APPLICATION OF THE REAXFF MOLECULAR SIMULATION METHOD FOR INVESTIGATING HYPERGOLICITY OF ENERGETIC IONIC LIQUIDS

A Thesis in
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by
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ABSTRACT

The conventional fossil fuels that are currently used for energy generation in different areas are non-renewable and harmful for the environment. This problem has made researchers and people around the world work towards finding alternatives to these fuels. One special area of application for certain type of fuels is their use as hypergolic space propellants. Hypergolic in the context of propellants refers to the process of spontaneous ignition upon contact with an external species such as an oxidizer. The most common hypergolic propellants in use today are a mixture of fuels like Hydrazine, Monomethyl Hydrazine (MMH) and Unsymmetrical Dimethyl Hydrazine (UDMH) along with oxidizers like White Fuming Nitric Acid (WFNA), Red Fuming Nitric Acid (RFNA), Inhibited Red Fuming Nitric Acid (IRFNA) and Nitrogen Tetroxide (NTO). Since hydrazines are carcinogenic, have a high vapor pressure, are low density fuels, evaporate easily and can be highly toxic if inhaled or internally ingested, there is a significant need for the development of new fuels with matching performance properties and lower toxicity.

The high chemical reactivity of hypergolic fuels makes it extremely difficult to measure their reaction chemistry and reaction kinetics with certainty. Computer simulations like molecular dynamics (MD) methods can help us identify the intermediates and predict the reaction chemistry at an atomistic level. Results obtained using MD in analyzing combustion and thermal decomposition problems coupled with convincing results have prompted this study at the atomistic level to be performed in probing hypergolic behavior among ionic liquids.
In this thesis, the ReaxFF reactive force field is used for performing MD simulations on a number of ionic liquid and oxidizer species combinations. We predict the reaction chemistry of these energetic IL’s and correlate it with earlier results published using QM calculations. Primary cation is 1-butyl-3-methyl imidazolium and anion is dicyanamide. Oxidizer species used are nitric acid (HNO$_3$) and nitrogen tetroxide (N$_2$O$_4$). We have first trained the force field for nitric acid by training it against a set of available QM and experimental data. Then we use this force field to perform simulations and extract the data obtained from the output to retrain the force field. Drop-test simulations on a fuel and oxidizer combination and analysis of the chemistry are performed. We analyze the trajectory of the different cation and anion to find out the crucial intermediates from the reaction.

In our simulations, we observe that when the fuel droplet comes in contact with the oxidizer at a velocity of 9-12 km/s, it undergoes vigorous reactions leading to the formation of key reaction intermediates HC$_2$N$_3$ and HC$_2$N$_4$O$_3$. Cookoff simulation involving a steep temperature ramp-up of 2000K carried out with HC$_2$N$_4$O$_3$ in a nitric acid environment eventually led to the formation of dinitrobiuret (H$_3$C$_2$N$_5$O$_6$). This reaction mechanism observed through ReaxFF is in good agreement with that proposed in QM and experimental studies [15, 32] indicating that ReaxFF provides a feasible computational approach for designing and analyzing hypergolic ionic liquid formulations.
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<td>CDT</td>
<td>Chemical Delay Time</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>DNB</td>
<td>Dinitro Biuret</td>
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<td>HDCA</td>
<td>Hydrogen Dicyanamide (HC$_2$N$_3$)</td>
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<tr>
<td>HDCA.NO$_3$</td>
<td>HC$_2$N$_4$O$_3$ (HC$_2$N$_3$-NO$_3$)</td>
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<td>IL</td>
<td>Ionic Liquid</td>
</tr>
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<td>IRFNA</td>
<td>Inhibited Red Fuming Nitric Acid (83% HNO$_3$ + 14% N$_2$O$_4$ + 2.5% H$_2$O + 0.5-0.6% HF)</td>
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<td>MD</td>
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<td>Mononitro Biuret</td>
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<td>Nitrogen Tetroxide (N$_2$O$_4$)</td>
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<td>Quantum- Mechanical</td>
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</table>
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Chapter 1
INTRODUCTION

This introduction offers a general yet detailed description of the different concepts involved with this research work. It covers broad topics about the material being investigated and about the computational tools being used for deriving the results. There is a special focus on ReaxFF, which is the computational tool used here for the simulation and analysis work.

1.1 Ionic Liquids

Ionic Liquids (ILs) have attracted a wide interest as a new class of materials. Industrial applications of ILs have increased manifold complemented with new properties for them being discovered gradually. ILs are salts that are composed of ions that have melting points below 100°C. While salts which are ionic in nature and composition have been known for more than a century, the new phenomenon surrounding their interests lies in the synthesis of these liquids with flexible properties. Specific IL compositions can be synthesized based on the user’s need and the desired physical, chemical and biological properties. ILs consisting of 1,3-dialkyl imidazolium and N-alkyl pyridinium have been found to possess favorable properties like low toxicity, low flammability, low volatility and referred to as green fuels for use in the future [1].
ILs can exhibit certain desirable physical properties, such as high solvency, wide liquidus range and negligible vapor pressure, which merit the consideration of ILs as solvent replacements. ILs are evolving from electrochemical and general solvents [2] [3] to novel materials in diverse applications such as lubricants [4] [5] [6], thermal fluids [7], propellants [8] [9] etc. ILs provide a platform through which we can individually modify the cation or anion while retaining the core desirable features of the IL [10].

Anions in ILs are usually weak basic inorganic or organic compounds that have a diffuse or protected negative charge. The lowest viscosity ionic liquids are formed from small anions that have a diffuse negative charge and do not participate in hydrogen bonding [11]. Typical ionic liquid cations include N-butylpyridinium, 1-alkyl-3-methylimidazolium or 1,3-dialkylimidazolium. Common anions are $[\text{Cl}]^-$, $[\text{Br}]^-$, $[\text{PF}_6]^-$, and $[\text{BF}_4]^-$.

Thermodynamic properties of ILs are conveniently determined by thermogravimetric/differential scanning calorimetry (TGA/ DSC) techniques [12]. Also used for probing reaction mechanisms of energetic ILs are Fourier Transform Infra Red and ToF techniques [13].

Cations are generally organic and heavier of the two species. The effect of different anions on an IL is more prominent and wide-ranging than a corresponding variation in cation. There is a further decrease in melting point as the length of the alkyl group on the cation increases in the region of three to five carbon atoms [11]. Figure 1-1 shows some examples of ionic liquids commonly used. Figure 1-2 shows a pictorial view of the melting point of some IL combinations.
Figure 1-1: Commonly used cations and anions in ionic liquids.

Common cations:

- Phosphonium
- Imidazolium
- Ammonium
- Pyridinium

Common anions:

- $\text{F}_3\text{CO}_2\text{S}^-$
- $\text{N}^+\text{SO}_2\text{CF}_3^-$
- $\text{PF}_6^-$
- $\text{CF}_3\text{SO}_3^-$
- $\text{BF}_4^-$

Figure 1-2: Melting points of imidazolium based Ionic Liquids [14].

('R' represents alkyl and 'X' represents anionic group).
1.2 Hypergolic Ionic Liquids

Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. This makes them highly useful for spacecraft and satellites, which need to fire their rocket engines hundreds or even thousands of times during their lifetime. In a salt system, the positive charge of the cation makes it resistant towards oxidation. Electron and fuel rich anions are much easier to oxidize and hold the potential to promote hypergolic ignition [15].

There are a number of different fuel-oxidizer combinations used in hypergolic bipropellant formulations, where the fuel typically is hydrazine or one of its derivatives. Hydrazine based propellants are hazardous and need careful handling. Recently, a novel class of ILs with high nitrogen content has received significant attention as novel energetic materials due to very high heats of formation [16]. Energetic ILs possess a number of advantages over conventional hypergolic propellants such as high density, good oxygen balance, improved stability, low vapor pressure that results in reduced loss of material and decreased hazards through formation of explosive fumes [16].

Designing novel IL hypergolic systems requires a fundamental understanding of pre-ignition and ignition stages. The interaction of physical phenomena (mixing and interfacial transport) and chemical kinetics (key initiation reactions, preignition intermediates, and ignition events) is important to facilitate development of new ILs for application as hypergolic propellants [16].
Earlier investigations into hypergolic behavior have shown that fuel rich anions have a marked reactivity towards oxidizer whereas the same family of cations shows no appreciable reactivity characteristics. In our research, we have primarily focused on using Dicyanamide anions (C$_2$N$_3^-$) for the simulations since the ILs based on DCA anions tend to have the lowest viscosities among known ILs. In propellant systems and fuel delivery systems, viscosity is an important property to consider for these ILs to qualify as propellant fuels. Imidazolium-based IL was first considered because they generally possess greater stability than their triazolium or tetrazolium analogues [15].

In the area of replacement for hypergolic fuels, there is a long list of aliphatic amines that are less toxic than UDMH and MMH. The task is to not only develop a new and broad range of ILs that can replace or supplement the existing propellants but also to develop non-destructive techniques like computational chemical simulation methods for investigating their behavior. This would save time and reduce production costs on ILs.

1.3 Modeling and Simulation

Modeling and simulation greatly aids in understanding the complex phenomenon associated with combustion events. A simulation generally refers to a computerized version of the model which is run over time to study the implications of the defined interactions. Simulations are mostly iterative in nature. One develops a model, performs the simulations, learns from the results, revises the model, and continues the iterations until a desired level of understanding is developed. Computational Chemistry uses the results from theoretical chemistry and incorporates the associated potentials and
parameters into computer programs. Upon compilation, structures are calculated and properties co-relating the interaction between atoms and molecules are studied.

1.3.1 Molecular Dynamics

Molecular Dynamics is a form of computer simulation to study the time dependent motion of a molecular system as they interact under specific conditions, providing us the atom positions, velocities and accelerations. Use of statistical mechanics allows us to translate this information into other macroscopic properties like pressure, heat capacities etc. An experiment is usually made on a macroscopic sample that contains an extremely large number of atoms or molecules which sample a large number of conformations. In statistical mechanics, averages corresponding to experimental observables are defined in terms of ensemble averages. An ensemble would be a collection of all possible systems which have different microscopic states but have an identical macroscopic or thermodynamic state.

