)

Figure 4.1: Structures of 1-Ethyl-3-Methyl-Imidazolium nitrate, 1-Methyl-Imidazole and 1-Ethyl-Imidazole

4.1 Thermal Decomposition of [emim]Br and [emim]Cl

Numerous screening attempts were made in order to identify the temperature at which rapid thermolysis occurred of the two imidazolium halides [emim]Br and [emim]Cl. These two salts have melting points of 76.5 and 77-79°C, respectively. Evolution of gas-phase species at a rapid rate began to occur at temperatures near 390°C; at 350°C, no gaseous species were detected during a 5s time interval. The sample remained on the foil, and it showed no discoloration. Using a sample size of approximately 0.5mg, Fig. 4.2 shows the evolution of species from thermolysis of [emim]Cl at a temperature of 425°C.
As the two heaters came in contact, one notes a slight base-line shift in the spectral transmittance that serves as the indicator for the beginning of heating. Both ionic liquids are also very hygroscopic, which makes it very difficult to study the thermolysis behavior of pure compounds. Figure 4.2 shows that the band features evolve quite evenly and very early. Starting near 3,125 cm\(^{-1}\), the \(\equiv\text{C-H}\) stretching frequency is clearly observed in file 9. Near 2,980 and 2,950 cm\(^{-1}\), \(-\text{C-H}\) stretching frequencies are also observed. The absence of an \(\text{N-H}\) stretch near 3,500 cm\(^{-1}\) is also noted. In the range from 1,500 to 600 cm\(^{-1}\), the spectra are very complex and definite assignment is difficult without the use of calibration compounds.

To aid in the interpretation of the acquired spectra, Figure 4.3 shows the typical spectral transmittances of \(1\text{-H}-\text{methylimidazole (1-MeIm), 1-H-Imidazole (1-Im), N-ethylimidazole (N-EtIm), chloromethane (MeCl) and chloroethane (EtCl)\). The \(N\)-EtIm of 99.5\% purity was acquired from ww.vwr.com and used without further purification. The other compounds (\(>98\%\) purity) were acquired from Sigma-Aldrich and also used without further purification.
The 1-MeIm exists as a liquid under standard conditions, with a melting point of -60°C and a boiling point of 198°C. The FTIR spectrum of 1-MeIm in Fig. 4.3 was acquired in the thermolysis test rig at 281°C and 1 atm pressure under a nitrogen environment. A comparison between the known and observed rovibrational frequencies of various bonds in the molecule is presented in Table 4.1. All the vibrational modes in
the imidazole molecule are IR active and have been well-documented by Tatara et al. [1] using computational methods.

![FTIR spectra of [emim]Cl, N-EtIm, 1-MeIm, 1-Imidazole, Chloromethane and Chloroethane for identification of thermolysis products.](image)

The assignment of frequencies below 1,600 cm$^{-1}$ was in excellent agreement with previous work done by Sadlej et al. [2]. The $\equiv$C–H in-plane stretching vibrational frequency was slightly over-predicted. However, the C=C, C=N and C–H bending-in-plane (bip) stretching vibrational frequency bands matched perfectly with the computed frequencies. The C–N(1)–C bip and the C–H bending-out-of-plane (bop) frequencies were also well-predicted. In addition to the imidazole ring, the frequency of the C–H
stretch in the terminal methyl group was confirmed in a review of available data by Socrates [3].

Table 4.1: Comparison of rovibrational frequencies of 1-MeIm with standard data published in the literature [1-3].

<table>
<thead>
<tr>
<th>Description</th>
<th>Frequency (cm(^{-1})) (predicted)</th>
<th>Frequency band (cm(^{-1})) (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(=\text{C–H str} )</td>
<td>3273 / 3245 / 3242</td>
<td>3200-3100</td>
</tr>
<tr>
<td>C–H str in methyl group</td>
<td>2975-2950</td>
<td>2980-2940</td>
</tr>
<tr>
<td>C=(\text{C str} )</td>
<td>1555</td>
<td>1550-1475</td>
</tr>
<tr>
<td>C=(\text{C, C=N str, C–H bip} )</td>
<td>1496</td>
<td>1550-1475</td>
</tr>
<tr>
<td>C=(\text{C, C=N str} )</td>
<td>1430</td>
<td>1440-1400</td>
</tr>
<tr>
<td>C–N str, C–H bip</td>
<td>1282</td>
<td>1300-1200</td>
</tr>
<tr>
<td>C=(\text{C, C=N str} )</td>
<td>1092</td>
<td>1100-1060</td>
</tr>
<tr>
<td>C–((\text{N(1)}–\text{C bip, C–H bip}) )</td>
<td>1073</td>
<td>1100-1060</td>
</tr>
<tr>
<td>C–((\text{N(1)}–\text{C bip}) )</td>
<td>908</td>
<td>930-880</td>
</tr>
<tr>
<td>C–(\text{H bop} )</td>
<td>808</td>
<td>780-850</td>
</tr>
<tr>
<td>C–(\text{H bop} )</td>
<td>729</td>
<td>740-700</td>
</tr>
</tbody>
</table>

Examination of the spectral transmittances in Fig. 4.3 of the \(N\)-EtIm and 1-Im reveals significant similarities with 1-MeIm, in particular for the \(N\)-EtIm. The \(N\)-EtIm is a liquid at room temperature and has a listed boiling temperature of 79-81°C; studies here were conducted at 200°C. 1-Im has a melting point of 89-91°C and a boiling temperature of 257°C; studies here were conducted at 281°C. Clearly, the –C–H stretching frequency near 2,980 cm\(^{-1}\) must be associated with the carbon atom in the ethyl group attached to the ring nitrogen. Many of the observed bands from 1,600 to 600 cm\(^{-1}\) are associated with various vibrational modes of the ring as discussed previously; strengths of bands
associated with either the ethyl or methyl group appear to be moderately weak at best. Differences between 1-MeIm and \(N\)-EtIm are noted in the region from 1,460–1,325 cm\(^{-1}\). Additionally, the heterocyclic compounds were also subjected to thermolysis at higher temperatures, but it is clear that evaporation dominates and decomposition does not occur within the short residence time within the confined volume between the two heaters. The MeCl and EtCl are also highly stable compounds, as revealed in numerous decomposition studies [4]. In addition, the tests carried out using the FTIR spectrometer were found to be highly repeatable, with variations between transmittances staying below 15% for any compound. The variations were found to be largely caused by the difficulty in accurately selecting the exact mass due to the crystalline nature of the studied compounds.

Based on the results in Figs. 4.2 and 4.3, the thermolysis behavior of [emim]Cl involves two pathways. The first pathway involves the formation of MeCl and \(N\)-EtIm, whereas the second pathway involves the formation of EtCl and 1-MeIm. Proton transfer does not occur directly to form HCl, which is a highly IR-active species.

To verify the above findings using FTIR spectroscopy, results from ToF spectrometry are shown in Figs. 4.4 and 4.5. Averaging 10 consecutive spectra was found to provide a high degree of accuracy with the standard deviation of the intensities staying below a value of 5 units. The standard deviation at m/z=96 at 0.02s for [emim]Cl was found to be 3.7. The mass spectra in Figs. 4.4 and 4.5 appear at a first glance as quite complicated due to the fact that a high ionization potential is used. However, the use of such high ionization potential allows comparison with available mass spectral data bases for a wide range of chemical compounds. Figure 4.4 shows that the evolution of various species initially occurs at a fast rate, and then decays quickly. A closer inspection reveals
the abundance of EtIm at m/z=96 over MeIm at m/z=82. Examination of the m/z spectrum for MeCl in Fig. 4.5 shows that the fragmented charged species include largely the CH$_3^+$ group and is thus the major contributor to m/z=15 for [emim]Cl. The fragmentation of 1-MeIm also produces the CH$_3^+$, but to a much smaller extent compared to MeCl. The fragmentation of EtCl produces to a large extent many of the hydrocarbon ions near m/z=28; that is, the charge is largely carried with the ethyl group, and to a much smaller extent with the chlorine ion near m/z=35 or 37. Ionization of N-EtIm also produces charged species near m/z=28, but also large ions at m/z=68 and 81, corresponding to a loss of C$_2$H$_4$ and CH$_3$ groups, respectively. The appearance of m/z=54, 52, 42, and 41 suggests that the ring does fracture as well, largely due to the high ionization potential. The scope of this work does not permit detailed discussion of the fragmentation pathways, but the reader is directed to similar works [5]. Additionally, the mass spectra acquired by the ToF mass spectrometer of MeCl, EtCl, and 1-MeIm are in excellent agreement of those listed in the NIST data base [6]. Finally, metastable peaks are lacking in the spectra shown [7].
Figure 4.4: Mass spectra from rapid thermolysis of [emim]Cl at 420°C and 1atm Ar, He and residual air extracted at 0.02, 0.07, 0.12, 0.17, 0.22s (average of 10 spectra).

With the availability ToF mass spectra shown in Figs. 4.4 and 4.5, the thermolysis behavior [emim]Cl is quite clear: the dominant pathway involves the methyl group to form MeCl and N-EtIm. There is an abundance of CH$_3^+$ and MeCl at m/z=50 and 52, and there is an abundance of N-EtIm, 1-Im, m/z=81, as well as m/z=26-29.
Figures 4.6 and 4.7 show several ToF mass spectra from the rapid thermolysis of [emim]Br. Although not included here, the FTIR spectra are strikingly similar to those obtained from thermolysis of [emim]Cl. Inspection of Figs. 4.6 and 4.7 reveals that proton transfer does not occur to form HBr, but instead the decomposition pathways are equivalent to those of [emim]Cl. Here we include MeBr and EtBr mass spectra from the NIST data base [6]. Close review of the mass spectra and comparison with [emim]Cl reveals that the only changes in m/z positions are those associated with Br-containing charged species.

Figure 4.5: Mass spectra of [emim]Cl, 1-MeIm, N-EtIm, chloroethane, and chloromethane for identification of thermolysis products.
4.2 Thermal Decomposition of [emim]NO₃

[emim]NO₃ is a stable crystalline, hygroscopic solid under standard conditions, with a melting point of 39°C and a boiling point of around 300°C. Rapid thermolysis, defined by almost complete decomposition of the material in less than 5 seconds, was achieved above temperatures of 390°C. A small amount of a carbonaceous residue remains on the aluminum foil.
Figure 4.8 shows five consecutive spectra during rapid thermolysis of [emim]NO$_3$. The spectra were taken in time intervals of 50 ms at a temperature of 435°C and pressure of 1 atm. The evolution of products started with the twelfth spectrum, which was approximately 0.1s into the event. The rovibrational modes of various gaseous molecules that are easily identifiable in the spectra are listed in Table 4.2. Strong absorption bands of H$_2$O, CO$_2$, CO, NO, N$_2$O, CH$_3$OH and species containing a C=O bond are marked on the sixteenth spectrum. Aldehydes and ketones normally show strong features in the range from 1,700 to 1,750 cm$^{-1}$. H$_2$CO is also present, as its rovibrational features near 2,700 cm$^{-1}$ are visible. The spectra also contained the rovibrational bands

Figure 4.7: Mass spectra of [emim]Br, N-EtIm, 1-MeIm, Imidazole, C$_2$H$_5$Br, and CH$_3$Br for identification of thermolysis products.
seen in the spectra from 1-MeIm and \(N\)-EtIm. The presence of lines in the region 3,500-3,750 and 1,595 cm\(^{-1}\) was in part due to atmospheric water vapor in the background, which could not be completely eliminated due to high humidity levels in the laboratory. Additionally, the N-H stretch near 3,500 cm\(^{-1}\) is absent.

![FTIR spectra](image)

Figure 4.8: FTIR spectra showing the evolution of species from rapid thermolysis of [emim]NO\(_3\) at 435°C and 1 atm N\(_2\).
Figure 4.9 is a superposition of spectra obtained from thermolysis of [emim]NO$_3$ at 435°C, 1 atm in a N$_2$ environment, 1-MeIm at 281°C, 1 atm, N-EtIm and 1-Im. While comparing the spectra, the broadening of individual bands due to the elevated temperature of decomposition of [emim]NO$_3$ is evident. From 2800 to 3200 cm$^{-1}$, there is a noticeable agreement in the $\equiv$C-H stretch and the C-H stretch in the $-\text{CH}_3$ group between the spectra. Two distinct bands for the C=C and C=N stretch from 1,550 to 1,400 cm$^{-1}$ were easily recognizable. From 1,300 to 1,200 cm$^{-1}$, the frequencies for the C=N stretch and the C–H bip matched perfectly in the spectra. The C–N(1)–C bip with its prominent bands in 1,100-1,060 cm$^{-1}$ and 930-880 cm$^{-1}$ was noticeable. In addition, two C–H bip frequency bands around 800 cm$^{-1}$ and 730 cm$^{-1}$ were detected. The striking similarity between the spectra corroborated the formation of 1-MeIm and N-EtIm as products during thermolysis of [emim]NO$_3$. There are some differences in the details of the individual bands. These differences are attributed to the presence of a wide range of smaller molecular weight species in the gas-phase region in the case of thermolysis of

Table 4.2: Vibrational wavenumbers of experimentally observed gaseous products.

<table>
<thead>
<tr>
<th>Description</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>3657, 1595</td>
<td>[8]</td>
</tr>
<tr>
<td>HCN</td>
<td>3311, 712</td>
<td>[8]</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>2843, 2782, 1500, 1746,1249</td>
<td>[8]</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2349, 667</td>
<td>[8]</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>2224, 1285</td>
<td>[8]</td>
</tr>
<tr>
<td>NO</td>
<td>1875</td>
<td>[9]</td>
</tr>
<tr>
<td>CO</td>
<td>2143</td>
<td>[8]</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>3681, 3000, 2960, 2844, 1477, 1345, 1033</td>
<td>[8]</td>
</tr>
</tbody>
</table>
[emim]NO$_3$ causing broadening of lines, whereas broadening of lines of 1-MeIm is caused by N$_2$ and by 1-MeIm itself.

Figure 4.9: FTIR spectra of [emim]NO$_3$, N-EtIm, 1-MeIm, and Imidazole for identification of thermolysis products.

Results from the use of the ToF MS provide additional details on the rapid thermolysis behavior of [emim]NO$_3$. Figure 4.10 shows the temporal evolution of m/z spectra acquired at 1000Hz, and averaging of ten spectra. Hence the temporal resolution is 0.01 s. Examination of Fig. 4.10, along with Fig. 4.11, reveals that a nucleophilic transfer is likely to primarily involve the methyl group for two reasons. First, the extent of N-EtIm evolved is relatively large compared to 1-MeIm. Second, the extent of ionized CH$_3^+$ is relatively small. Third, subsequent reactions near the methyl group produces m/z=126, which is believed to be a methoxy-EtIm, involving H-abstraction from the C(2), C(4) or C(5) carbon on the ring. The methoxy itself is an intermediate that may also abstract H-atoms from other hydrocarbons, forming in part the small amount of MeOH.
that is detected. Fragmentation of this molecule yields the methoxy-MeIm as well as the methoxy-Im. Species near m/z=28 originate largely from fragmentation of N-EtIm, since HCN formation due to ring fracture is absent from the FTIR spectra; a strong peak at 712 cm\(^{-1}\) would otherwise be visible. Additionally, the peaks at m/z=56, 57, and 58 are likely caused by various aldehydes including acrolein H\(_2\)CCHCHO at m/z=56 and propionaldehyde H\(_3\)CCH\(_2\)CHO at m/z=58. Fragmentation of these aldehydes produces an appreciable fraction of the charged species in the range from m/z=25 to 30, but the parent molecule is also detected by the TOFMS.

Figure 4.10: Mass spectra from rapid thermolysis of [emim]NO\(_3\) at 420°C and 1atm Ar, He and residual air extracted at 0.02, 0.07, 0.12, 0.17, 0.22s (average of 10 spectra).
The complex structure of [emim]NO$_3$ and the extent of secondary reactions within the condensed phase make the prediction of the initial chemical kinetic steps under high temperatures a challenging task. Based on the results from decomposition of [emim]Br and [emim]Cl, the pathways are likely to involve the same initial steps. That is, nucleophilic transfer yields:

I.  [emim]NO$_3$ $\rightarrow$ CH$_3$ONO$_2$ + N-EtIm

It is the dominant pathway, with secondary steps initiated by

\[ \text{CH}_3\text{ONO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]

\[ \text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_2\text{O} + \text{HONO} \]

H-atom abstraction from one of the carbon atoms (e.g., from C(2)) on the ring follows quickly to yield the detected 1-ethyl-2-methoxy-1H-imidazole (EtMeOIm) at m/z=126

Figure 4.11: Mass spectra of [emim]NO$_3$, N-EtIm, 1-MeIm, and Imidazole for identification of thermolysis products.
NO₂ + N-EtIm → HONO + 1-ethyl-1H-imidazol-2-yl

CH₃O + 1-ethyl-1H-imidazol-2-yl → EtMeOIm

The carbon atom to which the methoxy is attached is not certain. Subsequent reactions between methoxy and nitrate also occur, to produce the detected water vapor, nitrous oxide, nitric oxide, methanol, carbon monoxide and dioxide. Detailed discussions of those are beyond the scope of this paper, and are generally contained in larger reaction mechanisms discussed by many authors, including gas-phase reactions [10,11] as well as condensed-phase reactions with consideration to the cage effect [12].