The molecular dynamics simulation method is based on Newton’s second law or the equation of motion, $F = ma$, where $F$ is the force exerted on the particle, $m$ is its mass and $a$, its acceleration. From knowledge of the force on each atom, it is possible to determine the acceleration of each atom in the system. Integration of the equations of motion then yields a trajectory that describes the positions, velocities and accelerations of the particles as they vary with time. From this trajectory, the average values of properties can be determined. Once the positions and velocities of each atom are known, the state of
the system can be predicted at any time in the future or the past. The integration of these
equations of motions can be done using the Verlet algorithm [17]. Mathematically:

\[ \vec{F}(t) = -\frac{dE}{d\vec{x}} = m \vec{a}(t) = m \frac{d^2 \vec{x}(t)}{dt^2} \Rightarrow \]

\[ \vec{x}(t) = \vec{x}(t_0) + \vec{v}(t_0) (t - t_0) + \int_{t_0}^{t} dt' \int_{t_0}^{t'} \frac{1}{m} \vec{F}(t'') dt''' \]

1.3.2 Types of Ensemble

In the context of quantum mechanics, an ensemble contains a state and several
dynamic variables by which we can impose a set of conditions in order to compare or
find out the probabilities of the outcome of certain events [19].

1) **Microcanonical ensemble (NVE)**: The thermodynamic state characterized by a fixed
number of atoms- \( N \), a fixed volume- \( V \), and a fixed energy- \( E \). This corresponds to an
isolated system.

2) **Canonical Ensemble (NVT)**: This is a collection of all systems whose thermodynamic
state is characterized by a fixed number of atoms- \( N \), a fixed volume- \( V \), and a fixed
temperature- \( T \).

3) **Isobaric-Isothermal Ensemble (NPT)**: This ensemble is characterized by a fixed
number of atoms- \( N \), a fixed pressure- \( P \), and a fixed temperature- \( T \).
In a MD simulation employing variable temperature or while maintaining
temperature constant, a thermostat is used. In the ReaxFF atomistic simulations that have
been performed in the research, the force field employs a Berendsen thermostat [20].

1.3.3 Berendsen Thermostat

The Berendsen thermostat [20] is an algorithm to re-scale the velocities of
particles in MD simulations to control the simulation temperature. To maintain the
temperature, the system is coupled to an external heat bath with fixed temperature $T_0$.
The velocities are scaled at each step, such that the rate of change of temperature is
proportional to the difference in temperature:

$$\frac{dT(t)}{dt} = \frac{1}{\tau} \left( T_0 - T(t) \right) \quad - (3)$$

where ‘$\tau$’ is the coupling parameter which determines how tightly the bath and the system
are coupled together. The ensemble generated using the Berendsen thermostat is not the
canonical ensemble. The thermostat suppresses fluctuations of the kinetic energy of the
system and therefore cannot produce trajectories consistent with the canonical ensemble.

1.3.4 Force Fields

The simulations we perform using MD employ a force field. A force field is a
functional set of parameters used for describing the potential energy of a system of
particles. The force field contains parameters to describe both the bonded interaction between atoms as well as the non-bonded interactions arising between the atomic species such as Coulombic (electrostatic) attraction and van der Waals force. The bonded terms include the energy from bond breaking and bond formation, angle rotation as well as dihedral torsion.

One of the most important characteristics of a force field is that it provides a mechanism for describing the potential energy surface for a large molecular system from components that can be parameterized on the basis of experimental information and/or the results of QM calculations. The reactive force field ReaxFF is trained primarily using QM data. The non-bonded terms in a force field are the more computationally expensive terms since they involve far more interactions per atom than the bonded terms. A force field that works for one or more atoms or molecule may not work for a different molecule depending on the transferability of the force field method. The drawback of creating a single force field for a large number of species is that enhanced transferability would require more substantial training against QM data. Discussion of reactive MD and the ReaxFF reactive force field follows.

1.3.5 Reactive Molecular Dynamics

Reactive molecular dynamics, or MD with reactive force fields, can be used to simulate chemical reactions in large atomic and molecular systems. Using this technique, it is possible to reach nanometer length scales while accounting for the effects of intermolecular interactions in condensed phases. As compared to a nonreactive force field, a
reactive force field such as ReaxFF employs a bond-order/bond-distance concept which allows it to simulate bond breaking and bond formation effectively.

For energetic materials, understanding their behavior towards thermal excitation and impacts at the atomic level requires an understanding of the reactive dynamics involved in such reactions, which includes: non-equilibrium heat/mass transfer, decomposition, phase transitions etc. ReaxFF allows for such conditions and parameters to be modeled and simulated.

1.4 ReaxFF

ReaxFF is a reactive force field for performing MD simulations at the atomistic level. The ReaxFF force field was developed by van Duin et al. [21]. ReaxFF is a reactive force field based on bond-order potentials and accurately describes bond formation and bond breaking with every iterative time step. Initially developed for hydrocarbons, ReaxFF has been successfully applied to a large set of chemical systems ranging from organic reactions\textsuperscript{a}, reactions of energetic materials (EMs), such as RDX and HMX under extreme conditions\textsuperscript{b,c} decomposition of improvised explosive devices such as TATP\textsuperscript{d}, thermal decomposition of polymers such as silicones and tribology of metal-metal oxide interfaces\textsuperscript{e}, catalytic formation of carbon nanotubes\textsuperscript{f}, storage of H\textsubscript{2} in Mg nanoclusters\textsuperscript{g}, Si/SiO\textsubscript{2} oxidation\textsuperscript{h}, crack propagation in silicon crystals\textsuperscript{i}, dissociation of H\textsubscript{2} on Pt surfaces\textsuperscript{j}, propene-selective oxidation over BiMoO\textsubscript{x} heterogeneous catalysts\textsuperscript{k}, and catalysis and ion transport in fuel cells\textsuperscript{l} [22].
Figure 1-3 shows the position of ReaxFF in the hierarchy of various computational methods.

QM studies have been most useful for understanding uni-molecular and simple bi-molecular processes of small molecules (<50 atoms), but QM is not practical for following the MD for the reaction pathways for systems containing 10,000 to 1,000,000 atoms over the periods of many nanoseconds. Knowledge of bond breaking and bond formation in chemically explosive species is important because the current experimental techniques are not able to predict the intermediate transition states and reaction kinetics.
sufficiently. This is due to the response time for experimental techniques such as mass spectrometry and chromatography, which can go as low to the order of milli seconds. But in hypergolic reactions such as the ones studied here between energetic materials, the time duration of existence of the intermediate products or transitional species is of the order of pico seconds. MD simulations using ReaxFF greatly help in learning about the chemistry that takes place in these short transition intervals based on a trained force field.

The bond orders are calculated on the basis of inter-atomic distances. The correct bond order is enforced using energy penalties for over-coordination and under-coordination of atoms. The bond order and charge is updated every iteration. The total potential energy of a system is given in Reax by: -

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{lone pair}} + E_{\text{overcoord}} + E_{\text{undercoord}} + E_{\text{valence}} + E_{\text{penalty}} + \\
E_{\text{conjugation}} + E_{\text{C2}} + E_{\text{torsion}} + E_{\text{H-bonding}} + E_{\text{vdW}} + E_{\text{Coulomb}} - (4)
\]

This includes the energies for bond distance, lone pair, over-coordination, under-coordination, valence interactions, energy penalty, conjugation, torsion, hydrogen-bonding, van der Waals and Coulomb interaction. Charge distribution in Reax is calculated using a geometry dependent polarizable charge calculation method known as Electronegativity Equalization Method [23].

There are some principles that are common to all force field methods, including ReaxFF. These features include: -

- The system energy is divided into contributions from bonded and non-bonded interactions.
- The bonded interactions are linked to the internal coordinates of the molecule, most commonly including bonds, angles and torsion angles.
• For each of these internal coordinates an equilibrium-state is defined (equilibrium bond length and equilibrium angle).

• An energy function is linked to the internal coordinate, describing the energy and force required to displace the internal coordinate from its equilibrium-state. Reactive molecular dynamic methods use bond-order concepts which allow a proper dissociation of the bonds. Non-bonded interactions are commonly divided into van der Waals and Coulomb contributions.

The charges used to calculate the Coulomb interactions can come from various sources; in protein force fields like CHARMM [24] and AMBER [25], these charges are kept fixed during the simulation. In most cases, non-bonded interactions are excluded between atoms sharing a bond, a valence angle or even a dihedral angle. These non-bonded exclusions completely separate the length-scale of the bonded (short length scales) and non-bonded interactions (long-range).

Once the set of empirical equations linking the molecular geometry to energy and forces is defined, one obtains a set of parameters (like force constants). If a direct link between an experimental parameter and a QM-based property exists, then we can formally assign the parameter a value. One can obtain the parameter values by fitting them to a database of experimental and/or QM-data (training set). The contents of the training set define the transferability of the force field; a force field that successfully reproduces data for a wide range of structure diversity can be expected to have a broader range of applications. The bond order/ bond distance approach provides FF-methods the ability to simulate connectivity changes and converge to the right dissociative bond limit. The bond-order correction scheme enables ReaxFF to use a slowly decaying bond-order
function, enabling the method to properly capture QM-transition state energies and not only predict reaction products but also describe reaction kinetics. In ReaxFF, separate bond distance/bond order relationships are used for the single (sigma), double (pi) and triple (double-pi) bond order and this information can be directly used to derive the hybridization effects on equilibrium angles and torsion angle force constants.

The training set used in our research is developed for nitric acid which incorporates several parameters related to reactions between OH, NO₂, HNO₃, HONO etc. Parameters for nitrogen and hydrogen atoms such as H₂ dissociation, O-O single/double bond dissociation and N-O single/double bond dissociation, have been added from the earlier training sets developed for nitramine [26], hydrazine [27] and ammonia borane [28].
Chapter 2

LITERATURE REVIEW

2.1 Ionic Liquids as Hypergolic fuels

The computational approach that has been developed during the course of this research has the foundation and support from earlier conducted experimental work on IL formulations which have shown promise and warrant the development of diagnostic and testing solutions for investigating hypergolic behavior in energetic ILs.

Schneider et al. [15] reported the first ignition tests carried out with fuel-rich azide anions \([N_3]^–\), though these did not reveal hypergolic properties. The violent nature of the reaction prompted further investigation. Using nitrate anions \([NO_3]^–\), with the imidazolium family of cations showed no reaction with IRFNA, RFNA or WFNA. The droplet tests (or drop tests) were carried out using the dicyanamide anions \([N(CN)_2]^–\) and cations from the 1-alkyl-3-methylimidazolium bromide family (where ‘R’ corresponds to allyl, 3-butenyl, propargyl, 2-butynyl and 2-pentynyl). The oxidizer was IRFNA or WFNA. Tests showed ILs with the allyl, 3-butenyl and propargyl to be hypergolic [15]. An IL based on the 1-methyl-4-amino-1,2,4-triazolium compound as well as three commercially available IL dicyanamides:- 1-butyl-3-methyl-imidazolium, 1-butyl-1-methyl-pyrolidinium, and \(n\)-butyl-3-methyl-pyridinium were all found to be hypergolic as well in this research. Figure 2-1 provides the structure for the imidazolium- dicyanamide ionic species, which is the IL being investigated in this research work.
2.1.1 Effect of Diluents on IL hypergolicity

Dambach et al. [29] suggest that the limit for dilution for BMIM/DCA based ILs with water (H₂O) is between 19.5 and 20%. Increasing the concentration of diluent tends to increase the ignition delay. BMIM/DCA does not ignite with 96%WFNA whereas AF-IL-617 (codename for IL developed by Air Force research lab) will ignite with 90%WFNA. The vacuum specific impulse and characteristic velocities of DCA based fuels are significantly lower than hydrazine fuels when reacted with WFNA.