The second and less important pathway involves transfer of the ethyl group:

II. [emim]NO₃ → C₂H₅ONO₂ + 1-MeIm

A wide variety of secondary steps take place, but products detected in the gas phase having a large molecular weight include the aldehydes, which are believed to be at m/z=44, 56, 57 and 58 as well as the strong presence of the C=O band at 1,730 cm⁻¹. Important steps include

C₂H₅ONO₂ → C₂H₅O + NO₂

C₂H₅O + NO₂ → CH₃CHO + HONO

A similar H-atom abstraction from a carbon atom on the ring (e.g. from C(2)) yields 1-methyl-2-ethoxy-1H-imidazole (MeEtOIm), with the same m/z value as 1-ethyl-2-methoxy-1H-imidazole (EtMeOIm).

NO₂ + 1-MeIm → HONO + 1-methyl-1H-imidazol-2-yl

C₂H₅O + 1-methyl-1H-imidazol-2-yl → MeEtOIm
It is believed that HNO$_3$, by deprotonation form C(2), C(4), or C(5), is not formed since some of it would be detected by the FTIR due to its strong IR-activity; ToFMS does not readily detect the HNO$_3$, however [13].

The preferential nucleophilic transfer between the methyl group and the nitrate group over the ethyl group and the nitrate group needs further elucidation. Molecular dynamics simulations by Voth et al. [14,15] using 216 ionic pairs and under working conditions of atmospheric pressure and 400K, showed that [emim]NO$_3$ was a strongly coupled ionic system with nitrate anions concentrated around the highly positive C(2)-H(2) bond. A closer inspection revealed that the nitrate ions reside nearer to the methyl group compared to the ethyl group. A study of [emim]Cl using ab initio techniques by Turner et al. [16] suggested that the chloride anion, located in the plane of the ring was located in the vicinity of the methyl group. However, a similar study on [emim]Br revealed that the bromide anion was most stable above the plane of the ring. Despite conducted at lower temperatures, these simulations of the most stable structures of [emim]NO$_3$ and [emim]Cl may provide information on the potential or most probable location of the atoms or molecular groups involved in the initial reaction steps in the condensed phase.

4.3 References


Chapter 5

AMINO-TRIAZOLIUM SALTS

The thermal decomposition of two energetic ionic liquids, formed by pairing the 4-amo-1,2,4-triazolium cation with chloride (4ATCl), and nitrate (4ATN) anions, was studied by confined rapid thermolysis. Rapidscan FTIR spectroscopy and time-of-flight mass spectrometry were utilized in conjunction to identify the products of decomposition. Decomposition was achieved under heating rates of 2,000K/s and temperatures up to $340^\circ$C for 4ATCl and 4ATN in an ambient inert gas at 1 atm. Whereas a proton transfer from the N$_1$ position primarily initiated decomposition in 4ATCl, the amino group was found to primarily participate in the initiation reaction in case of 4ATN. The parent molecule, 1-$H$-1,2,4-triazole, was detected during subsequent reactions. Ring fracture was also evident from the presence of HCN. The highly energetic nitrate salt formed copious amounts of H$_2$O and N$_2$O through multiple secondary reaction channels.

The salt of primary interest is 4-amino-1,2,4-triazolium nitrate (4ATN). Since the complexity of the secondary reactions is considerably higher for the oxygen-rich anion, the relatively simple salt 4-amino-1,2,4-triazolium chloride (4ATCl) has been studied initially. Extensive studies have also been conducted on the building blocks for these complicated molecules such as 4-amino-1,2,4-triazole (4AT), 3-amino-1,2,4-triazole (3AT), and 1-$H$-1,2,4-triazole (1TA), as shown in Fig. 5.1.
5.1 Thermal Decomposition Pathways of 4ATCl

4ATCl was procured from Sigma-Aldrich and subjected to confined rapid thermolysis without further purification. The salt is a white crystalline solid with a melting point of 147–148°C. Approximately 0.5mg of the sample was found to rapidly decompose above temperatures of 260ºC, leaving a small amount of solid yellowish residue on the aluminum foil.

The gaseous products from the decomposition of 4ATCl under 340ºC and an inert atmosphere of N₂ are shown in Fig. 5.2. The products identified in the FTIR spectrum are HCl, HCN, NH₃, and NH₄Cl. The vibrational frequencies of the experimentally observed species are listed in Table 5.1. The CO₂ detected was attributed to trace amounts left in the thermolysis chamber due to inadequate purging. Around 3,500 cm⁻¹, a strong N-H absorption band was observed. In order to identify the source of the band, 4AT (99% pure), 3AT (95% pure), and 1TA (98% pure) were acquired from Sigma-Aldrich and studied under temperatures around 340ºC. All the three compounds are crystalline white solids.
Table 5.1: Vibrational wavenumbers of experimentally observed gaseous products.

<table>
<thead>
<tr>
<th>Description</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>3657, 1595</td>
<td>[1]</td>
</tr>
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<td>HCN</td>
<td>3311, 712</td>
<td>[8]</td>
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<tr>
<td>HCl</td>
<td>2886</td>
<td>[8]</td>
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<tr>
<td>NH$_3$</td>
<td>3337, 1627, 950</td>
<td>[8]</td>
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<tr>
<td>HNO$_3$</td>
<td>3551, 1710, 1326, 879</td>
<td>[2]</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2349, 667</td>
<td>[8]</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>2224, 1285</td>
<td>[8]</td>
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<tr>
<td>NO</td>
<td>1875</td>
<td>[3]</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>1617, 1320</td>
<td>[2]</td>
</tr>
</tbody>
</table>

Figure 5.2: FTIR spectrum of species from rapid thermolysis of 4ATCl at 340°C and 1 atm N$_2$.

Figure 5.3 shows a comparison of the transmission spectra from the thermolysis of the three compounds. The difference between 3AT and 1TA is evident in the region
around 3,500 cm\(^{-1}\), where two bands due to a symmetric and an asymmetric stretch in the –NH\(_2\) group distinguishes 3AT. Similar stretches due to the presence of the –NH\(_2\) group are clearly visible in gas-phase transmission spectra from aniline. Though the =C–H stretching frequency is observed for both of these heterocyclic compounds around 3,125 cm\(^{-1}\), dissimilarities exist between 1,650 to 600 cm\(^{-1}\). The C–N stretches at 1,625 cm\(^{-1}\) and 1,550 cm\(^{-1}\), present in the gas-phase FTIR spectrum of 3AT is absent in case of 1TA.

![Figure 5.3: Comparison of FTIR spectra of 4AT, 3AT and 1TA.](image)

Whereas 3AT and 1TA were found to evaporate without decomposition, 4AT decomposed significantly to yield NH\(_3\), HCN and a heterocyclic compound. To assist in the identification of species evolving during the decomposition of 4AT, Fig. 5.4 shows the results from the thermolysis of 4AT under an inert atmosphere of Ar and He, acquired
under an ionization potential of 70eV and mass spectra acquisition at 1000Hz. Averaging 10 consecutive spectra was found to provide a high degree of accuracy with the standard deviation of the intensities staying below a value of 5 units. Besides the compounds detected by FTIR spectroscopy, N$_2$ was produced in profuse quantities.

The heterocyclic compound mentioned earlier was found to have a molecular weight of 69, and was established as 1TA. The IR-active vibrational modes of the triazole molecule have been documented by El-Azhary et al. [4] and are summarized in Table 5.2. The predicted C–N stretches at 1,524, 1,407, 1,255, and 1,175 cm$^{-1}$ were recognizable in the spectrum. The C–H deformation or bending-in-plane frequencies were identified too.

Figure 5.4: Mass spectrum from rapid thermolysis of 4AT.
In order to clearly identify the products of decomposition of 4ATCl in the region 1,500-600 cm$^{-1}$, spectra from 4ATCl, 4AT, 1TA, and NH$_4$Cl are compared in Fig. 5.5. 99.9% NH$_4$Cl from Sigma-Aldrich was heated to 525ºC in order to obtain its gas-phase spectrum. NH$_3$, HCN, and NH$_4$Cl are clearly discernable in the spectrum from 4ATCl. The presence of the NH$_3$ rotational lines from 1,200 to 750 cm$^{-1}$ proved to be a hindrance in clearly identifying the vibrational bands from 1TA in that region. However, the N-N stretch at 1,042 cm$^{-1}$ and the C-H wagging frequencies were recognized easily. Also visible was the ring torsion frequency at 710 / 706 cm$^{-1}$. The source of NH$_3$, present among the decomposition products of 4ATCl, could be attributed to either 4AT or NH$_4$Cl. In order to resolve this ambiguity and to explain the thermolysis of 4ATCl, the products were further analyzed by ToF mass spectrometry.

Table 5.2: Comparison of rovibrational frequencies of 1TA with standard data [4]

<table>
<thead>
<tr>
<th>Description</th>
<th>Frequency (cm$^{-1}$) (predicted)</th>
<th>Frequency band (cm$^{-1}$) (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>=C–H str</td>
<td>3157 / 3149</td>
<td>3175-3100</td>
</tr>
<tr>
<td>C–N str, C–H def</td>
<td>1524</td>
<td>1540-1480</td>
</tr>
<tr>
<td>C–N str, C–H def</td>
<td>1407</td>
<td>1475-1400</td>
</tr>
<tr>
<td>C–N str</td>
<td>1265 / 1255</td>
<td>1300-1240</td>
</tr>
<tr>
<td>C–N str, C–H def</td>
<td>1175</td>
<td>1190-1160</td>
</tr>
<tr>
<td>N–N str</td>
<td>1042</td>
<td>1075-1000</td>
</tr>
<tr>
<td>C–H wag</td>
<td>826</td>
<td>900-800</td>
</tr>
<tr>
<td>Ring torsion</td>
<td>710 / 706</td>
<td>740-650</td>
</tr>
</tbody>
</table>
Figure 5.5: FTIR spectra of NH$_4$Cl, 4AT, 1TA, and 4ATCl for identification of thermolysis products.

Figure 5.6 shows the results from the thermolysis of 4ATCl at 335ºC and an inert atmosphere of Ar and He. The various species are found to evolve at a fast rate and then decay immediately as the small amount of the sample is exhausted. A cursory glance at the spectra shows an abundance of HCl at m/z = 35, 36, 37, and 38. Also present are 1TA (m/z = 69) and HCN (m/z = 27). The signal at m/z = 70 was formed by the excess protonation of 1TA, due to the presence of H$^+$ ions in the flight tube of the ToFMS. The presence of atmospheric nitrogen, a species that is IR-inactive, obscured the evolution of N$_2$ during the actual decomposition of 4ATCl. The signals observed at m/z = 41, 42, and 43 were formed primarily by fragmentation of the ring due to the high ionization
potentials used. Detailed discussion of the fragmentation pathways can be found in similar works [5]. However, no signal was detected at m/z = 84 (4AT).

In order to elucidate the decomposition pathways of 4ATCl, the species evolution profiles were extracted from the FTIR spectra and displayed in Fig. 5.7. Since quantification of some of the evolved species, such as NH$_4$Cl, would be difficult owing to their tendency to condense out in the gas phase during measurement, the evolution of these species has been studied just qualitatively. After a fairly short induction period of

Figure 5.6: Mass spectra from rapid thermolysis of 4ATCl at 340°C and 1 atm Ar, He and residual air extracted at 0.02, 0.07, 0.12, 0.17, 0.22s (average of 10 spectra).
about 400 ms, HCl starts to desorb from the condensed phase at a very high rate, followed by HCN, 1TA, and NH₄Cl, after a significant delay. NH₃ appears considerably later than HCl and at a relatively slower rate.

Figure 5.7: Species evolution from rapid thermolysis of 4ATCl at 340°C and 1 atm N₂.

Pathway I: Proposed primary reaction pathway for 4ATCl

The presence of copious amounts of HCl very early in the event and relatively smaller amounts of HCN and 1TA indicate a hydrogen-transfer from the N₁ atom (pathway I), forming 4AT in the process. Though it remained undetected by the ToFMS,
4AT decomposes in the condensed phase under the applied temperatures, forming HCN, 1TA, NH₃, and N₂. NH₃, thus formed, recombines with HCl to form the detected NH₄Cl.

Pathway II: Proposed secondary reaction pathway for 4ATCl

A second, but minor reaction pathway (pathway II) involves the N₄–N bond cleavage to form 1TA and NH₂Cl, an extremely reactive species, which then proceeds to abstract hydrogen from the parent 4ATCl to form NH₄Cl. NH₂Cl was not detected in the gas phase due to its reactive nature. However, this pathway is less important, due to the lack of a suitable pathway leading to the formation of HCN. 1TA, a byproduct of the initial step of pathway II, and the most likely source of HCN, is a fairly stable molecule, and should remain intact despite the proton-scavenging capabilities of NH₂Cl.

5.2 Thermal Decomposition Pathways of 4ATN

4ATN, which is a white crystalline solid under standard conditions, has a melting point of 69ºC. Rapid thermolysis of the compound was found to occur at temperatures above 260ºC. Below that temperature, the sample remained on the foil without any
discoloration. Figure 5.8 shows the various species from thermolysis of 4ATN at 340°C and a pressure of 1 atm of N₂. The various products identified in the spectrum were HNO₃, with three strong bands from 1,700 cm⁻¹ to 900 cm⁻¹, and an overtone above 3,500 cm⁻¹, N₂O, CO₂, NO, and H₂O. Also evident are the N–H stretching frequency at 3,500 cm⁻¹, the =C–H stretch around 3,125 cm⁻¹. The presence of trace amounts of CO₂ was attributed to impurities in the sample and subsequent reactions with HNO₃. In the spectral range from 1,500 to 600 cm⁻¹, assignment was aided by calibration compounds 4AT and 1TA. Figure 5.9 shows the typical spectral transmittances of 4AT, 1TA, NH₃, and the gaseous products from 4ATN in the ‘fingerprint region’. From prior discussions, it was clear that the decomposition products of 4ATN contained the stable compound 1TA.

Figure 5.8: FTIR spectrum of species from rapid thermolysis of 4ATN at 340°C and 1 atm N₂.
The findings obtained from FTIR analysis were confirmed by ToF mass spectra. Figure 5.10 shows the evolution of species from the thermolysis of 4ATN at 335°C and 1 atm of argon and helium. The high ionization potential of 70 eV introduces certain levels of ambiguity in the spectra. The slight disadvantage is overshadowed by the ability to compare data with available mass spectral data bases. At a first glance, the copious amounts of HNO$_3$ detected from the FTIR spectra seem to be absent due to the lack of a strong peak at m/z = 63. However, previous studies [6] showed that HNO$_3$ readily decomposes under the high ionization potential used to form NO$_2^+$ (m/z = 46), NO$^+$ (m/z = 30), H$^+$ (m/z = 1) and a number of other smaller ions, which were present in the mass spectra acquired during the early stages of the event.

Figure 5.9: FTIR spectra of NH$_3$, 4AT, 1TA, and 4ATN at 340°C and 1 atm of N$_2$ for identification of thermolysis products.
The absence of a strong peak at \( m/z = 84 \) corroborates the absence of appreciable amounts of 4AT among the decomposition products. The larger peak at \( m/z = 70 \) was believed to be caused by excess protonation of 1TA (\( m/z = 69 \)) due to the presence of \( H^+ \) ions derived from fragmentation of HNO\(_3\). Tests conducted at lower pressures essentially eliminated the peak at \( m/z=70 \). The peak at \( m/z = 44 \) is attributed to N\(_2\)O, also present in the FTIR spectra. Occurrence of peaks at \( m/z = 41, 42 \) and, 43 was primarily due to the fragmentation of the ring.

Figure 5.10: Mass spectra from rapid thermolysis of 4ATN at 335°C and 1 atm Ar, He and residual air extracted at 0.02, 0.07, 0.12, 0.17, 0.22s (average of 10 spectra).
A study of the species evolution profiles, extracted from the FTIR spectra, reveals further information on the decomposition pathways of 4ATN. Figure 5.11 presents the profiles at 320°C. Similar to 4ATCl, HNO₃ was found to evolve at an extremely fast rate after a short induction period. The presence of the strongly oxidizing nitrate anion led to the formation of H₂O and N₂O, both of which evolved at a slower rate than HNO₃. Compared to 4ATCl, the major difference in the species profiles was the early evolution of 1TA, and the relatively low concentrations of HCN in the gas phase, implying an N₄-N bond scission as the primary initiation step.

![Figure 5.11: Species evolution from rapid thermolysis of 4ATN at 320°C and 1 atm N₂.](image)

The desorption of 1TA into the gas phase very early during the decomposition suggests that the transfer of a ring hydrogen to form HNO₃ is not a major pathway. Instead, the nitrate ion scavenges a proton from the amino group to form the large amounts of HNO₃ and 1TA, as shown by pathway III. The byproducts of the initiation reactions are NH₂ONO₂ and a combination of triazole and an imino radical, named 4ATz. The reactive species NH₂ONO₂ and 4ATz react through a series of steps to form H₂O and
N₂O as well as N₂. Also, deamination and successive formation of H₂O and N₂O was found to be a major reaction pathway during deamination of 4-aminotriazolium salts using nitrous acid [7].

Pathway III: Proposed primary reaction pathway for 4ATN

The variation of the initial reaction pathway due to presence of the nitrate anion needs to be clarified further. There are two probable reasons behind the formation of the protonated acids by deprotonation form two separate sites. The first of them being, the significant difference of the $pK_a$ values of HCl and HNO₃. Since HCl is a stronger acid than HNO₃, this leads to a larger basicity of the conjugate base, the nitrate anion over the chloride anion. Studies by Brill et al. [8] involving hydrohalide salts of the energetic molecule 5-amino-1\textit{H}-tetrazole illustrated the precedence of a radically different pathway of decomposition as the basicity of the halide anion was altered. Thus, similar trends can be expected in case of 4-amino-1\textit{H}-triazolium salts.
The second reason involves the molecular structure of 4ATN and 4ATCl in the condensed phase. According to crystal structures determined by Laus et al. [9], on an average, the chloride anion resides closer to the N$_1$–H, compared to the NH$_2$ group, thus increasing the probability of the formation of HCl by abstraction of the ring hydrogen during thermolysis. However, recent simulations by Cadena and Maginn [10] speculate that in case of 4ATN, the amino group is more readily accessible by the anion, as opposed to the ring hydrogens, thus providing a channel for the formation of HNO$_3$ via cleavage of the N$_4$-N bond. Similar discrepancies in initiation pathways based on different anions have been noted by Fischer et al. [11] while investigating thermal decomposition characteristics of 1,5-diamino-4-methyl-1-H-tetrazolium nitrate, dinitramide and azide. While decomposition was initiated by a proton transfer in case of the dinitramide and the azide salts to form the corresponding acids, a methyl group transfer was observed to be the initial process in case of the nitrate salt.

The secondary reaction pathway, as depicted by pathway IV, involves deprotonation at the N$_1$ position, to form nitric acid, and 4AT. Nitric acid produces the nitronium ion in the condensed phase, which produces N$_2$O and H$_2$O through deamination of 4AT. The 4H-1,2,4-triazol-4-yl radical, generated as a byproduct, abstracts a hydrogen atom from surrounding species to form the unstable 4H-1,2,4-triazole, which undergoes tautomerism to form 1H-1,2,4-triazole. The lack of significant quantities of HCN, a significant product of the decomposition of 4AT, in the gas phase spectra of 4ATN leads to the conclusion that the proposed pathway is indeed secondary.
Pathway IV: Proposed secondary reaction pathway for 4ATN

5.3 References


Chapter 6

METHYL-AMINO-TRIAZOLIUM SALTS

Thermal decomposition of the energetic ionic liquids 1-methyl-4-amino-1,2,4-triazolium iodide (Me4ATI), 1-methyl-4-amino-1,2,4-triazolium nitrate (Me4ATN), 1-amino-3-methyl-1,2,3-triazolium iodide (Me1ATI), and 1-amino-3-methyl-1,2,3-triazolium nitrate (Me1ATN) was studied by confined rapid thermolysis. Sub-milligram quantities of the compounds were subjected to decomposition under isothermal conditions achieved by initially heating the sample at rates of approximately 2000 K/s. The products formed by decomposition under the aforementioned conditions were sampled by rapidscan FTIR spectroscopy and time-of-flight mass spectrometry. Decomposition studies involving the iodide salts were carried out around 270–290ºC, whereas the nitrate salts were subjected to 320–340ºC. The amino group was found to be involved in the initiation reaction, forming copious quantities of ammonia from the iodide compounds and, N\textsubscript{2}O and H\textsubscript{2}O from the nitrate compounds. The extent of decomposition of the triazole ring was minimal at the considered temperatures.

The molecular structures of the molecules are shown in Fig. 6.1. Studies were also conducted on the building blocks for these rather complex molecules, including 4-amino-1,2,4-triazole (4AT), 1-methyl-1,2,4-triazole (1MeTA), and 1-amino-1,2,3-triazole.
6.1 Thermal Decomposition Pathways of Me4ATI

Me4ATI is a light orange crystalline solid under standard conditions, with a melting point of 101ºC [1]. Approximately 0.5 mg of the sample was rapidly thermolyzed in the temperature range of 230 to 300ºC. Figure 6.2a shows the products evolving from the decomposition of Me4ATI at a representative temperature of 270ºC and 1 atm. The vibrational frequencies of the experimentally observed species evolving from the compounds studied are listed in Table 6.1. As seen from Fig. 6.2a and Table 6.1, the major decomposition product is ammonia, with its rotational doublet near 900 cm\(^{-1}\), as well as peaks at 1626 cm\(^{-1}\) and 3336 cm\(^{-1}\). The rotational lines due to the protonated anion HI or the vibrational bands from CH\(_3\)I were not detected.
Figure 6.2: FTIR spectrum of species from rapid thermolysis of (a) Me4ATI at 270°C and 1 atm \( \text{N}_2 \), and (b) MeTA at 250°C and 1 atm \( \text{N}_2 \).

Table 6.1: Vibrational wavenumbers of experimentally observed gaseous products.

<table>
<thead>
<tr>
<th>Description</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>3657, 1595</td>
<td>[2]</td>
</tr>
<tr>
<td>HCN</td>
<td>3311, 712</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>3337, 1627, 950</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{CH}_3\text{I} )</td>
<td>2974, 1435, 1252, 882</td>
<td>[8]</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>3551, 1710, 1326, 879</td>
<td>[3]</td>
</tr>
<tr>
<td>MeONO(_2)</td>
<td>2962, 1667, 1291, 1019, 855</td>
<td>[4]</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2349, 667</td>
<td>[8]</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>2224, 1285</td>
<td>[8]</td>
</tr>
<tr>
<td>NO</td>
<td>1875</td>
<td>[5]</td>
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<tr>
<td>NO(_2)</td>
<td>1617, 1320</td>
<td>[2]</td>
</tr>
<tr>
<td>HNCO</td>
<td>3530, 2269</td>
<td>[6]</td>
</tr>
</tbody>
</table>
In order to identify the source of the rovibrational bands from 1500 cm\(^{-1}\) to 1000 cm\(^{-1}\), 1MeTA was acquired from Sigma-Aldrich and used without further purification, and the resulting FTIR spectrum of vaporized 1MeTA attained at 250\(^{\circ}\)C and 1 atm is displayed in Fig. 6.2b. 1MeTA was found to be stable under comparable conditions, as evident from the lack of detection of any smaller products, such as HCN or CH\(_3\)CN. Although the presence of the NH\(_3\) rotational lines from 1200 cm\(^{-1}\) to 750 cm\(^{-1}\) proved to be a hindrance in clearly identifying the vibrational bands from 1MeTA in that region, the presence of 1MeTA among the decomposition products of Me4ATI is recognized by the ring torsion frequency around 680 cm\(^{-1}\) and the strong band around 1500 cm\(^{-1}\). The lack of HCN among the products shows that the ring structure is intact at the applied temperatures. N\(_2\) could not be detected due to its IR-inactivity. Based on the prodigious quantities of ammonia liberated and the formation of 1MeTA, the initiation of decomposition occurs most likely through the amino group. Proton transfer does not occur directly to form HI.

To assist in the identification of species evolved during the decomposition of Me4ATI, Figs. 6.3a and 6.3b show the results from the thermolysis of Me4ATI under an inert atmosphere of Ar and He, acquired at 270\(^{\circ}\)C and 1 atm Ar, He and residual air, under an ionization potential of 70eV at 1000Hz. In order to provide better signal-to-noise ratios in the mass spectra, 10 consecutive spectra were averaged, providing a temporal resolution of 0.01 seconds. Although the mass spectrum in Figs. 6.3a and 6.3b, split in order to provide clarity, appears at a first glance as quite complicated due to the fact that a high ionization potential is used, it facilitates comparison with available mass spectral data bases for a wide range of chemical compounds [7].
The prominent peaks at m/z = 17 and m/z = 83 attest to the formation of ammonia and 1MeTA respectively. The signal at m/z = 84 was formed by the excess protonation of 1MeTA, due to the presence of H⁺ ions in the flight tube of the ToFMS. The fragmentation of the ring of 1MeTA is seen in Fig. 6.4a, with the most prominent one seen at m/z = 56, due to the loss of an HCN fragment. Similar fragments found in Fig. 6.3a substantiate the formation of 1MeTA during the decomposition of Me4ATI.

1MeTA also dimerizes to a limited extent, as seen by the peak at m/z = 166. The peak at

Figure 6.3a and b: Mass spectrum from rapid thermolysis of Me4ATI at 270°C and 1 atm Ar, He and residual air (average of 10 spectra).
m/z = 209 can be explained by the formation of methyl-iodo-triazole, produced as a by-product during the formation of ammonia from the amino group. The lack of a peak at m/z = 142 proves the absence of CH$_3$I. The peak at m/z = 28 has contributions from molecular N$_2$ as well as fragmentation of 1MeTA.

Figure 6.4a and b: Mass spectrum from rapid thermolysis of MeTA at 250°C and 1 atm Ar, He and residual air (average of 10 spectra).
The availability of the ToFMS data facilitates the determination of the decomposition pathways of Me4ATI. As postulated earlier, the presence of large quantities of ammonia and 1MeTA indicates the involvement of the amino group in the initiation stage of decomposition. The most probable initiation pathway, as shown in Scheme I, is the deamination of the Me4AT cation to form 1MeTA and NH$_2$I. Similar decomposition pathways were observed during the decomposition of 1-amino-4,5-dimethyl-tetrazolium iodide [8]. NH$_2$I being a reactive species [9], promptly reacts with the neutral 1MeTA to abstract an H-atom to form NH$_3$ and methyl-iodo-triazole. The exact location of abstraction is difficult to ascertain due to the existence of two similar locations on the ring carbon atoms (C$_3$ and C$_5$), as well as the methyl group. NH$_2$I subsequently decomposes to form NH$_3$, N$_2$ and molecular iodine. The lack of HI among the FTIR spectra or the mass spectra precludes the possibility of a proton transfer from the methyl group or the amino group as an initiation reaction. Also, due to almost
undetectable levels of CH$_3$I among the decomposition spectra, a nucleophilic transfer involving the methyl group to form CH$_3$I is neglected as a significant decomposition pathway.

6.2 Thermal Decomposition Pathways of Me4ATN

Unlike its iodide salt, the nitrate salt of the methyl-amino-triazolium cation is a clear viscous liquid with a melting point of −60°C. Thermal decomposition measured by DSC was initiated at 221°C [1]. Confined rapid thermolysis of approximately 0.5 µL of the sample was carried out at temperatures around 320°C. The hygroscopic nature of the salt made it difficult to clearly study the decomposition behavior of the compound. The sample was dried for 24 hours under vacuum (40 mtorr) and then stored in a sealed container to avoid contamination by moisture. Figure 6.5a depicts an FTIR spectrum of species from rapid thermolysis of Me4ATN at 320°C and 1 atm. Nitric acid (HNO$_3$), with several rovibrational bands from 1700 to 800 cm$^{-1}$ and an overtone above 3500 cm$^{-1}$, was immediately discernable as a major species. The other major species detected were H$_2$O, N$_2$O, and CO$_2$. Also identified were small quantities of HNCO and HCN. Figure 6.5b shows the spectrum obtained by vaporizing 1MeTA for identification of the bands in the ‘fingerprint region’. It was clear that the decomposition products of Me4ATN contained the stable compound 1MeTA, as evident from the presence of the C–H wags near 850 cm$^{-1}$, and the ring torsion near 680 cm$^{-1}$. As expected, methyl nitrate (CH$_3$ONO$_2$) was not detected among the products.
The findings obtained from FTIR analysis were confirmed by ToF mass spectra. Figure 6.6 shows a spectrum from the ToFMS acquired during the pyrolysis of Me4ATN at 320°C and 1 atm Ar, He and residual air. At a first glance, the HNO$_3$ detected from the FTIR spectra seem to be absent due to the lack of a strong peak at m/z = 63. However, previous studies [10] showed that HNO$_3$ readily decomposes under the high ionization potential used to form NO$_2^+$ (m/z = 46), NO$^+$ (m/z = 30), H$^+$ (m/z = 1) and a number of other smaller ions, which were present in the mass spectra acquired during the event. Similar to the decomposition of Me4ATI, the signal at m/z = 84 was formed by the excess protonation of 1MeTA, due to the presence of H$^+$ ions in the flight tube of the ToFMS. The peak at m/z = 44 is attributed to N$_2$O and CO$_2$, also present in the FTIR spectra. Additionally, the lack of a peak at m/z = 69 proves the absence of 1-$H$-triazole, a
by-product of the decomposition of 4-amino-triazole under similar conditions [11], hence negating the possibility of involvement of the methyl group during the initiation reaction.

Figure 6.6: Mass spectrum from rapid thermolysis of Me4ATN at 320°C and 1 atm Ar, He and residual air (average of 10 spectra).

As shown in Fig. 6.7, the species evolution profiles, extracted from the FTIR spectra acquired at 320°C, reveals further information on the decomposition pathways of Me4ATN. Although HNO₃ was found to be a major product during the decomposition of Me4ATN, its rate of evolution was significantly delayed compared to the faster rates of H₂O and N₂O. CO₂ and HCN were found to evolve at smaller quantities. The right vertical axis shows the absorbance of the band from 1100 to 1175 cm⁻¹ arising from 1MeTA. As seen from this plot, 1MeTA desorbs at a rate comparable to H₂O and N₂O from the condensed phase.
Figure 6.7: Species evolution from rapid thermolysis of Me4ATN at 320°C and 1 atm N₂.

Scheme II: Proposed reaction pathway for Me4ATN.
The nitrate anion and the complex structure of the amino-methyl-triazole results in a wide variety of reactions leading to the decomposition of Me4ATN. However, the formation of H$_2$O and N$_2$O early in the event, and the lack of methyl nitrate suggest that the initiation reaction involves the amino group. As shown in Scheme II, the initiation reaction is through an N$_4$-N bond scission to form 1MeTA and the reactive species, NH$_2$ONO$_2$. NH$_2$ONO$_2$ subsequently forms N$_2$O, H$_2$O and N$_2$ through secondary reactions with the parent molecule Me4ATN. Methyl-triazolium nitrate, formed as a byproduct during these reactions, decomposes to form the HNO$_3$ detected at a later stage, and additional 1MeTA. 1MeTA produced during the initiation and secondary steps is further reduced to a limited extent to CO$_2$, HCN, HNCO, H$_2$O and N$_2$ by the strong oxidizer, HNO$_3$.

6.3 Thermal Decomposition Pathways of Me1ATI

Me1ATI, an isomer of Me4ATI, is a light yellow crystalline solid under standard conditions. The decomposition temperatures for Me1ATI were found to be relatively similar to those of Me4ATI. Thermolysis tests were typically conducted at 290°C. Figure 6.8 shows the species evolving from rapid thermolysis at 290°C and 1 atm. As listed in Table 6.1, the principal product is ammonia, with its prominent rotational doublet and numerous rotational lines near 900 cm$^{-1}$, similar to the decomposition products of Me4ATI. Unlike Me4ATI, the lack of the reference compound 3-methyl-1,2,3-triazole (3MeTA) rendered accurately determining the peaks in the ‘fingerprint region’ difficult. However, the presence of a sharp peak at 760 cm$^{-1}$, typically attributed
to ring torsion, confirms the presence of a cyclic triazole. The presence of a \(-\text{CH}_3\) stretch near 3000 cm\(^{-1}\) indicates the possibility of the formation of 3MeTA. HCN and HI were not detected among the products. Due to overlapping of bands, it was not possible to accurately identify CH\(_3\)I in the spectra. As in the case of Me4ATI, the copious amounts of ammonia leads to the possibility of the involvement of the involvement of the amino group in the initiation reaction.

![FTIR spectrum of species from rapid thermolysis of Me1ATI at 290°C and 1 atm N\(_2\).](image)

**Figure 6.8:** FTIR spectrum of species from rapid thermolysis of Me1ATI at 290°C and 1 atm N\(_2\).

Results from the use of the ToFMS provide additional details on the rapid thermolysis behavior of Me1ATI. Figures 6.9a and 6.9b show a spectrum from the ToFMS acquired during the pyrolysis of Me1ATI at 290°C and 1 atm Ar, He and residual air. Careful observation of the spectrum reveals that m/z = 17 (NH\(_3\)) and m/z = 83 (3MeTA) are the major species. The peaks at m/z = 55, 54, 52, 42, and 27 were suspected to be formed due to fragmentation of 3MeTA. Similar to the fragmentation of 1MeTA, the large peak at m/z = 28 is partially formed by the fragmentation of 3MeTA. The major deviation from the mass spectra obtained from Me4ATI was the formation of the methyl iodide (CH\(_3\)I), evident from the peak at m/z = 142. This shows the presence of a
secondary reaction pathway through a nucleophilic methyl group transfer to the iodide anion. The smaller peaks at m/z = 209 and m/z = 166 account for methyl-iodo-triazole and the 3MeTA dimer, respectively.