Results also investigate dicyanamide based ILs suggesting that dicyanamide based fuels proved to be hypergolic with nitric acid. Adding water or methanol to BMIM/DCA increased the ignition delay. MMH has the shortest ignition delay of all conventional fuels. AF-IL-617 diluted down to 95% by the addition of a diluent such as water or methanol has vacuum specific impulse comparable to MMH.

Catoire [30] in his findings compares imidazoles, triazoles and tetrazoles. 1H-tetrazole had the highest experimental and calculated heat of formation. The tetrazoles
are followed by the pyrazole, imidazoles and then pyrrole. A reaction between 1-butyl-3-methyl imidazolium dicyanamide and WFNA has HNO₃, CO₂, N₂O and HNCO as the gas phase products formed/observed by FTIR. Traces of H₂O and NO₂ were also observed. Once the IL comes in complete contact with the oxidizer, there is a vigorous reaction, the release of energy causing products to be converted from the condensed phase into the gas phase. The gas phase products HNCO, CO₂ and N₂O continue reacting to form the crucial product dinitrobiuret (DNB) (NO₂NHCONHCONHNO₂). DNB upon thermal decomposition yields two intermediates- NO₂NHCONCO and NH₂NO₂ (nitramide).

\[ \text{NO}_2\text{NHCONHCONHNO}_2 \rightarrow \text{NO}_2\text{NHCONCO} \rightarrow \text{HNCO} + \text{N}_2\text{O} + \text{CO}_2 \]  
\[ \text{(5)} \]

\[ \text{NO}_2\text{NHCONHCONHNO}_2 \rightarrow \text{NH}_2\text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \]  
\[ \text{(6)} \]

The temperature and concentration of the end products listed above combined with HNO₃ and NO₂ are primary species that decide hypergolic ignition. The gas phase thermo-chemistry of nitro compounds have been validated and studied by Osmont et al. [31] and also Burcat et al. [32]. Catoire mentions an adiabatic flame temperature of greater than 2000K could be a criterion for considering hypergolic reactions. These results need to be validated since chemical species present in flame affects temperature and a model is needed to predict the temperature since experimental technique like Fourier Transform Infra Red cannot detect oxygen (O₂).
2.1.2 Reaction Mechanism for BMIM/DCA and HNO₃ reaction

Chambreau et al. [33] in their findings studying the hypergolic ignition of ILs report that the influence of the cation on the reaction is minimal and anions are the primary species responsible for driving reaction kinetics. It is found that the azide ion containing compounds do no react with WFNA, whereas DCA based ILs do. The reaction mechanism of the dicyanamide anion with nitric acid is a main topic of the Chambreau [15, 33] work and for the research presented in this thesis. The mechanism for the above reaction is discussed below and shown in Figures 2-2, 2-3 and 2-4.

The hydrogen atom from the nitric acid protonates the DCA at either of the two nitrile nitrogens (Figure 2-2 steps (a-c)). In case of WFNA, the nucleophile is NO₃⁻ in place of H₂O. The NO₃⁻ from the resultant deprotonation of nitric acid attacks at the electrophilic carbon (Figure 2-2 steps (d-e)) followed by the 1,3 migration of the NO₂ group to the terminal nitrogen (Figure 2-2 steps (f-g)).

The gas-phase proton affinity of the terminal nitrogen is approximately 7.6 kcal/mol greater than that of the central nitrogen. Increased electron density near the nitrogen atoms makes the carbon electron deficient susceptible to nucleophilic attack. The NO₂ migration leads to the formation of a C=O bond and this reaction is exothermic by approx 35 kcal/mol [33].
Protonation of the resultant structure above followed by nucleophilic attack and migration of \( \text{NO}_2 \) group leads to the eventual formation of DNB (Figure 2-3 and 2-4).
Figure 2-3: Reaction Pathway showing protonation of HDCA.NO$_3$ to form DNB ion [33].

Figure 2-4: Protonation of DNB ion on central nitrogen atom to form DNB complex [33].

Similar to this, the formation of mononitrobiuret (MNB) is also possible. The thermal decomposition of MNB and DNB has been studied by Geith et al. [34]. The
above formation of DNB and the crucial transition products as well as the products from the thermal decomposition of DNB (Figure 2-5), which are HNCO, N\textsubscript{2}O, CO\textsubscript{2} and H\textsubscript{2}O are observed through the ReaxFF analysis as well (described in detail in section 3.3.5).

CO\textsubscript{2}, N\textsubscript{2}O and HNCO are produced from the derivative intermediate NHNO\textsubscript{2}CONCO and N\textsubscript{2}O and H\textsubscript{2}O are produced from the nitramide derivative NH\textsubscript{2}NO\textsubscript{2}. This is a multistep process and the final products are not formed all at once. Chambreau also suggests that for such a reaction to be possible, it has to be acid-catalyzed (HNO\textsubscript{3} is a proton donor and is present in larger quantities than the IL). The presence of HCN or H\textsubscript{2}NCN is not observed using FTIR. Isomers of HNCO namely HOCN or HCNO are also not observed.

![Figure 2-5: Thermal decomposition of DNB complex [32].](image)

An intermediate identified from the biuret test is (HNO=CNHC=ONH\textsuperscript{-}), which further confirms the role of anion in initiating the hypergolic reaction. Heat released from this ignition tends to cause the cation to decompose. Small, unsaturated hydrocarbons (with C=C and C≡C bonds) accelerate the ignition phenomenon and adding functional
groups on the cation which aid in such development will prove to be useful in tailoring the IL for particular needs as propellants [34].

Chowdhury et al. [35] in their findings on the ignition behavior for hypergolic materials have performed the drop test and made measurements for ignition delay and done FTIR and ToF measurements. Drop test apparatus investigating reaction between EMIM/ DCA and WFNA suggest extremely exothermic reactions at the fuel-oxidizer interface. The temperature increases beyond the boiling point of WFNA. Findings state that the ignition kernel is formed 25 ms after the droplet impact. The oxidizer tends to form on the walls of the cuvette whereas the fuel tends to remain in condensed phase. Formation of soot is evident as well. The global ignition delay for a system comprising of 10 µL of EMIM/DCA and 160 µL of 90% HNO₃ was found to be 70 ms. Compared to 90% HNO₃, a smaller amount of HNO₃ (100 µL) was found to be sufficient for repeatable and reliable ignition with EMIM/ DCA. If the water produced in such an ignition is reduced by 10% , the rate of reaction in the condensed phase is much faster and the global ignition delay is reduced by almost 50% to 35 ms. In a test reaction between 70% HNO₃ and EMIMDCA under 50°C exposed to an inert atmosphere of N₂, the authors observe a similar range of products- CO₂, N₂O, H₂O, HNCO using an FTIR spectrum, which are in agreement with results from Schneider et al. [15], Geith et al. [34] and those found using the ReaxFF reactive force field (described here in chapter 3). An important result the authors find out is the presence of a dicyanamide derivative- [(NH₂CN)₂], which appears as a distinct peak in the spectrum.

Hampton and Smith [36] found that the chemical delay time (CDT) for conventional fuel mixtures mixed with a diluent such as methanol at certain
concentrations is smaller than that for just the pure fuel reacting with RFNA. Laser based diagnostics were used for establishing the CDT, which is a relevant parameter for gauging fuel/oxidizer combination. Non-IL chemical fuels include MMH, UDMH and anhydrous hydrazine. For a C/N (Carbon/ Nitrogen) ratio between 0-0.5, addition of MMH or UDMH to hydrazine does not yield satisfactory or significant behavior. Too much or too little carbon remarkably slows the reaction CDT in the case of C/N ratios between 0.5-1.0, especially with the addition of MMH. Hampton et al. [37] is of the view that adding an asymmetric polar compound might reduce the CDT for other amines and azides as well. Results state that for MMH/ Methanol mixtures < 23 mole% Methanol, the mixtures are chemically faster than pure MMH and for MMH/Methanol mixtures > 23 mole% Methanol, the CDT increases from that of pure MMH. Stable hypergolic ignition as observed for below 25 mole% methanol concentration.

Regarding the thermo-physical properties of imidazolium based ILs, Fredlake et al. [37] validate and state the thermo-physical properties of imidazolium based ILs for different anions. Considering the IL we have used for our research- BMIM/DCA, it has been found that the density of BMIM/DCA at 82.7°C to be 1.0258 gm/cm³, which is higher than water. Density for imidazolium based ILs decreases as the alkyl substituted chain length on the cation increases. Also, the density increases with increasing molecular weight of the anion. The energy in any chemical species can be stored in its translational, vibrational and rotational modes. The more atoms there are in the IL, the larger its heat capacity tends to be. Fredlake et al. [37] conclude that the thermal stability of imidazolium ILs increases with increasing anion size (which is found to increase the
onset and start temperature for thermal decomposition). Table 2-1 enlists the different properties for the BMIM/DCA ionic liquid.