Figure 6.9a and b: Mass spectrum from rapid thermolysis of Me1ATI at 290°C and 1 atm Ar, He and residual air (average of 10 spectra).
Scheme III: Proposed reaction pathway for Me1ATI

From the information revealed by the ToFMS and FTIR spectra, it is clear that the decomposition of Me1ATI proceeds primarily through a ring N1-N bond scission to form NH2I and 3MeTA. However, there exists a secondary reaction pathway, leading to the formation of CH3I and 1-amino-1,2,3-triazole (1ATA). 1ATA was found to be stable when subjected to thermolysis at 350°C. The FTIR and mass spectra of 1ATA are shown in Figs. 6.10 and 6.11, respectively. However, proton transfer to form HI is not a possibility. The NH2I formed in the initiation step reacts with 3MeTA at C4 or C5, or the methyl group to form methyl-iodo-triazole or iodo-methyl-triazole. The initiation reaction pathways and the subsequent secondary steps are shown in Scheme III. Decomposition of NH2I also takes place in a manner similar to those observed in Scheme I, forming NH3, N2, and I2.
6.4 Thermal Decomposition Pathways of Me1ATN

Me1ATN is a colorless crystalline solid with a high degree of hygroscopicity. Hence, this salt was also dried under vacuum for 24 hours and stored in a sealed desiccator. Me1ATN has a melting point of 86–88°C, and decomposition is initiated at 185°C, as measured by DSC [12]. Small quantities of the sample were thermolyzed at
temperatures near 340ºC. Figure 6.12 shows an FTIR spectrum of the gaseous products generated during thermolysis of Me1ATN at 340ºC and 1 atm. According to Table 6.1, the major species present among the decomposition products were HNO₃, H₂O and N₂O, similar to the FTIR spectra obtained from Me4ATN. Besides these principal species, smaller quantities of CO₂, NO₂, and HNCO were also detected. Though it was difficult to exactly ascertain the presence of 3MeTA, the band due to ring torsion around 760 cm⁻¹ and the −CH₃ stretch near 3000 cm⁻¹ indicate its formation. Due to overlapping of bands, it was not possible to exactly identify CH₃ONO₂, if present, among the products.

![FTIR spectrum](image)

Figure 6.12: FTIR spectrum of species from rapid thermolysis of Me1ATN at 340ºC and 1 atm N₂.

Figure 6.13 shows a ToFMS spectrum from the thermolysis of Me1ATN taken at 340ºC and 1 atm Ar, He and residual air. Similar to Me4ATN, the decomposition products include HNO₃, as seen from the peaks at m/z = 46 and m/z = 30. Although these peaks are also indicative of CH₃ONO₂, formation of this species is most likely limited due to lack of conclusive evidence. The peaks at m/z = 83 and m/z = 84 shows the presence of 3MeTA and its protonated form. The smaller species found in the FTIR
spectra, such as \( \text{H}_2\text{O} \) at \( m/z = 18 \), \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) at \( m/z = 44 \) are also present. The fragmentation of 3MeTA leads to the smaller peaks at \( m/z = 55, 54, 52, 42, \) and 27.

In order to further elucidate the decomposition pathways of Me1ATN, the species evolution profiles were extracted from the FTIR spectra at 340ºC and displayed in Fig. 6.14. The pattern of evolution of various species was found to be remarkable similar to Me4ATN, with \( \text{H}_2\text{O} \) and \( \text{N}_2\text{O} \) desorbing from the condensed phase at a fast rate, followed by \( \text{HNO}_3 \). As observed in case of Me4ATN, the evolution of \( \text{HNO}_3 \) is considerably delayed.
Scheme IV: Proposed reaction pathway for Me1ATN

Figure 6.14: Species evolution from rapid thermolysis of Me1ATN at 340°C and 1 atm N₂.
Based on the FTIR and ToFMS spectra, and the knowledge gained from studying the decomposition of Me1ATI and Me4ATN, the decomposition pathways of Me1ATN are shown in Scheme IV. The decomposition of Me1ATN was mostly similar to that of Me4ATN, barring the ambiguity regarding the involvement of the methyl group in the initiation reaction, as seen in Me1ATI. The primary reaction pathway involves the formation of NH$_2$ONO$_2$ and 3MeTA. The smaller species N$_2$O and H$_2$O are formed via fast secondary reactions. Methyl-triazolium nitrate, formed as a byproduct during these reactions, decomposes to form the HNO$_3$ detected at a later stage, and more 3MeTA. Additionally, 3MeTA was oxidized by nitric acid to form the smaller molecular weight species.

6.5 References


Chapter 7

TETRAZOLIUM SALTS

The initiation of decomposition of several energetic ionic liquids (EILs) was studied by confined rapid thermolysis. Rapidscan FTIR spectroscopy and time-of-flight mass spectrometry were utilized to identify the products evolved from sub-milligram quantities subjected to heating rates of about 2000 K/s. The compounds studied were 2-amino-4,5-dimethyl-tetrazolium iodide (2AdMTZI), 2-amino-4,5-dimethyl-tetrazolium nitrate (2AdMTZN), 1-amino-4,5-dimethyl-tetrazolium iodide (1AdMTZI), and 1-amino-4,5-dimethyl-tetrazolium nitrate (1AdMTZN). Decomposition studies involving the 2AdMTZ salts were carried out around 300ºC. The major decomposition pathway involves a nucleophilic transfer to the anion leading to the formation of methyl iodide and methyl nitrate, from 2AdMTZI and 2AdMTZN, respectively. Methyl iodide (m/z=142) was detected both in the ToFMS and FTIR spectra. Methyl nitrate (m/z=77) was visible in the FTIR spectra. The resultant nitrogen-rich amino-methyl-tetrazole (m/z=99) was found to decompose to form primarily molecular nitrogen and methyl isocyanide.

Unlike the 2AdMTZ salts, the 1AdMTZ salts were found to initiate decomposition at temperatures lower by at least 50ºC. Decomposition was found to proceed through three major pathways – formation of the corresponding methylated anion and 1-amino-5-methyl-tetrazole, formation of ammonia by the amino group, and expulsion of nitrogen from the tetrazole cation itself. 1-amino-5-methyl tetrazole was found to rapidly decompose to form mainly ammonia and nitrogen. The ammonia formed
in the condensed phase during the decomposition of 1AdMTZN was reduced by methyl nitrate, to form smaller molecular weight species, such as N₂O, H₂O, NO₂, NO, CO₂, and others.

The energetic salts of primary interest are 1AdMTZN and 2AdMTZN. Since the complexity of the secondary reactions is considerably higher for the oxygen-rich anions, the relatively simple iodides 1AdMTZI and 2AdMTZI have been studied initially. The molecular structures of the molecules are shown in Fig. 7.1.

![Figure 7.1: Structures of 2-amino-4,5-dimethyl-tetrazolium X (X = iodide and nitrate), and 1-amino-4,5-dimethyl-tetrazolium X (X = iodide and nitrate).](image)

7.1 Thermal Decomposition Pathways of 2AdMTZI

2AdMTZI is a dark brown crystalline solid under standard conditions, with a melting point of 124°C [1]. The sample was dried in a vacuum chamber (40 mtorr) for 24 hours and prepared for thermolysis. Approximately 0.5mg of the sample was found to rapidly decompose above temperatures of 250°C, leaving a small amount of spotted black residue on the aluminum foil. Thermolysis studies were carried out at temperatures around 300°C. Figure 7.2 shows the gaseous products from the decomposition of
2AdMTZI under 320°C and an inert atmosphere of N₂. The vibrational frequencies of the experimentally observed species are listed in Table 7.1.

![Figure 7.2: FTIR spectrum of species from rapid thermolysis of 2AdMTZI at 320°C and 1 atm N₂.](image)

The major product identifiable from the FTIR spectrum is methyl iodide (CH₃I), with a strong stretch at 1252 cm⁻¹, and several other rovibrational bands. Lack of the –NH₂ stretches near 3450 cm⁻¹ and the C–N stretch at 2260 cm⁻¹ precluded the presence of cyanamide (NH₂CN) among the gaseous products. The rotational lines of the protonated anion, HI were not detected. The band near 2160 cm⁻¹ is indicative of an azide N≡N stretch or an isocyanide N≡C stretch. Though an azide is a possible product during decomposition of tetrazoles, the azide N≡N stretch is accompanied by another prominent N–N stretch around 1150 cm⁻¹, thus negating its presence. Thus, the band was attributed to methyl isocyanide (CH₃NC) [2, 3]. However, as seen in Fig. 7.3, at temperatures
lower than 320°C, the N≡C stretch was not visible and further insights into its absence would be provided by the mass spectra.

Table 7.1: Vibrational frequencies of experimentally observed gaseous products.

<table>
<thead>
<tr>
<th>Description</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Reference</th>
</tr>
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<tr>
<td>H(_2)O</td>
<td>3657, 1595</td>
<td>[4]</td>
</tr>
<tr>
<td>HCN</td>
<td>3311, 712</td>
<td>[8]</td>
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<tr>
<td>NH(_3)</td>
<td>3337, 1627, 950</td>
<td>[8]</td>
</tr>
<tr>
<td>CH(_3)I</td>
<td>2974, 1435, 1252, 882</td>
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<tr>
<td>CH(_3)NC</td>
<td>3014, 2965, 2166, 1467</td>
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<td>MeONO(_2)</td>
<td>2962, 1667, 1291, 1019, 855</td>
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</tr>
<tr>
<td>CO(_2)</td>
<td>2349, 667</td>
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<tr>
<td>N(_2)O</td>
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<td>1617, 1320</td>
<td>[7]</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>3018, 1306</td>
<td>[8]</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>3681, 3000, 2960, 2844, 1477, 1345, 1033</td>
<td>[8]</td>
</tr>
</tbody>
</table>

Also prominent was the absence of the inversion doublet of NH\(_3\) (968 cm\(^{-1}\) and 933 cm\(^{-1}\)), HCN (712 cm\(^{-1}\)), and CH\(_3\)CN (2267 cm\(^{-1}\)), all of which are probable species during degradation of the tetrazole ring with an amino group. N\(_2\), which is a common product during the decomposition of tetrazole compounds, could not be detected due to its IR-inactivity. Based on the results of Figs. 7.2 and 7.3, the initiation of decomposition occurs most likely by the transfer of a methyl group from the cation to form CH\(_3\)I and the corresponding amino-methyl-tetrazole. Proton transfer does not occur directly to form HI.
To assist in the identification of species evolving during the decomposition of 2AdMTZI, Figs. 7.4 and 7.5 show the results from the thermolysis of 2AdMTZI under an inert atmosphere of Ar and He, acquired at 320°C and 1 atm. Ar, He and residual air, under an ionization potential of 70eV at 1000Hz. In order to provide better signal-to-noise ratios in the mass spectra, 10 consecutive spectra were averaged. Although the mass spectrum in Figs. 7.4 and 7.5, split in order to provide clarity, appears at a first glance as quite complicated due to the fact that a high ionization potential is used, it facilitates comparison with available mass spectral data bases for a wide range of chemical compounds.

Figure 7.3: FTIR spectrum of species from rapid thermolysis of 2AdMTZI at 300°C and 1 atm N₂.
Figure 7.4: Mass spectrum (m/z = 0-110) from rapid thermolysis of 2AdMTZI at 320°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).

Figure 7.5: Mass spectrum (m/z = 110-260) from rapid thermolysis of 2AdMTZI at 320°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).
The peak at m/z = 142 in Fig. 7.5 attests the formation of CH$_3$I, which primarily accounts for the fragmented charged ion, CH$_3^+$ at m/z = 15. A strong peak at m/z = 99 is observed in Fig. 7.4, which can be formed by a methyl and an amino group attached to the tetrazole ring, thus corroborating the hypothesis derived from the FTIR spectrum that the amino group was indeed intact during the initiation reaction. N$_2$ was produced in abundant quantities. The CH$_3$NC observed in the FTIR spectra was confirmed by the peak at m/z = 41. However, as discussed previously, the relative intensity of this peak was smaller compared to the peak at m/z = 43 at lower temperatures, as shown by the mass spectra obtained at 300°C in Figs. 7.6 and 7.7, coinciding with the disappearance of CH$_3$NC from the FTIR spectra. The appearance of peaks at m/z = 71, 69, 58, 56, 43, and 42 suggest the ring is fractured, both by the high ionization potentials used and the temperatures to which the amino-methyl-tetrazole was subjected. Detailed discussions of the possible fragmentation pathways of di-substituted tetrazoles are well-documented by Forkey et al. [8]. The resultant amino-methyl-tetrazole dimerizes to a limited extent to form a di-tetrazole detected at m/z = 198.
Figure 7.6: Mass spectrum (m/z = 0-110) from rapid thermolysis of 2AdMTZI at 300°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).

Figure 7.7: Mass spectrum (m/z = 110-260) from rapid thermolysis of 2AdMTZI at 300°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).
The availability of the ToFMS data facilitates the determination of the decomposition pathways of 2AdMTZI. As discussed earlier, the nucleophilic transfer involves the formation of CH₃I and the corresponding amino-methyl-tetrazole. Since in general the bond dissociation energies of ring-\textit{exo} C–C bonds are greater than ring-\textit{exo} N–C bonds, the methyl group attached to the N(4) atom was preferably extracted to form CH₃I and 5-methyl-tetrazol-2-amine (2A5MeTZ). The theoretical results obtained for determination of the initiation reactions for 2AdMTZI at B3LYP/6-31++G** level are listed in Table 7.2. Reactions 1 and 3 show that the abstraction of the methyl group attached to the ring nitrogen is favorable over the abstraction from the ring carbon. The other explanation behind the selection of this initial step is that the reverse of this reaction is the synthesis procedure for 2AdMTZI [62]. As depicted by reaction 2, the secondary pathway, involving deamination to form NH₂I and 1,5-dimethyl-tetrazole (dMeTZ), is also energetically spontaneous. However, the absence of NH₂I, both in the FTIR spectra and the ToFMS spectra, lead to the conclusion that the minute quantities generated in the condensed phase engage in further secondary reactions to form other products. Due to almost undetectable levels of HI among the decomposition spectra, proton transfer from a methyl or amino group as an initiation reaction has been neglected as part of the calculations. Also neglected was ring-nitrogen expulsion as an initiation pathway, owing to the absence of two consecutive N atoms free from substituent groups.
It is well-established that thermal decomposition of tetrazoles is achieved by ring opening through either N₂ and/or azide elimination [9-11]. But, 2,5-disubstituted tetrazoles rarely undergo decomposition through splitting off an azide, and instead decompose through a ring-nitrogen expulsion to form an intermediate nitrilimine [12]. Besides, the formation of the amino azide would entail the subsequent formation of ammonia, which is not observed in the FTIR spectra. At higher temperatures, the unstable nitrilimine stabilizes through the formation of methyl isocyanide and nitrogen. At lower temperatures, since the byproduct methyl isocyanide is absent and the peak at m/z = 43

Table 7.2: Theoretical reaction enthalpies and free energies for 2AdMTZI at B3LYP/6-31++G** level.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>∆H&lt;sub&gt;R&lt;/sub&gt; (kcal/mol)</th>
<th>∆G&lt;sub&gt;R&lt;/sub&gt; (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 5-methyl-tetrazol-2-amine (2A5MeTZ)</td>
<td>-9.96</td>
<td>-22.7</td>
</tr>
<tr>
<td>2. 1,5-dimethyl-tetrazole (dMeTZ)</td>
<td>-12.9</td>
<td>-25.1</td>
</tr>
<tr>
<td>3. 4-methyl-tetrazol-2-amine (2A4MeTZ)</td>
<td>36.24</td>
<td>25.18</td>
</tr>
</tbody>
</table>
dominates, it is possible that the nitrilimine forms N-methyl methanimine or an isomer through a second nitrogen elimination.