<table>
<thead>
<tr>
<th>Property (Units)</th>
<th>Remarks</th>
<th>Value for BMIM/DCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (gm/cm³)</td>
<td>T = 24 ± 0.1 °C</td>
<td>1.0580 ± 0.0010</td>
</tr>
<tr>
<td></td>
<td>T= 39.8 ± 0.1 °C</td>
<td>1.0525 ± 0.0011</td>
</tr>
<tr>
<td></td>
<td>T= 51.2 ± 0.1 °C</td>
<td>1.0466 ± 0.0011</td>
</tr>
<tr>
<td></td>
<td>T= 60.8 ± 0.1 °C</td>
<td>1.0415 ± 0.0010</td>
</tr>
<tr>
<td></td>
<td>T= 71 ± 0.1 °C</td>
<td>1.0340 ± 0.0010</td>
</tr>
<tr>
<td>Melting Point Temperature</td>
<td></td>
<td>-6 °C</td>
</tr>
<tr>
<td>Cold Crystallization Temperature</td>
<td></td>
<td>-29 °C</td>
</tr>
<tr>
<td>Glass-Transition Temperature</td>
<td></td>
<td>-90 °C</td>
</tr>
<tr>
<td>Onset Temperature (moisture drying) for thermal decomposition</td>
<td></td>
<td>300 °C</td>
</tr>
<tr>
<td>Start Temperature for thermal decomposition</td>
<td></td>
<td>240 °C</td>
</tr>
<tr>
<td>Heat capacity (J/mol.K)</td>
<td>T = 25 °C</td>
<td>364.6 ± 13.85</td>
</tr>
<tr>
<td></td>
<td>T = 50 °C</td>
<td>370 ± 14.06</td>
</tr>
</tbody>
</table>

### 2.2 Nitric Acid Crystal

Nitric Acid (HNO₃) has a crystal structure. The crystal structure of HNO₃ was published by Luzzati [38]. Anhydrous HNO₃ crystallizes at -41°C. The structure is monoclinic with a P2₁/a- C₂ᵥ₅ symmetry and β=90° (which makes it orthorhombic). The dimensions of the unit cell are: a = 16.23 ± 0.05 Å; b = 8.57 ± 0.03 Å; c = 6.31 ± 0.01 Å. Each crystal of HNO₃ has 4 unit cells comprising 16 HNO₃ molecules (Figure 2-6).
The position of hydrogen atoms in the above structure was not reported by Luzzati. The location of hydrogen atoms within the unit cell was later determined by Ortega et al. [39]. The average O–H bond distance in the unit cell is 1.013 ± 0.009 Å and the N-O-H angle is 105.49° ± 0.025°. The elongation of the O–H bond and the opening of the N-O-H angle indicate the creation of hydrogen bonding between the ‘H’ atom and a neighboring ‘O’ atom of another HNO₃ unit in the crystal. The unit cell contains four hydrogen bonds, two with a bond length of 1.75 Å and two with a bond length 2.30 Å. The density of nitric acid crystal at 20°C is 1.895 gm/cm³, whereas the density of nitric acid in the liquids phase at room temperature is 1.41 gm/cm³. Liquid HNO₃ has a boiling point of 122°C and melting point of -42°C.
Chapter 3

DROPLET TEST SIMULATION

3.1 Introduction

The droplet test simulation presented here is a computational modeling of the experiment done by Schneider et al. [33]. The drop-test experiment is chosen because it serves to act as a reference against which the force field can be tested and optimized. Literature data enable us to observe many of the chemical phenomena that we see from the simulation. Further in the chapter (section 3.2), the primary setup has been discussed. This is followed by results and analysis work from the drop test simulation (section 3.3.1-3.3.3), cookoff simulations for the HDCA.NO₃ reaction product (section 3.3.5), comparison of the performance of HNO₃ and N₂O₄ (section 3.3.6) as well as snapshots from the ReaxFF simulation.

3.2 Development of simulation model

3.2.1 Experimental Setup

The experimental setup consists of a syringe filled with 10 µL of fuel (1-propargyl-3-methyl imidazolium and silver dicyanamide) and a cuvette containing 1 ml of oxidizer (IRFNA/ WFNA). The fuel droplet from the syringe is dropped upon the pool
of oxidizer from a certain height and the resultant chemical reaction is observed through a high-speed camera. The reaction between the ionic liquid and oxidizer happens vigorously as soon as the ionic liquid droplet is completely immersed into the oxidizer. The chemical reaction is hypergolic in nature and the ignition delay period is of the order of ms. Figure 3-1 shows the experimental hypergolic ignition process captured using a high speed camera.

Figure 3-1: Hypergolic reaction of 1-propargyl-3-methyl-imidazolium dicyanamide and WFNA. Images are captured using a high-speed video [15].

3.2.2 Computational Analogy

For atomistic-scale simulations using ReaxFF, a periodic box is created in which the fuel-oxidizer combination is placed at a certain distance apart from each other. The computational model for the drop test simulation is shown in figure 3-2.
In the initial set of simulations, a fuel droplet consisting of 16 cations (BMIM) and 16 anions (DCA) are placed around the center of the periodic box which acts as a cuvette. An oxidizer bed of 380 HNO₃ molecules are placed at the bottom surface of the box. The HNO₃ supercell is made from the HNO₃ crystal unit cell, the dimensions of which were reported by Luzzati [38]. The bottom ‘z’ surface of the periodic box is reflective in nature; when any species strikes the ‘-z’ surface, it is reflected back in the ‘+z’ surface following the laws of reflection. The atoms in the fuel droplet are given a velocity in the ‘-z’ direction which makes the fuel blob to approach the oxidizer bed like...
a fuel droplet has been dispensed on WFNA. ReaxFF simulates the breaking and formation of chemical bonds in the structure as the reaction progresses.

The input files for running the ReaxFF force field simulations contain the several parameters that are specified before the start of the program. There are primarily five input files- control, geo,ffield, vels and exe. Table 3-1 gives a brief description of the functions these files serve.

<table>
<thead>
<tr>
<th>control</th>
<th>Parameters for molecular dynamic and physical conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>geo</td>
<td>Geometry file for the system in biograf format.</td>
</tr>
<tr>
<td>ffield</td>
<td>Parameters for force field.</td>
</tr>
<tr>
<td>vels</td>
<td>Contains the initial set of position, velocities and accelerations for the set of atoms that are to be given the impact velocity.</td>
</tr>
<tr>
<td>exe</td>
<td>Executing script for the Reax program.</td>
</tr>
</tbody>
</table>

### 3.3 Results

#### 3.3.1 Procedure

(1) The fuel droplet and oxidizer are separately energy minimized using the force field in a periodic box which measures 32.46 x 32.46 x 200 Å³.

(2) Following this, both the fuel and oxidizer are now placed within the same box of the above dimensions such that the fuel droplet hangs approx 30 Å above the oxidizer bed. The system is further energy minimized briefly in the combined setup. Using a NVT
ensemble, a temperature of 100K, time step of 0.25 fs and similar box dimensions, the system is allowed to undergo a MD run of 150,000 iterations to let it equilibrate under a constant temperature regime. Figure 3.3 (a) and (b) show the initial and final stages of the MD-NVT equilibration process. Equilibration allows the fuel and oxidizer to reach a configuration where the system energy has become constant with time. After equilibration, the system is ready for being simulated for the drop test. Figure 3-4 shows the potential energy and temperature in the system as leveling out with time.

Figure 3-3: BMIM/DCA + HNO₃ system at the (a) start and (b) end of MD-NVT simulation.
Since system temperature is kept constant at every iteration (~ 100K), kinetic energy will remain constant, which will result in decreasing potential energy based on law of energy conservation. Graph in figure 3-4 verifies this trend.

(3) The drop test involves a MD run using a NVE ensemble. Hence, the total energy of the system will remain constant. When the fuel particle reacts with the oxidizer, a lot of heat is generated and the temperature (and hence kinetic energy) increases. Potential energy decreases. As the reaction progresses, temperature decreases and potential energy increases again for that duration. Figure 3-5 (a)-(d) gives a visualization of the NVE simulation reaction along different times.
(a) Initial Fuel- Oxidizer setup.

(b) Fuel droplet approaching the oxidizer.
Figure 3-5: Time spaced visualization of drop test simulation (BMIM/DCA + HNO$_3$).

(c) Fuel droplet mixing in the oxidizer pool.

(d) Fuel- Oxidizer vigorous reaction.
3.3.2 Species - Energy - Temperature Analysis

The fuel droplet is given four different impact velocities of 2, 4, 8, 12 and 16 km/s respectively. There was found to be no hypergolic behavior at velocities of 8 km/s or below. Following the drop test run at 12 km/s, a species analysis of the reaction products is provided in figure 3-6.

Figure 3-6: Species observed in drop test simulation (NVE) at T=100K, V_{fuel}= 12 km/s.
(Quantity of HNO₃ is shown on the secondary y-axis).

From figure 3-6, it can be seen that the HNO₃ population steadily decreases as soon as the fuel droplet comes in contact with the oxidizer. Protonation of the DCA anion occurs via the ‘H’ from HNO₃. This subsequent removal of proton increases the NO₃
An interesting observation here is that the population of the BMIM cation remains constant throughout the simulation. Despite the hypergolic behavior of the reaction, the cation is found to not participate in the reaction. The anion- DCA (C$_2$N$_3$) initiates the reaction, which is in agreement with observations made by Chambreau et al. [33]. As the NO$_3$ and DCA population decreases with time, water (H$_2$O) and nitrous oxide (N$_2$O) are generated. These probably result from nitric acid decomposition reactions resulting from the high local temperatures associated with the fuel particle impact. Protonation of DCA by hydrogen atom leads to the formation of HDCA (HC$_2$N$_3$). Near the end of the reaction, HDCA.NO$_3$ is also formed in the system. This can be attributed to the NO$_3$ attacking the electrophilic carbon on HDCA molecule thereby forming HDCA.NO$_3$. The potential energy and temperature variation with time for $V_{fuel}=12$ km/s simulation is shown in figure 3-7.

Figure 3-7: Potential Energy and Temperature variation for drop test simulation at T=100K, $V_{fuel}=12$ km/s.
The potential energy scan as the reaction progresses shows a spike in the initial phase which is the period when the fuel droplet is approaching the oxidizer. After the ignition delay, as the combustion starts, we see a drop in the energy and the temperature of the system tends to stabilize itself with time. As expected, change in potential energy and kinetic energy (hence, temperature) are complementary to each other.

Species analysis for the case $V_{\text{fuel}} = 16 \text{ km/s}$ is present in figure 3-8.

Compared to the case with lower fuel impact velocity ($12 \text{ km/s}$), it is seen that the increase in fuel impact velocity leads to a more vigorous reaction, which is explained by the rapid increase in the formation of $\text{H}_2\text{O}$ and $\text{NO}_2$. We also observe that at such high
impact velocities, the cation begins to participate in the reaction process. Closer inspection reveals that the ring structure in the imidazolium cation opens up and dissociates into smaller fragments. This is not congruent with literature data [33] and suggests that 16 km/s might not be the optimum velocity for analyzing reaction kinetics. HDCA and HDCA.NO\textsubscript{3} are also generated in the reaction but only for a brief time. At 16 km/s, the temperature plays a bigger role in governing reaction chemistry than the chemical interaction between atomic species itself.

![Figure 3-9: Potential Energy and Temperature variation for drop test simulation at T=100K, V_{fuel}=16 km/s.](image)

Compared to figure 3-8, the initiation and equilibrium temperature reached in the system for $V_{fuel}= 16$ km/s (Figure 3-9) is higher than that reached for $V_{fuel}= 12$ km/s.
The results from the drop test simulation lead to the conclusion that impact velocities equal to or between the range of 10-12 km/s predict chemistry agreeable with literature data. Figure 3-10 (a-c) show snapshots of some of the species generated from the 12 km/s drop test simulation. These species will be analyzed further in the next sections 3.3.3 and 3.3.4.

(a) HDCA and H₂O molecules (encircled).  
(b) Isolated HDCA.NO₃ molecule captured.  
(c) HDCA.NO₃ molecule structure.

Figure 3-10: Snapshot of major species generated during drop test at \( V_{\text{fuel}} = 12 \) km/s.  
(Red- Oxygen; Blue- Nitrogen; Green- Carbon; White- Hydrogen).
3.3.3 Cation - Anion consumption in Drop test reaction

To understand the contribution of each component of the ionic liquid in the reaction chemistry, individual analysis of the cation and anion consumption during the reaction was studied.

Figures 3-11 and 3-12 show the cation and anion consumption cases individually for all five fuel impact velocities.

![Graph showing cation consumption in Drop test reaction](image)

Figure 3-11: Variation in quantity of BMIM cations during drop test simulation at different fuel velocities.
Figure 3-12: Variation in quantity of DCA anions during drop test simulation at different fuel velocities.

Figure 3-11 and 3-12 show that at lower impact velocities (2 and 4 km/s), the BMIM/DCA IL does not exhibit hypergolic behavior with HNO₃ on the time scales of our simulation. As the impact velocity increases (12 km/s and above), we see that the DCA molecule starts participating in the reaction. The BMIM is still mainly unreactive at 12 km/s. 16 km/s impact velocity provides reaction energy equivalent to a temperature of 5000K that destructs all the BMIM and DCA molecule. Within the time scales of ReaxFF, impact velocity of 8-12 km/s will prove the most informative.
3.3.4 Reaction Pathway for Fuel - Oxidizer reaction

Chambreau et al. investigated the hypergolic behavior of ILs with HNO$_3$ and proposed a reaction pathway through which the IL reacts with HNO$_3$ and further combustion takes place [33]. This scheme has been described in chapter 2 of this thesis. A similar analysis was performed on the species present in the periodic box. Species analysis of the drop test simulations have shown that molecules like HDCA, HDCA.NO$_3$ are being produced in the system besides water and other products. Visual analysis of the drop test was done using Visual Molecular Dynamics (VMD) [41] and Molden [42]. Figures 3-13 (a-f) show the trajectory of a dicyanamide anion as it progresses with time and reacts with other species around it. All the other atoms have been given a constant color (yellow/gold) to aid the tracking.
(c) NO$_3^-$ attacks adjacent electrophilic ‘C’ atom to form HDCA.NO$_3$.

(d) NO$_2$ dissociates from NO$_3$ leaving OHC$_2$N$_3$.

(e) Dissociated NO$_2$ group revolves around OHC$_2$N$_3$ attracted to terminal ‘N.

(f) NO$_2$ attaches to terminal ‘N’ to form HDCA.NO$_3$ (more stable than (c)).

Figure 3-13: Reaction Pathway for formation of HDCA.NO$_3$ from DCA + HNO$_3$ via HDCA.

The ReaxFF chemistry traces a pathway in agreement with literature results reported by Chambreau et al. [33] and discussed in chapter 2. The ability of ReaxFF to produce the same reaction pathway aids in validating the other results obtained from the drop test simulations, discussed elsewhere in chapters 3 and chapter 4.

Understanding the critical role of DCA in initiating reaction, a detailed analysis of the trajectory followed by 15 DCA molecules present in the system was studied. A
diagram was prepared which enables us to see the major products that each DCA molecule is a part of or converts into from the beginning to the end of the MD run.

In figure 3-14, the length of the arrows represents approximately the relative time period for which the particular reactant (preceding the arrow) exists in the mixture before converting into the respective product (following the arrow). Observation shows that four molecules convert into HC$_2$N$_3$.NO$_3$, three molecules lead to formation of OH(HC$_2$N$_3$), two molecules form OH(HC$_2$N$_3$)H, two more DCA form HC$_2$N$_3$.NO$_2$, two DCA molecules remain unreactive and one molecule interacts with BMIM. Probability of occurrence of HDCA.NO$_3$ is greater than for other products. The HDCA.NO$_3$ formed at
the end of the simulation is in all four cases formed by the rearrangement of ‘NO₂’ from the HDCA.NO₃ to form a more stable species. A common intermediate species formed in eight of the 16 molecules is OH(C₃N₃). In most cases, this species is relatively stable during the course of the reaction suggesting that it might be a valid intermediate species being generated during the course of the hypergolic reaction.

3.3.5 Cookoff Simulations

The drop-tests indicate that HDCA.NO₃ complexes are the main stable intermediates formed during the BMIM/DCA interactions with HNO₃. However, the relatively low concentration of HDCA.NO₃ generated during the drop-test simulations hinder the investigation of subsequent reactive events. In order to increase the statistical sampling, a cookoff simulation was performed. A mixture of 10 HDCA.NO₃ and 100 HNO₃ molecules was heated in 35 ps. of MD-simulation from T= 500 K to T= 2500K. The procedure for the simulation is similar to drop test simulation. We place the mixture together in a box, energy minimize the system to reach a density of approximately 1.1 gm/cm³, equilibrate at 500K, using a Berendsen thermostat and then steadily ramp up the temperature form 500 K to 2500 K. The trajectory of HDCA.NO₃ was analyzed.
Reaction chemistry shown in figure 3-15 indicates the occurrence of a rapid protonation/de-protonation sequence, where the carbonyl oxygen is protonated by the nitric acid. A protonation on the terminal nitrogen atom is observed, and this rare reactive event triggers a second oxidation pathway, similar to the earlier HDCA.NO₃ formation. This leads to the formation of a dinitrobiuret anion, as proposed by Chambreau et al. [33]. This anion later is oxidized at the carboxyl carbon, leading to the formation of a weakly-bound CO₂ molecule that quickly releases itself from the dinitrobiuret compound. ReaxFF indeed allows us to establish the reaction pathways in complex reaction environments. To further validate this mechanism, further DFT-studies should be performed to demonstrate its validity.
Thermal decomposition of DNB: A MD simulation of 10 DNB complexes with 100 HNO₃ molecules was studied. ReaxFF has a temperature function program (file named ‘tregime.in’) in it by which the rate of temperature change can be specified. In this cookoff simulation, temperature of each atom was linearly increased from 300 K to 2300 K in 150,000 iterations with a time step of 0.2 fs (i.e., @ 0.013 K/iteration). Figure 3-16 shows the reaction scheme from the observed analysis.

The end products formed in the reaction of nitric acid with dinitrobiuret following the temperature ramp us shows formation of smaller product species like H₂O, HNCO and N₂O. The formation of unstable intermediate C₂HO₂N₃ and nitramide is in agreement with the thermal decomposition proposed by Chambreau et al. [33].
3.3.6 Comparison of Nitric Acid and Nitrogen Tetroxide as oxidizers

The use of HNO$_3$ has been well established as a suitable oxidizer for promoting hypergolic behavior. Another oxidizer in current use is nitrogen tetroxide (N$_2$O$_4$). Drop test simulations were performed for an IL consisting of 16 BMIM cations and 16 DCA anions. The fuel droplet was placed in a periodic box with 320 N$_2$O$_4$ oxidizer molecules. The drop test was conducted at an initial temperature of 100 K and for four different fuel impact velocities of 8, 9, 10 and 11 km/s. A comparison of the cation and anion consumption was carried out for two impact velocities of HNO$_3$ (8 and 9 km/s) and two for N$_2$O$_4$ (9 and 12 km/s). This graph is shown in figure 3-17.

Figure 3-17: DCA consumption for two different fuel impact velocities with HNO$_3$ and N$_2$O$_4$ as oxidizers.
Preliminary results show that the rate of consumption of DCA with N₂O₄ is higher than that with HNO₃. Experimental results and findings on IL tests with HNO₃ and N₂O₄ have revealed the opposite [29]. A thorough investigation of each DCA anion trajectory and the different compounds it reacts with was performed. A bond-order/bond-length study on the DCA anions reveals that the DCA anion does not actually bind with NO₂. N₂O₄ primarily breaks into NO₂ + NO₂. This NO₂ tends to revolve in the system without actually attaching to the DCA complex. Filtering out the N₂O₄ breakup events leads us to the plot the actual N₂O₄ consumption as seen in figure 3-18.

![Figure 3-18: DCA consumption for two different fuel impact velocities for HNO₃ and N₂O₄ oxidizers after filtering out the DCA molecules that unreactive with N₂O₄.](image)

Figure 3-18 shows that N₂O₄ is unreactive with DCA in the drop test reaction whereas HNO₃ proves to be a suitable oxidizing molecule. To reinforce the reaction chemistry of BMIM/DCA complex with N₂O₄, a species analysis of the drop test
simulations at two different fuel impact velocities of $V_{\text{fuel}} = 9$ and 10 km/s were carried out. MD-run is performed with an NVE ensemble for a time period of 50 ps at an initial temperature of $T = 100 \text{K}$ on a system comprising of 16 BMIM/DCA and 320 $N_2O_4$ molecules. The disturbance (or noise) that we see in figures 3-17 and 3-18 for each set of readings can be attributed to the small size of the fuel system that is being investigated. $HNO_3$ has a tendency to de-protonate and $NO_3$ has a tendency to form $HNO_3$ back again.

Species analysis for the two cases is presented in Figures 3-19 and 3-20.