![Chemical Reaction Diagram]

Pathway I: Considered secondary reaction pathways for 2AdMTZI

If, for the sake of argument, formation of amino iodide (NH$_2$I) is indeed a major initiation step, and CH$_3$I is produced by a substitution reaction with the methyl group attached to the C(5) atom, forming 1-methyl-5-amino-tetrazole in the process, the FTIR spectra should have revealed NH$_3$, in accordance with the observations of Lesnikovich et al. [13]. If the substitution had occurred on the methyl group attached to the N(1) atom, forming 1-amino-5-methyl-tetrazole instead, large quantities of NH$_3$ should have been detected too, as will be elaborated in the following section.
7.2 Thermal Decomposition Pathways of 1AdMTZI

1AdMTZI, an orange-colored crystalline solid under standard conditions, was thermally less stable than the 2-substituted tetrazolium salt. With a melting point similar to 2AdMTZI (121°C), decomposition was initiated at temperatures 50°C lower than 2AdMTZI. Thermolysis tests on the compound were typically conducted at 250°C, leaving spotted black residues on the aluminum foil. Figure 7.8 shows the species evolving from rapid thermolysis at 250°C and 1 atm. As listed in Table 7.1, the principal product is ammonia, with its prominent rotational doublet and numerous rotational lines near 900 cm\(^{-1}\). Also detected in the spectrum are vibrational bands from CH\(_3\)I. The strong absorption band near 3000 cm\(^{-1}\) is due to the \(-\text{CH}_3\) group. Unlike 2AdMTZI, the important species CH\(_3\)NC was not present among the decomposition products. Also absent were HI, HCN, CH\(_3\)CN, NH\(_2\)CN, and HN\(_3\). However, a weak band near 2104 cm\(^{-1}\) suggests the possible formation of CH\(_3\)N\(_3\), whose rovibrational bands were listed by Fisher et al. [14]. The formation of CH\(_3\)I indicates an initiation reaction comparable to 2AdMTZI, proceeding through a methyl group transfer to the iodide anion, and leading to an amino-methyl-tetrazole, which reduces to smaller molecular weight species in subsequent steps. However, the prodigious amounts of NH\(_3\) liberated leads to the possibility of the involvement of the amino group in the initiation reaction.
Results from the use of the ToFMS provide additional details on the rapid thermolysis behavior of 1AdMTZI. Figures 7.9 and 7.10 show the results from an average of ten mass spectra acquired at 1000Hz. Hence the temporal resolution is 0.01 seconds. Careful observation of the spectra reveals that $m/z = 142$ (CH$_3$I), 15 (CH$_3^+$), 99 (an amino-methyl-tetrazole), and 17 (NH$_3$) are the major species. Also noticeable is the large peak of N$_2$ at $m/z = 28$. Smaller peaks at $m/z = 113$ and 198 (amino-methyl-tetrazole dimer) are also present, confirming similarities with 2AdMTZI. Smaller fragments from the tetrazole ring were identified at $m/z = 69, 56, 41, 42,$ and 43. Their formation can be explained through familiar fragmentation pathways of 1,5-disubstituted tetrazoles [8]. The peak at $m/z = 58$ formed by the fragmentation of the amino-methyl-tetrazole detected in the mass spectra obtained during the thermolysis of 2AdMTZI was
found to be absent in Fig. 7.9, thus confirming the presence of the amino group on a different N atom on the ring.

Figure 7.9: Mass spectrum (m/z = 0-110) from rapid thermolysis of 1AdMTZI at 250°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).

Figure 7.10: Mass spectrum (m/z = 110-260) from rapid thermolysis of 1AdMTZI at 250°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).
From the information revealed by the ToFMS and FTIR spectra, it is clear that the decomposition of 1AdMTZI proceeds through multiple reaction channels. The enthalpies and free energies of the possible initiation reactions calculated at B3LYP/6-31++G** are listed in Table 7.3. From the experimental results and theoretical calculations, it is clear that, as opposed to 2AdMTZI, the process of decomposition is not dominated solely by the methyl group transfer involving the cleavage of a ring-\textit{exo} N–C bond, forming CH$_3$I and 5-methyl-tetrazol-1-amine (1A5MeTZ), as shown in reaction 1. Though the scission of the C–C bond to form CH$_3$I and 4-methyl-tetrazol-1-amine (1A4MeTZ) via reaction 6 was found to be energetically unfavorable and hence discarded, the copious quantity of ammonia and molecular nitrogen detected leads to the possibility of two additional significant decomposition pathways. The first one, reaction 2, is initiated by the extraction of a hydrogen atom by the amino group from the neighboring methyl group to form NH$_3$ and 5-iodomethyl-tetrazol-1-amine (5IdMeTZ). The second one, reaction 3, is instigated by the removal of N$_2$ from the ring, and suggested by the decomposition characteristics of 5-amino-tetrazolium halides [15]. The remaining unstable species decomposes rapidly in the condensed phase to produce smaller products. The relative importance of the three pathways can be adjudged by further theoretical calculations to estimate their respective activation energies. As shown by reaction 4, the abstraction of the amino group to form NH$_2$I was also found to be plausible.
Table 7.3: Theoretical reaction enthalpies and free energies for 1AdMTZI at B3LYP/6-31++G** level.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>∆HR (kcal/mol)</th>
<th>∆GR (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. H₂N⁺N⁺N⁺N⁻N⁻CH₃ → CH₃⁻ + 5-methyl-tetrazol-1-amine (1A5MeTZ)</td>
<td>-4.13</td>
<td>-15.69</td>
</tr>
<tr>
<td>2. H₂N⁺N⁺N⁺N⁻N⁻CH₃ → NH₃ + 5-(iodomethyl)-1-methyl-1H-tetrazole (5IdMeTZ)</td>
<td>-17.73</td>
<td>-28.38</td>
</tr>
<tr>
<td>3. H₂N⁺N⁺N⁺N⁻N⁻CH₃ → N₂ + HN=NH⁻CH₃</td>
<td>-29.55</td>
<td>-41.56</td>
</tr>
<tr>
<td>4. H₂N⁺N⁺N⁺N⁻N⁻CH₃ → NH₂⁻ + 1,5-dimethyl-tetrazole (dMeTZ)</td>
<td>-7.95</td>
<td>-20.26</td>
</tr>
<tr>
<td>5. H₂N⁺N⁺N⁺N⁻N⁻CH₃ → NH₃ + 1-amino-4-methyl-tetrazol-5-ylidene (1A4MeTZ)</td>
<td>22.92</td>
<td>12.25</td>
</tr>
<tr>
<td>6. H₂N⁺N⁺N⁺N⁻N⁻CH₃ → CH₃⁻ + 1-amino-4-methyl-tetrazol-5-ylidene (1A4MeTZ)</td>
<td>26.07</td>
<td>14.40</td>
</tr>
</tbody>
</table>
A complete enumeration of the numerous secondary reactions in the condensed phase is considerably challenging. However, the major secondary steps are shown in pathway II. The di-substituted tetrazole, 1A5MeTZ, rapidly decomposes under these conditions, aided by a ring N–N bond scission to form an isomeric azide [16, 17], which releases nitrogen and a singlet nitrene. The nitrene proceeds to form NH$_3$ and other products, confined mainly to the condensed phase, in a manner similar to the decomposition of 1,5-diaminotetrazoles [50, 66]. 5IdMeTZ decomposes either through the elimination of methyl azide and iodoacetonitrile, which remains in the condensed phase, or through the elimination of N$_2$ and CH$_3$I to form similar products during the decomposition of 1A5MeTZ.
7.3 Thermal Decomposition Pathways of 2AdMTZN

2AdMTZN is a white crystalline solid with a melting point of 94°C, considerably lower than the corresponding iodide salt. The hygroscopic nature of the salt made it difficult to study the decomposition behavior of the compound. The sample was dried for 24 hours under vacuum (40 mtorr) and then stored in a sealed container to avoid contamination by moisture. Small quantities of the sample were thermolysed at temperatures near 300°C, with a sooty black residue left on the aluminum foil. Figure 7.11 shows an FTIR spectrum of the gaseous products generated during the thermolysis of 2AdMTZN at 300°C and 1 atm. Methyl nitrate (CH$_3$ONO$_2$), with several rovibrational bands from 1700 to 800 cm$^{-1}$ was immediately discernable as the principal species. Also detected were H$_2$O, CO$_2$, and a small quantity of HCN. The common oxides of nitrogen, NO, N$_2$O, and NO$_2$ were surprisingly absent in Fig. 7.11. The double bands around 2260 cm$^{-1}$ and 2310 cm$^{-1}$ were identified as a combination of methyl isocyanate (CH$_3$NCO) and CH$_3$CNO, respectively. Around 1750 cm$^{-1}$, a strong band due to a species containing a C=O bond was detected. Aldehydes and ketones normally show strong features in the range from 1,700 to 1,750 cm$^{-1}$. As found in the FTIR spectra of 2AdMTZI, CH$_3$NC was present with a band at 2160 cm$^{-1}$.
Figure 7.12 shows a spectrum from the ToFMS acquired during the pyrolysis of 2AdMTZN at 300°C and 1 atm Ar, He and residual air extracted 0.12s after the two heaters came into contact. Although CH$_3$ONO$_2$ is absent from the mass spectrum at a cursory glance, its presence was confirmed by prominent peaks of CH$_3^+$ (m/z=15), NO$_2^+$ (m/z=46), and NO$^+$ (m/z=30), corroborated by Fischer et al. during thermal decomposition of 1,5-diamino-4-methyl-tetrazolium nitrate [66]. The peak at m/z = 99 was confirmed as an amino-methyl-tetrazole, and after a brief study of the fragments, was identified as 2A5MeTZ. The smaller molecular-weight species of N$_2$ and H$_2$O were also present in Fig. 12. The larger peak at m/z = 57, in comparison to the mass spectra obtained during thermolysis of 2AdMTZI indicates that other species are present besides the fragments of 2A5MeTZ. The FTIR spectra confirm that these species are indeed
CH$_3$NCO and CH$_3$CNO. The aldehyde present in the FTIR spectrum was recognized as acetaldehyde (m/z = 44) after deliberation.

Ab initio theoretical calculations at the B3LYP/6-31++G** level, shown in Table 7.4, corroborates that the major reaction channel remains unaltered from the one observed for 2AdMTZI. The affinity of the nitrate group for the methyl group over the amino group has also been established while studying decomposition behavior of 1,5-diamino-4-methyl-1$H$-tetrazolium nitrate [66].
The possible secondary reactions between the products formed are outlined in Pathway III. Majority of the generated CH$_3$ONO$_2$ in the condensed phase promptly escapes into the gas phase, while the remaining amount reacts with 2A5MeTZ and its various intermediates. Subsequent reactions between CH$_3$ONO$_2$ and 2A5MeTZ replace the methyl group on 2A5MeTZ to form 2-amino-5-methoxy-2$H$-tetrazole, detected by a minor peak at m/z = 115 in Fig. 12, and methyl nitrite, CH$_3$ONO. Similar substitution reactions were observed during the thermolysis of di-alkyl-substituted imidazolium nitrates [18]. The methoxy tetrazole undergoes a decomposition process similar to

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \Delta H_R ) (kcal/mol)</th>
<th>( \Delta G_R ) (kcal/mol)</th>
</tr>
</thead>
</table>
| 1. \( \begin{array}{c} 
\text{H}_2\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{CH}_3 \\
\end{array} \rightarrow \begin{array}{c} 
\text{CH}_3\text{ONO}_2 + \\
\text{H}_3\text{C} \\
\text{N} \\
\text{N} \\
\text{NH}_2 \\
\text{N} \\
\text{CH}_3 \\
\end{array} \) 5-methyl-tetrazol-2-amine (2A5MeTZ) | -3.42 | -16.24 |
| 2. \( \begin{array}{c} 
\text{H}_2\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{CH}_3 \\
\end{array} \rightarrow \begin{array}{c} 
\text{NH}_2\text{ONO}_2 + \\
\text{H}_3\text{C} \\
\text{N} \\
\text{N} \\
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\end{array} \) 1,5-dimethyl-tetrazole (dMeTZ) | 5.07 | -6.68 |
| 3. \( \begin{array}{c} 
\text{H}_2\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{CH}_3 \\
\end{array} \rightarrow \begin{array}{c} 
\text{CH}_3\text{ONO}_2 + \\
\text{H}_3\text{C} \\
\text{N} \\
\text{N} \\
\text{NH}_2 \\
\text{N} \\
\text{CH}_3 \\
\end{array} \) 4-methyl-tetrazol-2-amine (2A4MeTZ) | 42.78 | 31.64 |
2A5MeTZ to form the species CH$_3$NCO and CH$_3$CNO through nitrogen elimination. Besides, CH$_3$ONO$_2$ and CH$_3$ONO partially decompose under the temperatures applied to form smaller molecules. Detailed discussions of these reactions, as well reactions involving partial decomposition of CH$_3$ONO$_2$ are beyond the scope of this paper. 2A5MeTZ itself also decomposes through previously described pathways.

Pathway III: Considered secondary reaction pathways for 2AdMTZN

Pathway III: Considered secondary reaction pathways for 2AdMTZN

7.4 Thermal Decomposition Pathways of 1AdMTZN

While the three tetrazolium salts studied prior to 1AdMTZN were all solids, this is a liquid under standard conditions with a melting temperature of -59ºC. Confined rapid
thermolysis on approximately 0.5 μL of the sample was carried out at temperatures around 250°C. Figure 7.13 depicts an FTIR spectrum of species from rapid thermolysis of 1AdMTZN at 250°C and 1 atm.

![FTIR spectrum of species from rapid thermolysis of 1AdMTZN at 250°C and 1 atm N₂.](image)

Figure 7.13: FTIR spectrum of species from rapid thermolysis of 1AdMTZN at 250°C and 1 atm N₂.

The spectrum is dominated by the rotational structures of H₂O, centered at 1595 cm⁻¹, making it difficult to ascertain the rovibrational bands present in the region 1200 to 2000 cm⁻¹. In order to determine the species present with water, the concentration of H₂O was calculated using a data reduction procedure and the amount of H₂O present was synthetically subtracted to yield the cleaner spectrum shown in Fig. 7.14. Consequently, the species that were identified are CH₃ONO₂, NO, NO₂, N₂O, CH₃CNO, and CH₃NCO. Also detected in smaller quantities were CO, CO₂, CH₄, and CH₃OH. Although not detected among the decomposition products of 1AdMTZI, HCN with its strong Q-branch at 712 cm⁻¹, was identified in Fig. 7.14. The large quantities of NH₃ found in the FTIR
spectra of 1AdMTZI were oxidized by methyl nitrate formed during the initiation step. An aldehyde was identified by the prominent band near 1750 cm\(^{-1}\). Additionally, the N≡C stretch from the isonitrile, CH\(_3\)NC was found at 2160 cm\(^{-1}\).

Figure 7.14: FTIR spectrum of species from rapid thermolysis of 1AdMTZN at 250°C and 1 atm N\(_2\) (H\(_2\)O subtracted for clarity).

Figure 7.15 shows a ToFMS spectrum from the thermolysis of 1AdMTZN, taken 0.09 seconds after initiation of heating at 250°C and 1 atm Ar, He and residual air. Similar to 2AdMTZN, the decomposition products include CH\(_3\)ONO\(_2\). Also present are 1A5MeTZ at m/z = 99, NO\(_2\) at m/z = 46, N\(_2\)O and CO\(_2\) at m/z = 44, NO at m/z = 30, CO and N\(_2\) at m/z = 28, HCN at m/z = 27, and H\(_2\)O at m/z = 18. The peak at m/z = 57 corroborates the presence of CH\(_3\)NCO and CH\(_3\)CNO.
Based on the FTIR and ToFMS data, and the previous knowledge gained from studying the decomposition of 1AdMTZI, the primary reaction pathways and their associated free energy changes calculated at the B3LYP/6-31++G** level have been tabulated in Table 7.5. As expected, three major pathways – a nucleophilic transfer involving the methyl group attached to the ring nitrogen to form 1A5MeTZ and CH$_3$ONO$_2$ (reaction 1), ammonia formation by the amino group through a proton abstraction from the neighboring methyl group (reaction 2), as well as ring nitrogen elimination (reaction 3), were all found to be thermodynamically feasible processes. As found before in the case of 1AdMTZI, the formation of 1A4MeTZ was found to be unfavorable in reaction 6.