Figure 3-19: Population of major species during BMIM/DCA + $N_2O_4$ drop test at $T=100 \text{K}, V_{\text{fuel}}= 10 \text{ km/s}$. 

```
Figures 3-20 show that most of the N$_2$O$_4$ dissociates into NO$_2$, which has almost double the population as N$_2$O$_4$. The cation is completely unreactive in the course of the reaction. The other components that are formed (although in small amounts) are C$_2$O$_2$N$_4$ (C$_2$N$_3$ + N$_2$O$_4$), CO$_2$ and N$_2$. The NO$_2$ group attaching and dissociating from the DCA molecule has been captured by ReaxFF in VMD as a visual supplement to the theory that N$_2$O$_4$ is not hypergolic with the BMIM/DCA combination (Seen in frames (a-e) of figure 3-21). Simulating the system with a different N$_2$O$_4$ configuration (ONO-NO$_2$ and not NO$_2$-NO$_2$) should be investigated.
Figure 3.21: Reaction pathway showing NO2 hopping during BMIM/DCA + N2O4 drop test simulation.
4.1 Introduction

The force field used for conducting the atomistic-scale simulations has to be trained in predicting the reaction chemistry correctly for the elements and compounds it means to simulate. In this research, the primary atoms which are undergoing combustion are hydrogen, oxygen, nitrogen and carbon. The ReaxFF force field works by training and optimizing different parameters against a set of values derived from QM computations and experiments. The HNO\textsubscript{3} force field is developed here as part of getting ReaxFF to predict the hypergolic combustion chemistry between IL-Oxidizer species as described in chapter 3 of this thesis. In the coming sections, the general methodology involving force field optimization has been discussed.

4.2 Methodology

The force field optimization process in ReaxFF consists of reducing the total cumulative error (called the cost function) that is calculated based on the difference in values between quantum experiments derived data and that produced by the ReaxFF force field. The force field contains parameters which define the bond lengths, bond
angles, torsion angles etc. between different elements that the force field uses for predicting the chemistry. These parameters are optimized based on the quantum-mechanically computed values that serve as reference point. The primary files needed for the optimization process and their functions are as follows:

1) **control**: Contains the external input/run parameters needed for carrying out the energy minimization. For eg. the minimization criterion, periodic box dimensions etc.

2) **geo**: Contains the geometry of all the structures that are present in the dataset for the force field to train against.

3) **ffield**: This is the initial force field that has been optimized previously for some other set of species but serves as a good starting field needed for preparing the new force field. The initial force field should have been prepared with the same atomic elements for which we primarily need the new version. For eg. the current force field contains input data for bond lengths, bond angles, torsion angles, hydrogen bonds for carbon, hydrogen, nitrogen and oxygen.

4) **params**: This file tells ReaxFF about the different parameters that need to be optimized.

5) **trainset.in**: This file contains the dataset for charges, heat of formation, geometry, cell parameters and energies against which the initial force field bases its optimization upon. A point to note here is that, the geometry of the different species mentioned in trainset file has to be correspondingly present in the ‘geo’ file bearing the same name. For eg. if the trainset file contains a line for the reaction between \((\text{HNO}_3 \rightarrow \text{H} + \text{NO}_3)\) having a QM energy of ‘x’ kcal/mol, then during the optimization process, the geometries of HNO\(_3\), H and NO\(_3\) are read from the ‘geo’ file and the respective structures are energy
minimized and the corresponding Reax energy is calculated. Depending on how off-set the QM and Reax energies are, the error is calculated. The cumulative error is simply calculated by adding up the error for each entry made in the trainset file.

6) **exe**: Contains the executable script for running the complete optimization process.

7) **fort.99**: Contains the output file giving the individual and cumulative error for every entry in the trainset file. This enables us to see the efficiency of the cost function.

The optimization routine includes a single-parameter based parabolic extrapolation method [43] using successive parameter optimization cycles to resolve the parameter correlation and subsequently reduce the cost function to an acceptable level.

The following sections describe various categories of data that were included in the force field development.

### 4.3 Equation of State

Equation of state enables us to understand the relation between the thermodynamic parameters which represent the state of the material. These parameters are pressure, volume, temperature and derived parameters such as density. Figures 4-1 and 4-2 represent the equation of states for the BMIM/DCA system and HNO$_3$ crystal respectively.
Figure 4-1: Equation of state for BMIM/DCA system.

Figure 4-2: Equation of state for HNO₃ crystal system.
In the equation of state curve prepared for the BMIM/DCA system, the ReaxFF trend is in very good agreement with the results obtained using the APPLE&P force field [44]. APPLE&P stands for ATOMISTIC POLARIZABLE POTENTIAL FOR LIQUIDS, ELECTROLYTES & POLYMERS. APPLE&P is an accurate and transferable many body polarizable force field for performing classical molecular dynamics simulations. The inclusion of many body polarization effects allows APPLE&P to accurately capture electrostatic interactions in highly polar and polarizable environments. Figure 4-1 shows that the ReaxFF gives good agreement with the APPLE&P force field in the case of BMIM/DCA.

Figure 4-2 shows the energy vs density relation for HNO₃ crystal supercell, which is obtained by allowing the supercell to expand and compress in a low temperature MD scan after an energy minimization run. The optimum density of nitric acid predicted with ReaxFF came to around 1.4 gm/cm³ (or kg/dm³). Experimental density calculations for the HNO₃ crystal cell reveal a density of 1.5 gm/cm³.

### 4.4 Binding Energy

The binding energies for the BMIM/DCA system were calculated using ReaxFF and compared with that obtained through literature data. A system comprising of one and two molecules of BMIM + DCA (Figure 4-3) dissociating into individual BMIM cations and DCA anions was studied. Table 4-1 shows us the comparative energy for these systems using ReaxFF and QM methods. Values stand in good agreement for both cases.
Figure 4-3: Systems comprising one and two BMIM cations and DCA anions.

Table 4-1: Binding Energy for proton transfer in BMIM/DCA systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Binding Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMIM/DCA → BMIM⁺(g) + DCA⁻(g)</td>
<td>89.80</td>
</tr>
<tr>
<td>2 BMIM/ 2DCA → 2BMIM⁺(g) + 2DCA⁻(g)</td>
<td>198.8</td>
</tr>
</tbody>
</table>

4.5 HNO₃/ DCA/ H₂O chemistry

In order to develop a ReaxFF description for HNO₃, a QM-based training set was developed based on the following cases:

1) HNO₃ proton affinities relative to DCA
2) HNO₃ proton transfer in water
3) Proton transfer in a HNO₃ dimer
The ReaxFF training sets that have been developed for RDX-initiation [45] and for proton transfer reactions in water [46] were included in the parameterization to ensure that the training set covered all the force field parameters.

4.5.1 HNO₃ proton affinities relative to DCA

The reaction energies associated with proton transfer from HNO₃ to DCA anion forming H-DCA was studied. Proton transfer by HNO₃ is the first step in the combustion process involving a fuel species and an oxidizer. Data in Table 4-2 suggests that protonation at the terminal ‘N’ atom is relatively easier than protonation at the central ‘N’ atom. ‘H’ atom is easier to dissociate from DCA-H when the ‘H’ is attached to the central ‘N’ atom of DCA. Attachment of the ‘H’ at the terminal nitrogen atom reduces the electron density at the nearby carbon atom making it susceptible to attack.

<table>
<thead>
<tr>
<th>Reaction pathway</th>
<th>Energy (kcal/ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QM</td>
</tr>
<tr>
<td>HNO₃ → NO₃⁻ + H⁺</td>
<td>318.5⁺</td>
</tr>
<tr>
<td>DCA-H (terminal N) → DCA⁻ + H⁺</td>
<td>302.8⁺</td>
</tr>
<tr>
<td>DCA-H (central N) → DCA⁻ + H⁺</td>
<td>310.4⁺</td>
</tr>
<tr>
<td>HNO₃ + DCA⁻ → NO₃⁻ + H-DCA (terminal N)</td>
<td>8.10ᵃ</td>
</tr>
<tr>
<td>HNO₃ + DCA⁻ → NO₃⁻ + H-DCA (central N)</td>
<td>15.7⁺</td>
</tr>
</tbody>
</table>

Table 4-2: Energy involving HNO₃ proton affinities relative to DCA [15, 32].
4.5.2 HNO$_3$ proton transfer in water

Nitric acid in a system containing excess water was studied (Figure 4-4). HNO$_3$ acts as proton donor in lower concentrations of water, whereas in higher concentrations of water, HNO$_3$ tends to de-protonate.

The proton affinities are in good agreement with the literature. To train ReaxFF for simulations of HNO$_3$ in water, DFT calculations on the proton transfer reaction in a system comprising of HNO$_3$/H$_2$O and HNO$_3$/6H$_2$O were performed using the B3LYP/6-311G** level basis set.

The hydrogen from HNO$_3$ is found to jump from one water molecule to the other forming a ring structure which is congruent with literature findings. Table 4-3 enlists the comparative results for two cases with different water content.
### Table 4-3: Comparison of QM and Reax energies for HNO₃ proton affinity in H₂O.

<table>
<thead>
<tr>
<th>Reaction pathway</th>
<th>Energy (kcal/mol)</th>
<th>QM</th>
<th>ReaxFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ + H₂O → NO₃⁻ + H₃O⁺</td>
<td>24.0</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>HNO₃ + 6H₂O → NO₃⁻ + H₃O⁺ + 5H₂O</td>
<td>-8.0</td>
<td>-4.7</td>
<td></td>
</tr>
</tbody>
</table>

4.5.3 Proton Transfer in a HNO₃ dimer

A scan involving H-proton transfer between a nitric acid dimer was performed.

\[
\text{HNO}_3 + \text{HNO}_3 \rightarrow \text{H}_2\text{NO}_3 + \text{NO}_3
\]

Underestimating the proton transfer energy can lead to unwanted formation of NO₂ at higher temperatures via water release from H₂NO₃. Hart et al. [48] suggest that the most stable structure for a HNO₃ dimer is a cyclic C₂ᵥ structure (Figure 4-5) in which the monomers are bound by two strong, nearly linear O-H---O hydrogen bonds.

![Figure 4-5: Most stable HNO₃ dimer configuration [48].](image-url)
ReaxFF produces the energy vs O-H bond distance trend well as shown in figure 4-6.

![Figure 4-6: Potential Energy surface for decreasing (O-H) bond distance in HNO₃ dimer.](image)

### 4.6 DCA-HNO₃ Potential Energy Scan

Chambreau et al. [33] have performed experimental studies on the hypergolic ionic liquids system of BMIM/DCA in which the initiation of reaction by the anionic species and the pathway following protonation by the ‘H’ from HNO₃ has been mentioned. A potential energy scan of this pathway by ReaxFF and QM calculations using the [B3LYP/aug-cc-pVZQ] basis set presented in figure 4-7 reveals that ReaxFF indeed produces the same trend as that obtained from QM based simulation.
4.7 \( \text{H}_2 + \text{NO}_2 \) reaction

The training set for the force field was describes the interaction between oxygen and hydrogen atom (O-H) correctly. QM and Reax simulations were performed on a \( \text{H}_2 + \text{NO}_2 \) system. For the QM study, the H-H molecule was made to approach the NO\(_2\) from a direction that enabled formation of H + cis-HNO\(_2\). For the ReaxFF cases, the H-H molecule was made to approach from two directions in separate cases in order to enable formation of ‘cis’ isomer. A reaction coordinate diagram plotting the potential energy surface was made. Figure 4-8 shows a comparison between ReaxFF and QM energies for the proton transfer from \( \text{H}_2 \) to \( \text{NO}_2 \).
Figure 4-8: Potential Energy scan for O-H exchange with ReaxFF and QM.

Table 4-4 shows the setup and method of approach for the O-H transition between NO\(_2\) and H\(_2\). The final product HONO is the cis-isomer.

Table 4-4: ReaxFF-QM study to determine optimum O-H bond length during proton transfer.

<table>
<thead>
<tr>
<th>Reaction: H-H + O=N=O → H + O=N-O-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>ReaxFF</td>
</tr>
</tbody>
</table>
4.8 Nitrogen, oxygen and hydrogen species chemistry

The reaction chemistry of nitric acid oxidizer with the dicyanamide anion involves formation of several intermediate species as well as products, some of which are OH, HONO, HNOO, cyclic HNOO, H radical during proton transfer, H₂, H₂O₂, H₂O, NO₂, NO₃, NO, HOONO etc. The chemistry involving these structures has been studied and incorporated into the existing force field to enable Reax to predict the hypergolic reaction kinetics more accurately. Owing to the extremely short ignition delay involved in hypergolic reactions and the vigorous nature of the HNO₃ oxidizer, experimental techniques are not sufficiently able to capture the transient and radical species that are formed during the reaction. The reaction pathways and kinetics involving the above mentioned species has been studied using QM calculations by Boughton et al. [49], Lin et al. [50], Chakraborty et al. [51], and Nguyen et al. [52].

Table 4-5 gives a comparison of the reaction energies obtained using QM theory and ReaxFF. Structures for the different species in Table 4-5 are present in Table 4-7.
Table 4-5: ReaxFF-QM comparison of Activation energy for reaction pathways.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Pathway</th>
<th>Activation Energy (kcal/mol)</th>
<th>QM</th>
<th>ReaxFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + HNO₃ → H₂ + NO₃</td>
<td>20.59</td>
<td>10.441</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>OH + NO₂ → HNO₃</td>
<td>48.14</td>
<td>44.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OH + NO₂ → HOONO</td>
<td>9.16</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>HOONO → HO₂ + NO</td>
<td>-18.06</td>
<td>-18.44</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>OH + NO₂ → HO₂ + NO</td>
<td>-8.91</td>
<td>-7.24</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>OH + NO → HONO</td>
<td>51.73</td>
<td>45.9</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>H + NO₂ → HNO₂</td>
<td>75.19</td>
<td>66.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H + NO₂ → HONO</td>
<td>78.70</td>
<td>73.4</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>HONO → HNO₂</td>
<td>-3.50</td>
<td>-7.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>HNO₂ → cyclic_HNO₂</td>
<td>-71.22</td>
<td>-78.6</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>cyclic_HNO₂ → HNOO</td>
<td>12.48</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>HNOO → HN + O₂</td>
<td>-16.75</td>
<td>-17.9</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>OH + cis_HONO → OH + trans_HONO</td>
<td>-1.41</td>
<td>-0.4</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>OH + cis_HONO → H₂O + NO₂</td>
<td>24.06</td>
<td>38.6</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>OH + cis_HONO → NO + H₂O₂</td>
<td>5.18</td>
<td>-0.1</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>OH + cis_HONO → H + HNO₃</td>
<td>-30.88</td>
<td>-23.99</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>OH + cis_HONO → ONOH + OH (1)</td>
<td>16.92</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>OH + cis_HONO → HOH--ONO (1)</td>
<td>39.76</td>
<td>40.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>----------------------------------------------</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (2)</td>
<td>6.12</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{HOH--ONO} ) (2)</td>
<td>36.95</td>
<td>39.7</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (3)</td>
<td>6.16</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (4)</td>
<td>3.18</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (5)</td>
<td>2.93</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (6)</td>
<td>7.92</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (7)</td>
<td>7.91</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (8)</td>
<td>7.41</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ON(OH)}_2 ) (2)</td>
<td>14.96</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ON(OH)}_2 ) (3)</td>
<td>14.96</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (9)</td>
<td>5.64</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>( \text{OH} + \text{cis-HONO} \rightarrow \text{ONOH} + \text{OH} ) (10)</td>
<td>14.79</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>( \text{ONOH} + \text{OH} ) (1) ( \rightarrow ) ( \text{HOH--ONO} ) (1)</td>
<td>22.83</td>
<td>31.4</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>( \text{ONOH} + \text{OH} ) (1) ( \rightarrow ) ( \text{ONOH} + \text{OH} ) (5)</td>
<td>-13.99</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>( \text{HOH--ONO} ) (1) ( \rightarrow ) ( \text{H}_2\text{O} + \text{NO}_2 )</td>
<td>-15.69</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>( \text{ONOH} + \text{OH} ) (2) ( \rightarrow ) ( \text{HOH--ONO} ) (1)</td>
<td>33.63</td>
<td>35.5</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>( \text{ONOH} + \text{OH} ) (2) ( \rightarrow ) ( \text{HOH--ONO} ) (2)</td>
<td>30.83</td>
<td>34.6</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>( \text{ONOH} + \text{OH} ) (3) ( \rightarrow ) ( \text{ONOH} + \text{OH} ) (5)</td>
<td>-3.23</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>( \text{ONOH} + \text{OH} ) (3) ( \rightarrow ) ( \text{ONOH} + \text{OH} ) (4)</td>
<td>-2.98</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>( \text{ONOH} + \text{OH} ) (6) ( \rightarrow ) ( \text{ONOH} + \text{OH} ) (7)</td>
<td>-0.01</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>( \text{ONOH} + \text{OH} ) (7) ( \rightarrow ) ( \text{OH} + \text{cis-HONO} )</td>
<td>-7.90</td>
<td>-6.8</td>
<td></td>
</tr>
</tbody>
</table>
Besides the major and intermediate reaction species added to the training set above, there are certain transition states that have been identified by Boughton et al. [49], Lin et al. [50], Chakraborty et al. [51], and Nguyen et al. [52].

As a chemical reaction progresses from the initial state to a product, it follows a certain pathway, the progress of which can be explained by varying a certain parameter called the reaction coordinate. Reaction coordinate can be a geometric parameter that changes during the course of a reaction. For eg. a particular bond length, bond angle, torsion angle or any combination of either.

Because of the rules of quantum mechanics, the transition state cannot be captured or directly observed; the population at that TS point is zero. The quantum-chemical methods such as DFT etc. are used by the authors to find the transition state. It is the point of highest energy along the reaction pathway. The transition state theory and Arrhenius rate law is used to determine energies for the reaction barrier. Reaction energies for the TS structures are trained against the QM values during the force-field optimization. Consecutive structures before and after the transition state are added in the optimization process to allow the force field to recognize the highest energy state much more accurately. Table 4-6 presents the reaction pathway and energy for transition states.

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>ONOH + OH (8) → ONOH + OH (2)</td>
<td>-1.30</td>
</tr>
<tr>
<td>41</td>
<td>ON(OH)₂ (2) → ON(OH)₂ (3)</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

4.9 Transition State chemistry for HNO₃ force field
Table 4-6: ReaxFF and QM activation energies for reaction pathways with transition states.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Pathway (Initial → Transition → Final)</th>
<th>Activation Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>QM</td>
</tr>
<tr>
<td>1</td>
<td>H + HNO₃ → H₂--NO₃ (ts1) → H₂ + NO₃</td>
<td>7.6⁺</td>
</tr>
<tr>
<td>2</td>
<td>H + HNO₃ → H--HNO₃ (ts2) → ON(OH)₂ (1)</td>
<td>2.2⁺ Barrierless</td>
</tr>
<tr>
<td>3</td>
<td>ON(OH)₂ (1) → HONO--OH (ts3) → OH + cis_HONO</td>
<td>9.1⁺</td>
</tr>
<tr>
<td>4</td>
<td>HONO → cyclic_HONO (ts4) → HNO₂</td>
<td>54.7ᵇ</td>
</tr>
<tr>
<td>5</td>
<td>HNO₂ → OONH (ts5) → cyclic_HNO₂</td>
<td>103.3ᵇ</td>
</tr>
<tr>
<td>6</td>
<td>cyclic_HNO₂ → OONH (ts6) → HNOO</td>
<td>34.7ᵇ</td>
</tr>
<tr>
<td>7</td>
<td>ONOH + OH (1) → ONOH--OH (ts7) → HOH--ONO (1)</td>
<td>-1.4ᶜ</td>
</tr>
<tr>
<td>8</td>
<td>ONOH + OH (2) → ONOH--OH (ts8) → HOH--ONO (1)</td>
<td>4.5ᶜ Barrierless</td>
</tr>
<tr>
<td>9</td>
<td>ONOH + OH (1) → ONOH--OH (ts9) → ONOH + OH (5)</td>
<td>15.2ᶜ</td>
</tr>
<tr>
<td>10</td>
<td>ONOH + OH (3) → ONOH--OH (ts10) → ONOH + OH (5)</td>
<td>11.7ᶜ</td>
</tr>
<tr>
<td>11</td>
<td>ONOH + OH (5) → ONOH--OH (ts11) → HOH--ONO (2)</td>
<td>4.9ᶜ</td>
</tr>
<tr>
<td>12</td>
<td>ONOH + OH (2) → ONOH--OH (ts12) → HOH--ONO (2)</td>
<td>2.9ᶜ</td>
</tr>
<tr>
<td>13</td>
<td>OH + trans_HONO → ONOH--OH (ts13) → H₂O₂ + NO</td>
<td>13.6</td>
</tr>
<tr>
<td>14</td>
<td>ONOH + OH (6) → ONOH--OH (ts14) → ONOH + OH (7)</td>
<td>19.3</td>
</tr>
<tr>
<td>15</td>
<td>OH + cis_HONO → ONOH--OH (ts15) → OH + trans_HONO</td>
<td>12.5ᶜ</td>
</tr>
<tr>
<td>16</td>
<td>ONOH + OH (8) → ONOOH (ts16) → ON(OH)₂ (2)</td>
<td>1.7ᶜ</td>
</tr>
<tr>
<td>17</td>
<td>ON(OH)₂ (2) → H--HNO₃ (ts17) → H + HNO₃</td>
<td>35.53ᶜ</td>
</tr>
</tbody>
</table>

⁻ - Becke3LYP/6-311G(d,p) DFT level; ᵇ - B3LYP/ 6-311++G(d,p) level; ᶜ - Becke3LYP/6-311G(d) level.

Barring three transition states (ts3, ts14, ts15), ReaxFF predicts the other transition states with good agreement. The elevated temperatures at which the hypergolic
reaction occurs, approx. 2000K, an energy difference of ±5 kcal/mol between QM and ReaxFF is agreeable in such high pressure- high temperature conditions. Figures 4-9 to 4-25 report the ReaxFF and QM values plotted against each other for the initial, transition state and final product species.