Figure 7.15: Mass spectrum from rapid thermolysis of 1AdMTZN at 250°C and 1 atm Ar, He and residual air extracted at 0.10s (average of 10 spectra).
Table 7.5: Theoretical reaction enthalpies and free energies for 1AdMTZN at B3LYP/6-31++G** level.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \Delta H_R ) (kcal/mol)</th>
<th>( \Delta G_R ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.98</td>
<td>-10.68</td>
</tr>
<tr>
<td>2.</td>
<td>-15.86</td>
<td>-25.9</td>
</tr>
<tr>
<td>4.</td>
<td>8.64</td>
<td>-3.31</td>
</tr>
<tr>
<td>5.</td>
<td>32.19</td>
<td>21.72</td>
</tr>
<tr>
<td>6.</td>
<td>31.18</td>
<td>19.4</td>
</tr>
</tbody>
</table>
A detailed description of the secondary reactions leading to the detected species has been given in pathway IV. 1A5MeTZ dissociates with an N₂ ejection to form mainly ammonia. Unlike the decomposition of 2AdMTZN, where most of the generated CH₃ONO₂ desorbed into the gas phase, majority of the nitrate from 1AdMTZN oxidizes NH₃ to liberate a number of smaller molecular weight species, namely N₂O and H₂O, as well as CO, NO, CO₂, and NO₂. A portion of CH₃ONO₂ reacts through the formation of 1-amino-5-methoxy-1H-tetrazole to form CH₃NCO and CH₃CNO, forming CH₃ONO in the process. Besides these primary reactions, numerous other secondary reactions involving the intermediate nitrenes, CH₃ONO₂, and CH₃ONO also take place to form the smaller molecular weight gases.
Pathway IV: Considered secondary reaction pathways for 1AdMTZN
7.5 References


Chapter 8

KINETICS OF DECOMPOSITION

The Arrhenius-type reaction rate parameters for the initiation reactions governing the thermal decomposition of several energetic ionic liquids were determined by numerical techniques. The compounds chosen for this purpose were the energetic 4-amino-1,2,4-triazolium nitrate (4ATN), and 1-hydroxyethyl-hydrazinium nitrate (HEHN). The supplementary compounds studied for comparison were 4-amino-1,2,4-triazolium chloride (4ATCl) and ammonium nitrate (AN), shown in Fig. 8.1. The reaction rate parameters were obtained by an evolutionary genetic algorithm that compared the difference between the experimental and simulated species evolution profiles from the decomposition process. The experimental data were generated by confined rapid thermolysis. The decomposition process was simulated by applying conservation equations to the condensed and gas phases individually. The optimization module recovered the experimental species profiles with reasonable accuracy for all the compounds studied. The processes governing the decomposition of these energetic compounds were found to be autocatalytic in nature, and the autocatalytic agents were the strong acids generated by the initial decomposition step. The activation energy and pre-exponential factor for the unimolecular decomposition step for 4ATN, HEHN, and 4ATCl were 40–45 kcal/mol and $10^{16}$, respectively, similar to previously determined values for AN.
8.1 Selection of Primary Reaction Steps

Both of the representative compounds, AN and 4ATCl, were procured from Sigma Aldrich and used without further purification. Confined rapid thermolysis of approximately 0.5mg of AN was carried out in the temperature range of 300–320ºC and under an inert atmosphere of N₂ at one atmospheric pressure. Figure 8.2 shows the species evolution profiles extracted from the FTIR spectra generated during thermal decomposition of 0.510 mg of AN at 310ºC. It is clear from the evolution of gases from the condensed phase that HNO₃ and NH₃ are the major species produced during the initiation step. However, as the concentrations of these two species increase in the cooler gas-phase region, a gas-phase recombination reaction occurs to form NH₄NO₃. Hence, after 600 ms, the slope of the HNO₃ and NH₃ evolution curves suffer a gradual decline. H₂O and N₂O, which are produced after a series of secondary reactions in the condensed phase, occur after a significant delay and at slower rates than the initial products.
Although significant efforts have been made to develop a complete decomposition mechanism for AN [1–3], it is widely accepted that the initiation step is the dissociation of AN via a proton transfer from the ammonium cation to the nitrate anion to form HNO$_3$ and NH$_3$. Thus, this step is incorporated as the first step in the chemical reaction model. The acid generated in the process has been suggested to act as an autocatalytic agent [3,4], further aiding the decomposition process. In case the single reaction model fails to describe the early stages of the decomposition chemistry of AN accurately, a second autocatalytic step, as shown in scheme I, would be added to the reaction scheme. Since the goal of this study is the exploration of the kinetics of the primary reaction pathways, the subsequent steps leading to the formation of N$_2$O and H$_2$O were omitted from the scheme. The temporal range covered in the optimization module was restricted from 0 to 600ms, during which time secondary reactions between NH$_3$ and HNO$_3$ were minimal.

Figure 8.2: Species evolution from rapid thermolysis of 0.510 mg of AN at 310°C and 1 atm N$_2$. 
Additionally, the effects of the gas-phase recombination reactions were effectively eliminated by undertaking such a measure.

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3
\]

\[
\text{NH}_4\text{NO}_3 + \text{HNO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3 + \text{HNO}_3
\]

Scheme I: Proposed reaction scheme for AN

A detailed description of the decomposition mechanism of 4ATCl and 4ATN has been covered in our previous studies [5]. However, the species evolution profiles presented in the previous case was observed when the decomposition of 4ATCl and 4ATN were carried out without a confinement of the products in the gas phase. The species profiles extracted during the decomposition of 0.404 mg of 4ATCl at 290ºC and 1 atm pressure under the revised circumstances are depicted in Fig. 8.3. HCl is the first species to escape into the gas phase, followed by HCN. The NH\textsubscript{3} that enters the gas phase after a considerable delay, and approximately coinciding with the evolution of HCN, immediately reacts chemically with HCl to condense out as NH\textsubscript{4}Cl, which is recorded by the FTIR spectra. Consequently, minimal amounts of NH\textsubscript{3} were detected in the FTIR spectra. This phenomenon causes the sudden negative slope in the HCl evolution curve. Thus, the temporal regime during the study of 4ATCl decomposition kinetics was bound from 0 to 450 ms.

As discussed earlier, the initial step in the decomposition of 4ATCl is the proton transfer from the N\textsubscript{1} position to form HCl and 4AT. 4AT then proceeds to form NH\textsubscript{3}, HCN, 1TA (1-\textit{H}-triazole), and N\textsubscript{2} through multiple reaction steps. Other possible initiation reactions of minor importance are also ignored while setting up the reaction scheme II. Due to reasons stated earlier, the secondary reaction steps were also omitted.
However, HCl being a stronger acid than HNO$_3$, the possibility of an autocatalytic effect could not be overruled, and was provided in the reaction scheme.

![Reaction Scheme II](image)

As in the case of 4ATCl, the revised species profiles observed during thermolysis of 0.466 mg of 4ATN under 290°C and 1 atm N$_2$ are shown in Fig. 8.4. As reported earlier, HNO$_3$ is the first species to desorb from the condensed phase, followed by H$_2$O and N$_2$O at slower rates. CO$_2$ and smaller quantities of HCN were also detected among the secondary reaction products. Contrary to the cases of AN and 4ATCl, NH$_3$ is neutralized in the condensed phase before reaching the gas phase. Hence, it does not pose
a threat by combining with the nitric acid already present in the gas phase. Instead, the
1TA produced during the decomposition process attacks the HNO$_3$, forming triazolium
nitrate in the process, and leading to the subsequent disappearance of HNO$_3$, and setting
the temporal bound for the kinetic study at 750 ms. The onset of decomposition occurs
through a proton scavenging by the nitrate ion from the amino group on the 4-amino-
triazolium cation, forming HNO$_3$ and the remaining species, named 4ATz, which is a
combination of 1TA and the imino radical. The reaction scheme III is provided as an
input to the kinetic optimization module. As in the previous cases, an autocatalytic step is
included as a distinct possibility.

Figure 8.4: Species evolution from rapid thermolysis of 0.466 mg of 4ATN at 290°C and
1 atm N$_2$. 
Unlike AN, 4ATCl, and 4ATN, no published material was found to be available in the literature describing the decomposition mechanism of HEHN. Since a complete narration of the numerous reactions occurring in the condensed phase during the decomposition of the energetic liquid is not feasible under the present study, and a brief description of the reaction mechanism is provided in scheme IV. Figure 8.5 shows the species profiles collected during the decomposition of 0.610 mg of HEHN at 290ºC and 1 atm pressure. Unlike the other compounds, where a significant portion of the acid evolved into the gas phase, extremely small quantities of HNO₃ were detected. The hydrazine derivatives produced in the decomposition reacted quickly with HNO₃. This aspect was verified by the violent reaction that occurred when hydroxy-ethyl-hydrazine (HEH) was brought in contact with 90% HNO₃ solution at room temperature.

As seen in Fig. 8.5, H₂O is the major product during the decomposition of HEHN. Since the material was known to be hygroscopic, the compound was dried under a 10 mTorr vacuum for 48 hours, and stored in the desiccator immediately, to dispel any incongruity about the concentrations of water detected in the gas phase. Repeatable results were obtained after two samples were dried separately and tested. Besides H₂O, other major products were N₂O, N₂, and NH₃. Minor quantities of CO₂ and NO were also
present among the products. A separate study of the hypergolic reaction between HEH and HNO₃ revealed that NH₃ was not a product of the hypergolic reaction, and was instead generated due to the decomposition of HEH at the high reaction temperatures.

![Figure 8.5: Species evolution from rapid thermolysis of 0.610 mg of HEHN at 290°C and 1 atm N₂.](image)

As shown in scheme IV, the initiation of decomposition was similar in nature to the other compounds, through a proton transfer to form HNO₃ and HEH. Similar to the previous reaction mechanisms, an autocatalytic step was added to the reaction scheme.

Scheme IV : Proposed reaction scheme for HEHN

\[
\begin{align*}
\text{NO}_3^- & \rightarrow \text{H}_3\text{N}^+ \cdot \text{NH} \cdot \text{CH} \rightarrow \text{H}_2\text{N} \cdot \text{NH} - \text{CH} \rightarrow \text{H}_2\text{N} \cdot \text{NH} - \text{CH} \rightarrow \text{H}_2\text{N} \cdot \text{NH} - \text{CH} + \text{HNO}_3 \\
\text{NO}_3^- & \rightarrow \text{H}_3\text{N}^+ \cdot \text{NH} \cdot \text{CH} \rightarrow \text{H}_2\text{N} \cdot \text{NH} - \text{CH} \rightarrow \text{H}_2\text{N} \cdot \text{NH} - \text{CH} + \text{HNO}_3 + \text{HNO}_3 \\
\text{H}_2\text{N}^+ \cdot \text{NH} \cdot \text{CH} \rightarrow \text{H}_2\text{N} \cdot \text{NH} - \text{CH} + \text{HNO}_3 & \rightarrow 2.5 \text{H}_2\text{O} + 0.42 \text{N}_2\text{O} + 1.08 \text{N}_2 + 0.042 \text{O}_2 + \text{CH}_3\text{CHO}
\end{align*}
\]
The global reaction mechanism describing the reaction between HEH and HNO$_3$ omits NH$_3$ as a product. The individual ratios of various products were determined by observing the FTIR-generated species profiles at different reaction temperatures. The ratio of H$_2$O to N$_2$ was determined from ToFMS spectra obtained from the decomposition of HEHN under comparable conditions. In order to introduce simplicity, the alcoholic moiety was kept intact in the reaction scheme, despite the fact that a more extensive scheme would involve its oxidation.

8.2 Selection of Best Fit Parameters

The reaction schemes outlined in the previous sections were utilized with the genetic algorithm optimization module to deduce the best fits of the experimental data obtained during the thermolysis of the ionic compounds. Figures 8.6 to 8.9 depict the experimental and the theoretical species evolution profiles within the considered temperature and temporal ranges for AN, 4ATCl, 4ATN, and HEHN, respectively. In the figures, the symbols represent the experimental mole fractions, normalized by the individual sample mass, the profile at a particular set temperature being the arithmetic average of at least three separate tests. The error bars are drawn at one standard deviation, representing a 68.3% confidence interval. The simulated species evolution profiles are reasonably comparable to the FTIR-generated profiles. The induction periods for all the compounds were recovered quite accurately. However, the predicted profiles tend to diverge from the actual ones at higher temperatures and towards the end of the temporal cutoff bounds for AN, 4ATCl, and 4ATN, the underlying causes being the incidence of
secondary reactions in the condensed phase as well as recombination reactions in the gas phase between HNO$_3$ and NH$_3$ in case of AN; HCl and NH$_3$ in case of 4ATCl; and HNO$_3$ and 1TA in case of 4ATN. HEHN was the only compound unaffected by recombination reactions in the gas phase, possibly due to the absence of sizeable quantities of HNO$_3$. As expected, due to increase in temperature, the reaction rates increased exponentially, leading to faster species evolution rates. In general, an approximate increment of 10ºC in temperatures was found to double the reaction rates.

Figure 8.6: Comparison of experimental and calculated gas phase normalized mole fractions of HNO$_3$ during thermal decomposition of AN at 300ºC, 310ºC, and 320ºC and 1 atm N$_2$. 

![Graph showing the comparison of experimental and calculated gas phase normalized mole fractions of HNO$_3$.](image-url)
Figure 8.7: Comparison of experimental and calculated gas phase normalized mole fractions of H$_2$O during thermal decomposition of HEHN at 270ºC, 280ºC, and 290ºC and 1 atm N$_2$.

Figure 8.8: Comparison of experimental and calculated gas phase normalized mole fractions of HNO$_3$ during thermal decomposition of 4ATN at 250ºC, 260ºC, 270ºC, and 280ºC and 1 atm N$_2$. 
The principal advantage of using genetic algorithms to optimize a set of kinetic parameters over a non-linear gradient-based iterative fitting method lies in the flexibility to search the entire parameter space for local minima’s and then select the global minima among the pertinent values. The parameter regimes explored for the unimolecular decomposition step for all four compounds were $30^{-50}$ kcal/mol and $10^{12}-10^{20}$ s$^{-1}$ for the activation energy and the pre-exponential factor, respectively. However, the exclusive usage of this step in the primary reaction mechanism led to unnaturally large values of the pre-exponential factor, although the experimental species evolution profiles were accurately recovered. In case of AN decomposition, the sole use of the initial dissociation step yielded an activation energy of 55.9 kcal/mol and a pre-exponential factor of $8.0 \times 10^{19}$ s$^{-1}$, which were unreasonable and also exceeded previously deduced values, given in Table 1. The incorporation of the autocatalytic step in the reaction mechanism
shown in scheme I led to the best-fit reaction parameters given in Table 3. The parameter bounds for the autocatalytic step were from 10⁻³⁰ kcal/mol and 10⁵⁻¹⁰¹⁵ (mol/cc×s)⁻¹ for the activation energy and the pre-exponential factor, respectively. As discussed before, the values reported by Rubtsov et al. [3] were 47.2 kcal/mol and 2.5×10¹⁴ s⁻¹ for the first step, and 24.0 kcal/mol and 2×10⁷ (mol/cc×s)⁻¹ for the second step. Except the pre-exponential factor for the autocatalytic step, the other parameters were found to be appreciably close. The difference may be attributed to variations in experimental conditions, especially reaction temperatures, which were higher by approximately 100ºC, leading to faster vaporization and thus, lesser accumulation of HNO₃, the autocatalytic agent.

The deduced kinetic rate parameters for 4ATCl, 4ATN, and HEHN are given in Table 8.1. The parameter bounds utilized to deduce the best-fit parameters for the initiation and autocatalytic steps were identical to that of AN. The global reaction in the decomposition scheme IV of HEHN had the bounds of 0⁻¹⁰ kcal/mol and 10²⁻¹⁰¹⁰ (mol/cc×s)⁻¹ for the activation energy and the pre-exponential factor respectively. They were chosen in a manner to assign a value for the activation energy as close to zero as possible, considering the hypergolicity of the reaction.

A comprehensive elucidation of the underlying reasons behind the inherent variations in the Arrhenius-type rate parameters recovered for the compounds studied is extremely complex. The causes behind such variations are most likely tied to various physico-chemical properties of the compounds, namely structural effects, bond strengths, and electronegativity of the ions, as well as the liquid-phase properties of the reactants and products, such as dielectric constant, viscosity, nucleophilicity and electrophilicity,
cohesion, and the influence of hydrogen bonding. However, it is clear from the deduced parameters that there exist some notable similarities and dissimilarities.

Table 8.1: Estimated Arrhenius-type parameters of decomposition.

<table>
<thead>
<tr>
<th>Reaction Mechanism</th>
<th>Activation energy (kcal/mol)</th>
<th>Preexponential Factor$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$NO$_3$ → NH$_3$ + HNO$_3$</td>
<td>45.3</td>
<td>3.9 × 10$^{15}$</td>
</tr>
<tr>
<td>NH$_4$NO$_3$ + HNO$_3$ → NH$_3$ + HNO$_3$ + HNO$_3$</td>
<td>21.1</td>
<td>3.5 × 10$^{10}$</td>
</tr>
<tr>
<td>4ATCl → 4AT + HCl</td>
<td>42.5</td>
<td>7.9 × 10$^{16}$</td>
</tr>
<tr>
<td>4ATCl + HCl → 4AT + HCl + HCl</td>
<td>23.3</td>
<td>1.5 × 10$^{12}$</td>
</tr>
<tr>
<td>4ATN → 4ATz + HNO$_3$</td>
<td>41.9</td>
<td>1.4 × 10$^{16}$</td>
</tr>
<tr>
<td>4ATN + HNO$_3$ → 4ATz + HNO$_3$ + HNO$_3$</td>
<td>28.6</td>
<td>5.7 × 10$^{13}$</td>
</tr>
<tr>
<td>HEHN → HEH + HNO$_3$</td>
<td>43.7</td>
<td>2 × 10$^{16}$</td>
</tr>
<tr>
<td>HEHN + HNO$_3$ → HEH + HNO$_3$ + HNO$_3$</td>
<td>29.8</td>
<td>3.9 × 10$^{12}$</td>
</tr>
<tr>
<td>HEH + HNO$_3$ → 2.5 H$_2$O + 0.42 N$_2$O + 1.08 N$_2$  + 0.042 O$_2$ + CH$_3$CHO</td>
<td>5.8</td>
<td>8.3 × 10$^5$</td>
</tr>
</tbody>
</table>

$^a$Units are s, cm$^3$, mol

The activation energies of the unimolecular decomposition step as well as the autocatalytic steps for 4ATCl and N$_2$H$_5$Cl are remarkably similar, since both processes involve deprotonation to form HCl. A similar comparison between 4ATN and N$_2$H$_5$NO$_3$ reveals that the activation energies for the primary steps are in considerable agreement, since HNO$_3$ abstraction is the key step for both compounds. The activation energy for the unimolecular step for HEHN was computed to be slightly higher than that of 4ATN and N$_2$H$_5$NO$_3$. Despite the presence of anions with varying electronegativities, 4ATN and
4ATCl were found to have analogous activation energies for the initiation step, which was found to be the case for \( \text{N}_2\text{H}_5\text{NO}_3 \) and \( \text{N}_2\text{H}_5\text{Cl} \) as well. Another interesting fact was observed on extrapolating the reaction rate constants for the unimolecular step for all compounds to a common temperature of 300ºC. The values obtained for 4ATCl, 4ATN, and HEHN were found to be to two orders of magnitude higher than those of AN. The rate constant for AN was found to be similar to those obtained previously [74,4,6].

8.3 References

Chapter 9

HYPERGOLIC DICYANAMIDE SALTS

9.1 Introduction

Bipropellant pairs that spontaneously ignite without any external heat source are categorized as hypergolic. These materials rely on highly exothermic reactions in the liquid and gas phases to initiate combustion. Hypergolic materials are used in applications where repeatability of ignition is required, often involving a simplified delivery system. Hence, hypergolic rocket engines are used extensively in orbital maneuvering subsystems and altitude control of spacecrafts and satellites. Since their development more than 50 years ago,[1] extensive experimental efforts led to the development of hydrazine derivatives, such as mono-methyl-hydrazine (MMH), unsymmetrical di-methyl-hydrazine (UDMH), aerozine (mixture of hydrazine and UDMH), as fuels and nitrogen tetroxide, nitric acid, or hydrogen peroxide as oxidizers. However, the high vapor pressure of these fuels, combined with their carcinogenic nature, entails costly and burdensome handling procedures to address personal as well as environmental hazards. Hence, there is considerable interest to develop suitable replacements to the hydrazine family of hypergolic fuels [2, 3].

Though initial focus on energetic ionic liquids was concentrated on development of monopropellants by coupling nitrogen-rich cations, such as imidazoles, triazoles, and tetrazoles with oxygen-rich anions such as nitrates, nitramides, and perchlorates, it has
been partially shifted to bipropellant systems with the recent discovery of the hypergolicity of a series of ionic compounds based on the anion dicyanamide [4]. But before these hypergolic fuels can be employed in a practical setting, critical performance parameters, such as ignition delay and specific impulse, must be calculated and optimized to match existing bipropellants. Ignition delay for a particular hypergolic pair is defined as the elapsed time between the fuel-oxidizer contact and the appearance of a luminous flame, and is determined by a complex interplay between various physical and chemical factors. Typically, while protracted ignition delays are avoided in order to prevent catastrophic ‘hard starts’ [5] and ensure smooth operation of the propulsion system, extremely short ignition delays are undesirable to prevent possible damage to injectors. In case of a liquid bipropellant pair, the global ignition delay may be broadly divided into the physical ignition delay and the chemical ignition delay. The physical delay is dominated by the atomization and evaporation processes for the individual components, whereas the chemical delay is governed by chemical reactions in the condensed and the gas phases.

Since the pre-ignition condensed phase chemistry is a significant contributor towards the global ignition delay, a thorough understanding of the chemical processes leading to gaseous species that initiate combustion in the flame zone is of paramount importance. In particular, the elucidation of the complex condensed-phase chemical kinetics using drop tests [6] and impinging jet devices [7] is considerably challenging due to ignition delay times on the order of a few milliseconds or less. Early efforts by Jain et al. [8] involved identification of reaction intermediates through quenching the pre-ignition reactions by diluting the thiocarbonohydrazone fuels by adding inert glass powder and
adding the nitric acid oxidizer to it, and finally, chemically analyzing the products. Patil et al. [9] recorded and analyzed FTIR spectra of gaseous products evolving from hypergolic reactions between nitric acid and various solid fuels, namely p-phenylenediamine and thiocarbohydrazide derivatives, in a modified variable-pressure thermolysis cell. The temperature profiles acquired from the reaction zone demonstrated that the neutralization, nitration, and oxidation reactions involved in the formation of the smaller gas phase species were highly exothermic in nature.

Ignition studies of various amine-acid systems by Schalla and Fletcher [10] showed that the initial step in a well-mixed system was an exothermic neutralization process. The heat generated during this step was utilized in achieving elevated temperatures, which induced decomposition and oxidation of the products formed in the first step, leading to ignition. Pre-ignition reaction products in hydrazine-based systems with NO$_2$ as the oxidizer were obtained by inducing the fuel to come in contact with the gaseous oxidizer within a cooled glass-jacketed reaction chamber by Mayer et al.[11] Saad et al. [12] studied similar reactions by adding N$_2$O$_4$ to various hydrazine-based fuels at a fixed temperature of $\text{\textdegree}20^\circ\text{C}$ in the inert solvent, CCl$_4$. The products formed due to the reactions in the condensed phase were analyzed by mass spectrometry, gas chromatography, and infrared absorption spectroscopy. Pre-ignition chemistry of dicyanamide-based ionic liquids with nitric acid as the oxidizer was probed using Fourier transform infrared (FTIR) spectroscopy by Chambreau et al. [13].

The principal goal of this study is to formulate a suitable reaction mechanism for the pre-ignition condensed phase reactions that can be fitted with appropriate Arrhenius-type parameters, and utilized to simulate the condensed phase behavior. However, the
study would remain incomplete without a thorough investigation of the gas phase reactions, interaction between the gas phase and condensed phase species, and reactions between vaporized fuel and oxidizer. Hence, the ultimate objective is to synergize the condensed phase reaction scheme obtained using a modified confined rapid thermolysis setup with the temperature profiles and the global ignition delay times extracted from a traditional drop test apparatus, to generate a comprehensive physico-chemical model of the hypergolic ignition process. The fuels chosen for this purpose were 1-ethyl-3-methylimidazolium dicyanamide (EmimDCA) and 1-butyl-3-methylimidazolium dicyanamide (BmimDCA), both potential replacements for the hydrazine family of fuels. The oxidizers were nitric acid of varying strengths, 70%, 90%, and white fuming nitric acid (WFNA). Figure 9.1 depicts the structures of the fuels.

Figure 9.1: Structures of 1-ethyl-3-methyl-imidazolium dicyanamide, and 1-butyl-3-methyl-imidazolium dicyanamide.
9.2 Experimental Setup

9.2.1 Drop Test Setup

The experimental setup utilized for inducing contact between a hypergolic bipropellant pair and studying the subsequent phenomena leading to ignition is commonly termed as a drop test apparatus. The technique relies on opto-electrical devices for detecting the initiation of the event and identification of the ignition kernel, and on thermo-electrical devices for recording the temperatures traces in the gas phase above the condensed phase reaction zone. A schematic diagram of the line-of-sight apparatus is presented in Fig. 9.2. An excess amount of the oxidizer, approximately 160 µl, is deposited at the bottom of a 10 mm glass cuvette. A section of the cuvette is removed beforehand to facilitate the placement of the thermocouples necessary for the measurement of temperature. The bare wire fine-gage K-type thermocouples, 0.002 inches in diameter, are mounted on individual Teflon plates stacked vertically. Though lexan was initially used as the material for constructing the plates, Teflon was found to provide better corrosion resistance to the nitric acid spilled during the drop test. The plates are recessed in order to position the cuvette accurately below a syringe containing approximately 10 µl of fuel. Special care is taken to align the syringe above the thermocouple assembly to ensure the drop of fuel avoids the thermocouple wires while traveling towards the oxidizer pool.

The event is initiated by pressing the plunger on the syringe through a friction-guided cylindrical block. A He-Ne laser, and a corresponding photodiode, placed underneath the syringe, but above the thermocouple assembly, triggers the data
acquisition system through a reduction in the photodiode signal as the drop of fuel descends across the line-of-sight. In a series of separate tests, a second laser and photodiode pair placed just above the surface of the oxidizer pool were used to identify the staring point of the measurement of ignition delays. The time of impact was repeatedly found to be 64 ms after the drop crossed the first laser-beam. Besides, the pulse width of the signal from the second photodiode serves as a means to calculating the impact velocity of the drop. The flash of luminosity from ignition, which occurs after the ignition delay, is detected by a series of photodiodes placed along the wall of the cuvette, thus clearly identifying the ignition delay for the particular fuel-oxidizer pair. The thermocouple traces at different heights above the reaction surface are routed through an amplifier and recorded by a Nicolet multipro data acquisition system. The thermocouples were found to be coated with combustion products after each test, and hence were discarded in favor of new thermocouples at the beginning of each successive test.
9.2.2 Modified Confined Rapid Thermolysis Setup

The present experimental setup for studying condensed-phase reactions leading to hypergolic ignition is a modification of an existing facility for confined rapid thermolysis (CRT), which is utilized to study the rapid thermal decomposition of energetic materials under isothermal conditions. The CRT/FTIR technique has been described in section 3.1.1. However, the shift in focus from studying decomposition of individual ingredients of energetic materials to hypergolic reactions between bipropellant pairs brought forth several complications. First, the initial alignment of small droplets intended to be studied in the CRT setup is important, and hence posed a design challenge. Second, the volatile
nature of the preferred nitric acid oxidizer, combined with the small drop size, may cause significant loss due to evaporation. The high vapor pressure of concentrated nitric acid implied that delay periods would have to be considerably reduced between the formation of the drop, and the completion of the reaction. To circumvent this issue, 70% and 40% aqueous solutions of nitric acid by weight were chosen over white fuming nitric acid (WFNA). The modified setup consists of the components for the hypergolic test housed in a constant pressure chamber and a Bruker IFS66/S FTIR spectrometer. The constant pressure chamber, resting on a rigid frame, has a height of 27.5 cm and an inner diameter of 5 cm approximately. 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.

An exploded, three-dimensional view of the assembly for studying gaseous products of condensed-phase hypergolic reactions is shown in Fig. 9.3. The semicircular top sample holder contains one of the components of the hypergolic pair, while the other is retained by the bottom sample holder. Metal foils are attached to the top sample holder via 3M transfer tape, and are wrapped around the bottom sample holder, to minimize conductive heat transfer resistance, and protect the copper heaters from degradation by coming in contact with oxidizing species in the condensed phase. Though it is possible to utilize different types of foils, an 11 µm thick aluminum foil is chosen over a 6 µm thick stainless-steel foil. The issue of proper alignment of the fuel and oxidizer droplets is resolved by employing a stainless-steel guiding piece, and two separate cylindrical jigs for the top and the bottom sample holders. The jigs are provided with matching indentations at the centre of their surfaces, which introduce aligned markings over the aluminum foils during preparation of the top and bottom sample holders. The samples are
placed on those markings. Finally, the top sample holder is placed in a recessed groove on the top of the guide, whereas the bottom sample holder is positioned exactly underneath the top sample holder through the semi-annular slit on the surface of the guiding piece, assuring appreciable physical contact and thorough mixing of the bipropellant pair. The 250 \( \mu \text{m} \) thickness of the center portion of the top sample holder separates the bottom heater from the top heater. It also provides an exit slit having the width and height dimensions of about 8mm \( \times \) 250 \( \mu \text{m} \), respectively, that allows the evolved gases to enter the modulated beam of the FTIR.
The mobile bottom heater is designed to raise the bottom sample holder, bring it in contact with the top sample holder, and press the assembly against the stationary top heater.
heater. Thus, the hypergolic reactants are brought in contact with each other to initiate the reaction sequence. Figure 9.4 shows the final assembled configuration of the heaters and the sample holders, to emphasize the relative positions of various components. An additional stainless-steel piece is attached to the top heater by a set screw, to prevent corrosive gases from coming in contact with copper.

![Figure 9.4: Cross-sectional view of the hypergolic test setup showing the relative positions of the hypergolic sample pair and the FTIR beam.](image)

In both heaters, high heating rates are achieved by using high-watt density cartridge heaters (*Omega CIR-1014/120V*). The cartridge heaters are sheathed in copper rods, 53 mm in height and 15.6 mm in diameter, to ensure isothermal conditions at the reaction zone. The temperature of the cartridge heaters is monitored by two 75 μm K-type thermocouples embedded in the copper sheaths. Isothermal conditions are established and controlled by proportional-integral-derivative (PID) controllers (*Omega CN8500*). There are two auxiliary systems, a pneumatic piston-cylinder for lifting the bottom heater and a purge gas system. The purging system using an inert gas, typically
nitrogen, serves a dual purpose. One, it purges the chamber of the decomposition products and prevents recirculation of products into the path of the modulated FTIR beam, and two, it prevents oxidation of the copper rods at elevated temperatures.

The gaseous products evolve into the path of the FTIR beam, which enters the chamber through two ZnSe (or KRS-5) windows, offering a spectral coverage of 500-10,000 cm\(^{-1}\). This wide range is truncated using a germanium coated KBr beamsplitter and a mercury-cadmium-telluride detector to the mid-IR range of 600-5,000 cm\(^{-1}\). The gases evolved during the thermolysis are detected, identified and quantified using FTIR transmission spectroscopy, discussed in section 3.1.1.

The hypergolic materials 1-ethyl-3-methyl-imidazolium dicyanamide (EmimDCA) and 70% nitric acid were chosen for demonstrating the capability of the setup. Both materials, especially nitric acid, are hazardous and must be handled with precaution. Approximately 0.5 µL of both liquids were extracted using Hamilton 7100-series syringes, and weighed by a Mettler Toledo XP26 scale with a resolution of 0.002 mg. The liquid droplets were deposited on the sample holders, with the oxidizer being on the top and the fuel at the bottom. The heaters were previously brought up to the pre-set temperature. After the entire assembly is placed inside the chamber, the chamber is purged for approximately two minutes, or till the initial atmospheric concentrations of CO\(_2\) and H\(_2\)O are reduced below detectable levels. After the background spectrum is acquired by the FTIR spectrometer, the bottom heater is raised by the pneumatic piston-cylinder till the sample holders make a firm but spring-loaded contact with surface of the top heater. The rapid-scan data acquisition is then initiated to acquire spectra for approximately 7 seconds. The gases generated gain access to the FTIR beam via a small
slit in the enclosed space between the two sample holders. After the event is concluded, the heaters are switched off, and the sample holders extracted to be weighed again, in order to ascertain the loss in mass of the reactants.

9.3 Results and Discussion

9.3.1 Results from the Drop Test Apparatus

The drop test apparatus is primarily utilized to test the hypergolicity and screen probable hypergolic bipropellant candidates, and is dissimilar in nature to an actual hypergolic engine where the fuel and oxidizer are brought in contact after being atomized through their respective injectors. Although as opposed to the drop test, where the mixing process is limited by the amount of kinetic energy imparted to the fuel drop and a slow diffusion process, the mixing process underwent by the bipropellant pair under engine conditions is further enhanced due to the smaller drop sizes and higher impact velocities, the essential processes controlling ignition, such as diffusion of one reactant into another, rapid exothermic condensed phase reactions leading to the generation of products and partial vaporization of the fuel and oxidizer, thermal interactions between the condensed and gas phases promoting further gas phase reactions, and finally the generation of free radicals that participate in a series of chain-branching reactions to initiate ignition, remains essentially the same. Hence, a thorough understanding of the individual processes that occur in the pre-ignition phase in the drop test setup would contribute towards improving efficiency and performance of hypergolic
engines. However, it is imperative that the various relevant factors affecting the ignition and the diagnostic processes be maintained at reasonable levels. These include, drop size and impact velocity, fuel impact into an oxidizer pool versus oxidizer impact into a fuel pool, pool depth in the cuvette, fuel to oxidizer ratio, initial temperatures of fuel and oxidizer, external ambient conditions, oxidizer concentration, and finally event triggering.

To temporally resolve the phenomena occurring as a 10 µl EmimDCA droplet plunges into a 80 µl WFNA pool, a series of images were captured at 2000 frames per second by an Olympus i-speed 3 high speed camera. The figures in Tables 9.1 and 9.2 show a series of selected frames as the event progresses from impact of the droplet to ignition and self-sustained combustion. The velocity of the droplet at the moment of impact was estimated to be approximately 1.1 m/s, assuming a spherical shape, which was corroborated by the video. The mixing process of the fuel droplet into the quiescent oxidizer pool can be modeled after the experiments of Dooley et al. [14], who studied the coalescence of a fluorescent dye-injected water droplet at a free water surface via high speed photographs of laser-excited fluoresce. The mixing between the liquids was found to occur through vortex rings generated at the interface. Similar vortices are expected to form at the EmimDCA–WFNA interface, constraining the condensed phase reactions to the central region of the pool, as seen by the second frame in Fig. 3, 3ms after the impact of the droplet. However, it should be noted that while the viscosities of the two fluids in the experiments reported were similar, the viscosity of EmimDCA is 21 cP, compared to 0.86 cP for WFNA at 20ºC.
Table 9.1: Selected frames acquired during ignition occurring after impingement of an EmimDCA droplet on WFNA.

\begin{align*}
&\text{t=−7.5 ms} & \text{t= 3ms} \\
&\text{t= 8ms} & \text{t= 13ms} \\
\end{align*}
As the two reactants come into intimate contact along the edges of the vortex, extremely rapid exothermic reactions were found to occur at the interface, forming a multitude of products, which will be discussed in the next section. The vigorous nature of the reactions raised the temperature in the liquid phase beyond the boiling point of WFNA, as evident from the formation of small bubbles in the pool along the reaction front. The third and fourth frames in Table 9.1 and the first frame of Table 9.2, taken 8 ms, 13 ms, and 22 ms after the droplet impact respectively, exhibit the violent nature of

Table 9.2: Selected frames acquired during ignition occurring after impingement of an EmimDCA droplet on WFNA.
the condensed phase reactions, which results in expulsion of small droplets into the gas phase ignition zone. The condensed phase reactions also evacuate WFNA from the centre of the pool, forcing sheets of the oxidizer to creep along the cuvette walls. The exact composition of these small droplets is subject to further investigation. However, it may be safe to speculate that the droplets are primarily composed of the oxidizer, because of the large oxidizer–fuel ratios employed in the tests, mixed with the fuel as well as the heavier molecular weight product species that tend to remain in the condensed phase. Besides these droplets, the gas phase also contains evaporated WFNA and EmimDCA.

After a certain period of accumulation of gases and globules in the gas phase above the reaction zone, the ignition kernel is formed 25 ms after the droplet impact. The kernel expands to a luminous flame within a short period of time, traveling downwards to consume the excess fuel and oxidizer, as well as upwards towards the open end of the cuvette, as shown by the third frame in Table 9.2. The combustion process is short-lived owing to constraints on the amount of fuel introduced into the system. Copious amounts of charred material are formed in the process, as detected along the walls of the cuvette after the event is over. An interesting observation may be witnessed from the last frame in Table 9.2, which shows the flame extinguishment as the event nears the end. At the centre of the cuvette, a smoldering drop of liquid was found to remain where the fuel had originally entered the oxidizer pool. Similar occurrences have been found repeatedly in other tests as well as with BmimDCA. This clearly demonstrates that the highly dense and viscous fuel diffuses to a limited extent into the oxidizer, which is simply pushed aside by the falling droplet. Efforts are underway to validate such a hypothesis by
injecting a fluorescent dye into the fuel to study the mixing between liquids with such widely varying viscosities.

Besides the high speed videos of the hypergolic ignition event, temperature profiles at three locations in the gas phase were also acquired to provide further assistance in resolving the gas phase phenomena. Figure 9.5 shows the variation of temperature in the ignition zone, coupled with a photodiode trace monitoring the visible emission during ignition, as a 10 µl drop of EmimDCA impinged upon 160µl of 90% HNO₃. The thermocouples were numbered one to three, in order of increasing distance from the oxidizer surface. As evident from the plot, no temperature rise is detected for approximately 35 ms after the droplet impact. This period, as corroborated by the Tables 9.1 and 9.2, is dominated by mixing between the two reactants, and subsequent condensed phase reactions along the mixing interface. After this initial phase, the gaseous products as well the condensed phase globules enter the gas phase. These elements combined with the heat feedback from the exothermic liquid phase reactions cause a sharp inflection point in the temperature profile recorded by the first thermocouple. The arrival of this point is delayed for the subsequent thermocouples due to the temporal lag introduced by the gas transport across the half-inch distance between consecutive thermocouples.
After the initial sharp increment in temperatures, the temperature at the first and the second thermocouples remain constant at approximately 100ºC and 90ºC for 35 ms, signaling an accumulation of gaseous species in the ignition zone. However, the thermocouple farthest from the reaction zone records a gradual rise in temperatures up to 60ºC. At the end of this period, which may be termed as an induction period, the ignition kernel is formed in the gas phase, and introduces the second inflection point in the temperature profiles. The ignition point was also clearly identifiable from the sharp rise in the photodiode signal. The global ignition delay for a system comprising of 10 µl of EmimDCA and 160µl of 90% HNO₃ was thus determined to be 70 ms. After the initiation of combustion, the temperatures of the first, second and the third thermocouples rose sharply to attain their maximum values of 900ºC, 1050ºC and 720ºC, respectively.

Figure 9.5: Temperature profiles and photodiode output from hypergolic reaction of an impinging EmimDCA droplet on 90% HNO₃.
The temperature profiles gradually declined after the combustion event was over, as identified by the return of the photodiode signal to its base level. The presence of several peaks in the photodiode signal was commensurate with the videos taken of the event with the high speed camera, where the flame front was found to grow and diminish over the duration of the combustion event.

The variation of ignition behavior of EmimDCA with varying strengths of nitric acid was studied by substituting 90% HNO$_3$ with WFNA. Compared to 90% HNO$_3$, a smaller amount of WFNA was found to be sufficient for repeatable and reliable ignition. Figure 9.6 shows the variation of temperature in the ignition zone, coupled with a photodiode trace monitoring the visible emission during ignition, as a 10 µl drop of EmimDCA impinged upon 100µl of WFNA. As expected, the absence of 10% water led to faster reactions in the condensed phase, and gases started to accumulate in the ignition zone as early as 20 ms. The global ignition delay was also found to be shortened to approximately half of the value obtained with 90% HNO$_3$, to 35 ms. After the ignition delay, the temperature traces from all three thermocouples increased rapidly to approximately 1000°C. However, the combustion event was vigorous enough to burn the thermocouples shortly after 60 ms, rendering the temperatures recorded after that point practically unusable. The post-ignition temperature profiles were found to be relatively similar to those obtained with 90% HNO$_3$. 
9.3.2 Results from the Modified Confined Rapid Thermolysis Setup

As discussed earlier, the development of a suitable condensed phase reaction mechanism that describes the liquid phase chemistry in the pre-ignition stages, and the determination of the appropriate Arrhenius-type rate constants is a major objective of this study. Chambreau et al. [13] utilized FTIR spectroscopy in order to examine the gas phase products in the pre-ignition stage during drop tests involving BmimDCA and WFNA. The species identified were CO$_2$, N$_2$O, H$_2$O, and HNCO, whereas HCN, HONO, NO, and CO were found to be absent. Similar products were observed before the hypergolic ignition of sodium dicyanamide with WFNA, suggesting minimal influence of
the nature of the cation on the condensed phase reactions. Biuret reaction tests conducted on the residue from the quenched reaction between sodium dicynanamide and 34% HNO$_3$ showed a positive result, thus suggesting the presence of a biuret as a reaction intermediate. A comprehensive set of ionic elementary reactions and global decomposition reactions were presented by the authors in an attempt to explain the reaction process between a dicyanamide and nitric acid. However, the determination of activation energies and the pre-exponential factors for the proposed reaction scheme being extremely difficult using the above-mentioned experimental setup, preliminary steps were taken to use ab initio computational methods to probe this area. This study attempts to lay the groundwork for experimentally determining the above-mentioned parameters.

Figure 9.7 shows a typical transmission spectrum of the gaseous products from the condensed-phase reaction between 70% HNO$_3$ and EmimDCA under 50ºC exposed to an inert atmosphere of N$_2$. The major products identifiable from the FTIR spectrum are CO$_2$, N$_2$O, and H$_2$O, with several strong rovibrational bands. Small amounts of HNCO were also detected. Although not present in large amounts, the spectrum shows the presence of HNO$_3$ and NO$_2$ in smaller amounts. The net transmittances of the products were high enough for the data reduction procedure to extract the mole fractions of the relevant species. Figure 9.8 shows the extracted species profiles for the same experiment. After an initial surge in the concentrations of HNO$_3$ after the two heaters are brought in contact, the bulk of the species, CO$_2$, H$_2$O, and N$_2$O evolve at a fast rate following a short chemical delay period.
The species evolution profiles at three different temperatures extracted after averaging a multitude of tests for the purpose of optimizing the reaction rate parameters are displayed in Fig. 9.9. Since quantification of HNCO in terms of mole fractions is a tedious job, it has been left out of the species list. Also, H$_2$O has been excluded due to the presence of 30% water in nitric acid, which however, increases the probabilities of third body reactions in the condensed phase.

Figure 9.7: FTIR spectrum of species from hypergolic reaction of EmimDCA with 70% HNO$_3$ at 50°C and 1 atm N$_2$. 
Figure 9.8: Species evolution from hypergolic reaction of EmimDCA with 70% HNO$_3$ at 50°C and 1 atm N$_2$.

Figure 9.9: Species evolution from hypergolic reaction of EmimDCA with 70% HNO$_3$ at 30, 40, and 50°C and 1 atm N$_2$. 
In order to further elaborate on the reactions leading to the formation of \( \text{N}_2\text{O} \) and HNCO among the final products, EmimDCA was brought in contact with 40\% H\(^{15}\)NO\(_3\) at 90°C. A representative spectrum obtained from the gas phase is displayed in Fig. 9.10. The principal rovibrational band at 2225 cm\(^{-1}\) due to \( \text{N}_2\text{O} \) was found to be shifted to a lower wavenumber. The bands in the spectrum corresponding to \( \text{N}_2\text{O} \) were found to be due to \(^{14}\text{N}\(^{15}\)NO\), thus proving that the \( \text{−NO} \) functionality in \( \text{N}_2\text{O} \) is derived from HNO\(_3\). The peak at 2270 cm\(^{-1}\) due to HNCO was found to unaffected by the presence of the isotopic nitrogen, showing that the nitrogen on HNCO is derived from the dicyanamide anion.

Figure 9.10: FTIR spectrum of species from hypergolic reaction of EmimDCA with 40\% H\(^{15}\)NO\(_3\) at 90°C and 1 atm N\(_2\).
A white residue was left on the foil after the test, which when subjected to further rapid thermolysis at 300ºC, yielded large quantities of HNCO, N₂O, H₂O, and CO₂, as shown in Fig. 9.11. Also present in the spectra were smaller quantities of NH₃. The major products of decomposition were found to be similar to those detected by Geith et al. [15] during the decomposition of dinitrobiuret under a heating rate of 1ºC/min. Besides the decomposition products mentioned above, a different product, dicyandiamide was detected during rapid thermolysis at higher temperatures. Figure 9.12 shows the FTIR spectra of the products obtained through thermal decomposition of the residue left after hypergolic reactions between EmimDCA with 70% HNO₃, and sodium dicyanamide with 70% HNO₃ at 400ºC. The presence of (NH₂CN)₂ was apparent from the presence of the dual peaks around 1500 cm⁻¹.
The comprehensive reaction mechanism leading to the formation of the key products, N$_2$O, CO$_2$, HNCO, and H$_2$O, was reduced to a model with five dominant reactions governing the pre-ignition condensed phase chemistry. The reduced reaction mechanism is detailed in the scheme shown below. The initiation reaction was presumed to be a neutralization reaction between EmimDCA and HNO$_3$, leading to the formation of EmimNO$_3$ and the protonated dicyanamide anion (HDCA). The next two steps involve reactions between HDCA and HNO$_3$, forming the intermediates, cyano-nitro-urea and

![FTIR spectrum](image)
dinitrobiuret, which subsequently decompose to form the smaller molecular weight products.

Figure 9.12: FTIR spectra of species generated during thermolysis of residue left after hypergolic reaction between EmimDCA and sodium DCA with 70% HNO₃ at 400°C and 1 atm N₂.
Pre-ignition condensed phase reaction scheme for \( \text{HNO}_3 \) and EmimDCA

9.4 References


Chapter 10

CONCLUSIONS

Confined rapid thermolysis studies with FTIR spectroscopy and ToF mass spectrometry as the diagnostic tools were conducted on various families of EILs. The thermal stability of the imidazolium family of salts was found to be the highest, followed by the triazolium and the tetrazolium family of salts.

10.1 Imidazolium Salts

In case of the imidazolium salts, analysis of the evolved gaseous species has shown that nucleophilic transfer involves primarily the methyl group and secondarily the ethyl group, whereas the ring remains largely intact although the temperatures employed reached 435°C. The formed species after proton transfer involving [emim]NO$_3$ are extremely reactive and produce small molecular weights products at a high rate. Studies involving [emim]Br and [emim]Cl produced no evidence of either HBr or HCl, both of which are strongly IR-active. Besides evidence of the formation of 1-MeIm and N-EtIm for the two latter ionic liquids, the proton transfer yields hydrocarbons containing methyl and ethyl groups. Further decomposition of the hydrocarbon halides is not evident.
10.2 Amino-triazolium Salts

In the triazolium family, deprotonation from the amino group initiated the decomposition for the more energetic 4ATN, with subsequent reactions leading to the formation of 1TA. No evidence of formation of 4AT was found, thus reducing the possibility of a proton transfer from the N$_1$ position. Multiple secondary reactions involving ring fracture were also apparent, leading to the formation of HCN. The species formed during the initial decomposition of 4ATN were extremely reactive, and produced smaller molecular weight species, such as H$_2$O and N$_2$O, at a fast rate.

10.3 Methyl-amino-triazolium Salts

The change in the ring structure from a 1,2,4-triazole to a 1,2,3-triazole did not have a significant effect on the thermal stability and the major decomposition pathways for the compounds. For both the iodide compounds Me4ATI and Me1ATI, the amino group was involved in the initiation reaction, leading to the formation of NH$_3$ and methyl-iodo-triazoles. However, unlike Me4ATI, in case of Me1ATI, the secondary initiation pathway involving a methyl group transfer to form CH$_3$I was found to be active. In case of the nitrate compounds, decomposition was initiated by the nitrate ion scavenging the amino group to form NH$_2$ONO$_2$ and the corresponding methylated triazole. NH$_2$ONO$_2$ reacted vigorously with the parent nitrates to form H$_2$O, N$_2$O and N$_2$ through secondary reactions. The methylated triazoles were subsequently oxidized by HNO$_3$ to form smaller molecular weight species.
10.4 Tetrazolium Salts

The relocation of the amino group from the N$_2$ position to the N$_1$ position lowered the thermal stability of the tetrazolium family of salts by 50ºC. While in case of 2AdMTZI and 2AdMTZN, the nucleophilic transfer primarily involved a methyl group, despite the presence of a more reactive amino substituent on the ring, in case of 1AdMTZI and 1AdMTZN, initiation reactions involved the methyl group extraction, hydrogen abstraction by the amino group, and ring nitrogen expulsion. The resultant amino-methyl-tetrazoles decomposed readily. 2A5MeTZ formed N$_2$ and CH$_3$NC as the principal products at higher temperatures, while 1A5MeTZ formed NH$_3$ and N$_2$. Methyl nitrate formed in the initial steps from the nitrate salts participated in a series of complex secondary reactions to form smaller species.

10.5 Kinetics Studies

The kinetics of the initiation reactions governing the thermal decomposition of several ionic compounds was investigated. The decomposition of the individual compounds was experimentally probed by confined rapid thermolysis/FTIR/ToFMS to determine the species profiles of the products in the gas phase being generated in the condensed phase, which were in turn provided as inputs to a genetic algorithm-based optimization module for determining the Arrhenius-type rate parameters for the constructed reaction mechanisms. The recovered activation energies of the unimolecular decomposition step and the subsequent autocatalytic step for AN were found to correspond to values published in the literature. Values for similar reactions were also
determined for the EILs 4ATCI, 4ATN, and HEHN. The versatility of the method applied in elucidating the chemical kinetics of the initiation steps allows its utilization in determining the entire chemical kinetics of decomposition of the EILs, as well as similar energetic materials.

10.6 Dicyanamide-based Salts

High speed videos and thermocouple measurements were used to determine the individual processes occurring during the ignition of EmimDCA when brought in contact with WFNA. The videos revealed that vigorous exothermic reactions in the condensed phase led to the expulsion of numerous globules of condensed matter into the ignition zone after an initial phase of mixing between the two reactants. Temperature profiles obtained at three distinct regions above the liquid surface demonstrated that the temperatures rose sharply to approximately 1000°C after remaining constant at 100°C in the pre-ignition stage. An ignition delay of 70 ms for the EmimDCA 90% HNO₃ system obtained from the temperature profiles was corroborated by the photodiode voltage profile monitoring the luminosity in the gas phase. A concise reaction scheme detailing the condensed phase pre-ignition chemistry was postulated to determine the pertinent chemical kinetic parameters, involving neutralization as the initiation step, and the subsequent formation and decomposition of cyano-nitro-urea and dinitro-biuret as intermediates.
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