Table 4-7: Geometrical structures for the different species described in Table 4-5 and 4-6. Structures are obtained from different ReaxFF simulation and viewed using Molden [41].

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Structure</th>
<th>No.</th>
<th>Species</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + HNO₃</td>
<td><img src="image1" alt="Structure" /></td>
<td>2</td>
<td>H₂ + NO₃</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>3</td>
<td>OH + NO₂</td>
<td><img src="image3" alt="Structure" /></td>
<td>4</td>
<td>HNO₂</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>5</td>
<td>HOONO</td>
<td><img src="image5" alt="Structure" /></td>
<td>6</td>
<td>HO₂ + NO</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>7</td>
<td>OH + NO</td>
<td><img src="image7" alt="Structure" /></td>
<td>8</td>
<td>HONO</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>Image</td>
<td></td>
<td>Reaction</td>
<td>Image</td>
</tr>
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</tr>
<tr>
<td>9</td>
<td>H + NO₂</td>
<td><img src="image1.png" alt="Image" /></td>
<td>10</td>
<td>cyclic_HNO₂</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>11</td>
<td>HNOO</td>
<td><img src="image3.png" alt="Image" /></td>
<td>12</td>
<td>HN + O₂</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>13</td>
<td>OH + cis_HONO</td>
<td><img src="image5.png" alt="Image" /></td>
<td>14</td>
<td>OH + trans_HONO</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>15</td>
<td>H₂O + NO₂</td>
<td><img src="image7.png" alt="Image" /></td>
<td>16</td>
<td>NO + H₂O₂</td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>17</td>
<td>ONOH + OH (1)</td>
<td><img src="image9.png" alt="Image" /></td>
<td>18</td>
<td>ONOH + OH (2)</td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>19</td>
<td>ONOH + OH (3)</td>
<td><img src="image11.png" alt="Image" /></td>
<td>20</td>
<td>ONOH + OH (4)</td>
<td><img src="image12.png" alt="Image" /></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>ONOH + OH (5)</td>
<td></td>
<td>ONOH + OH (6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>ONOH + OH (7)</td>
<td></td>
<td>ONOH + OH (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>ONOH + OH (9)</td>
<td></td>
<td>ONOH + OH (10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>HOH--ONO (1)</td>
<td></td>
<td>HOH--ONO (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>ON(OH)$_2$ (1)</td>
<td></td>
<td>ON(OH)$_2$ (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>ON(OH)$_2$ (3)</td>
<td></td>
<td>H$_2$--NO$_3$ (ts1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H--HNO₃ (ts2)</td>
<td></td>
<td>HONO--OH (ts3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td></td>
</tr>
<tr>
<td>33</td>
<td><img src="image1.png" alt="Image" /></td>
<td>34</td>
<td><img src="image2.png" alt="Image" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>cyclic_HON O (ts4)</td>
<td></td>
<td>OONH (ts5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td><img src="image3.png" alt="Image" /></td>
<td>37</td>
<td>OONH (ts6)</td>
<td></td>
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</tr>
<tr>
<td>38</td>
<td><img src="image4.png" alt="Image" /></td>
<td>39</td>
<td>ONOH--OH (ts7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td><img src="image5.png" alt="Image" /></td>
<td>41</td>
<td>ONOH--OH (ts8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td><img src="image6.png" alt="Image" /></td>
<td>43</td>
<td>ONOH--OH (ts9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td><img src="image7.png" alt="Image" /></td>
<td>45</td>
<td>ONOH--OH (ts10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td><img src="image8.png" alt="Image" /></td>
<td>47</td>
<td>ONOH--OH (ts11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td><img src="image9.png" alt="Image" /></td>
<td>49</td>
<td>ONOH--OH (ts12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td><img src="image10.png" alt="Image" /></td>
<td>51</td>
<td>ONOH--OH (ts13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figures 4-9 to 4-25 show the potential energy scans obtained from ReaxFF and QM calculated results. Energy values are plotted for the initial, transition and final product species. The corresponding ReaxFF structure at these points is embedded into the graphs. However, it is observed that the ReaxFF structures and QM structures match very well and stay in agreement with the QM pathway except for three cases.
Figure 4-9: Potential Energy scan for transition state 1 with ReaxFF and QM.

Figure 4-10: Potential Energy scan for transition state 2 with ReaxFF and QM.
Figure 4-11: Potential Energy scan for transition state 3 with ReaxFF and QM.

Figure 4-12: Potential Energy scan for transition state 4 with ReaxFF and QM.
Figure 4-13: Potential Energy scan for transition state 5 with ReaxFF and QM.

Figure 4-14: Potential Energy scan for transition state 6 with ReaxFF and QM.
Figure 4-15: Potential Energy scan for transition state 7 with ReaxFF and QM.

Figure 4-16: Potential Energy scan for transition state 8 with ReaxFF and QM.
Figure 4-17: Potential Energy scan for transition state 9 with ReaxFF and QM.

Figure 4-18: Potential Energy scan for transition state 10 with ReaxFF and QM.
**Figure 4-19:** Potential Energy scan for transition state 11 with ReaxFF and QM.

**Figure 4-20:** Potential Energy scan for transition state 12 with ReaxFF and QM.
Figure 4-21: Potential Energy scan for transition state 13 with ReaxFF and QM.

Figure 4-22: Potential Energy scan for transition state 14 with ReaxFF and QM.
Figure 4-23: Potential Energy scan for transition state 15 with ReaxFF and QM.

Figure 4-24: Potential Energy scan for transition state 16 with ReaxFF and QM.
There is a discrepancy in results predicted by Reax for two cases—ts3 (Figure 4-11) and ts14 (Figure 4-22). ReaxFF tends to overestimate the energy barrier for the ts3 transition state, whereas it underestimates the energy barrier for the ts14 transition state case. However, all other transition states predicted by ReaxFF are in the range of ±5-10 kcal/mol which suggests that the current force field should be able to describe the HNO₃ chemistry.

4.10 Cookoff on a HNO₃ + H₂ mixture with improved force field

To study the performance of the new force field that is developed as part of this research work, a cookoff simulation was performed on a mixture containing 150
molecules of nitric acid and 75 molecules of hydrogen. Summarizing the process, a system containing the 225 molecules (900 atoms) was placed in a periodic box of 70 x 70 x 70 Å³ dimensions. System density of 0.05 gm/cm³ translates to a gaseous system. The system was energy minimized to obtain a low energy configuration. A molecular dynamic simulation using an NVT ensemble involving a steep temperature ramp up from 100K to 4000 K on the minimized system was performed. This is done by scaling up the velocity of each individual atom with every iteration using the Verlet algorithm incorporated in ReaxFF. Visual representation of the MD simulation using VMD is shown in Figure 4-26, 4-27 and 4-28.

A graph of the potential energy of the system and the temperature variation with time was plotted in Figure 4-29. We see that the potential energy of the system decreases initially rapidly and then starts increasing gradually up to a temperature of approx. 3000 K. Investigation of the system approximately 8-10 ps into the simulation reveal that HNO₃ molecules form dimers, trimers and four membered HNO₃ complexes. The existence of HNO₃ dimers has been suggested by Taketa [57] and further verified by Dimitrova [58] and Hart [48]. Formation of strong and linear O-H-----O bonds between the HNO₃ molecules decreases the overall potential energy of the system. As temperature increases further, it is observed that these dimers, trimers etc. start breaking into individual HNO₃ molecules. HNO₃ further dissociates to reach an equilibrium state:

\[
\text{HNO}_3 \rightleftharpoons a \text{NO}_2 + b \text{H}_2\text{O} + c \text{O}_2
\]  

- (8)
Figure 4-26: Snapshot of initial system- 150 HNO₃ + 75 H₂ at T= 100K.

Figure 4-27: Snapshot of system- 150 HNO₃ + 75 H₂ at ~ T= 300K (~ t= 9ps). Formation of HNO₃ polymers is visible.
Figure 4-28: Snapshot of system $150 \text{HNO}_3 + 75 \text{H}_2$ at $T = 3500\text{K}$.

Figure 4-29: Potential Energy and Temperature ($y_2$ axis) variation with time for a $150 \text{HNO}_3 + 75 \text{H}_2$ cookoff simulation.
Figure 4-30 shows the variation of nitric acid (HNO$_3$), hydrogen (H$_2$), water (H$_2$O) and nitrous oxide (NO$_2$) with time during the cookoff simulation. There is an initial decrease in the quantity of HNO$_3$ for the initial 8-10 ps which signifies the formation of HNO$_3$ into dimers, trimers etc. With temperature increase, these polymers dissociate and number of HNO$_3$ increases. HNO$_3$ dissociation actually initiates around a temperature of 1600 K (~ 75 ps into the simulation), whereas H$_2$ starts dissociating around a temperature of 2100 K (~ 100 ps into the simulation). In b/w 75-100 ps, reaction is characterized by HNO$_3$ dissociating to form H$_2$O, NO$_2$, OH and NO$_3$ as well.

$$\text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2 \quad - (9)$$

$$\text{HNO}_3 \rightarrow \text{H} + \text{NO}_3 \quad - (10)$$
Figure 4-30 shows the variation of water ($H_2O$) and nitrogen dioxide ($NO_2$) with time and also temperature variation with time during the course of the cookoff simulation. Around 1600-1700K (75-85 ps), there is a rise in the production of $H_2O$ and $NO_2$ in the system, which can be explained by the fact that $HNO_3$ starts dissociating around the same mark and as soon as $H_2$ starts participating, the relative rate of generation increases initially as seen from the steep gradient around the 100 ps mark. The production increases as temperature is ramped upto ~3500 K, after which at such a high temperature, even the $H_2O$ and $NO_2$ starts breaking into smaller fragments - OH, ON, H, O, HON etc.

$$H_2 + 2 HNO_3 \rightarrow 2 H_2O + 2 NO_2 \quad - (12)$$

Heat of Reaction for (4) using ReaxFF $\Rightarrow \Delta E_f = E_{products} - E_{reactants} = -4.14 \text{ kcal/mol}$.

The reaction (4) is almost energy neutral leading to a release of 4 kcal/mol energy. This might explain why we do not see a drop in the potential energy in figure 4-29 even at a high temperature of ~3000 K.

These results show the improved force field is describing the reaction chemistry for nitric acid with an explosive fuel such as hydrogen with sufficient accuracy.
Chapter 5

CONCLUSIONS

A computational method for performing atomistic-scale molecular dynamic simulations on the hypergolic combustion chemistry between ILs and Oxidizers was developed. This computational method, a ReaxFF force field for HNO₃ and ILs was found to give very good agreement with existing literature data and other simulation models. The unique feature of ReaxFF is its ability to describe the transition states during the course of combustion reactions, which greatly aids in understanding the path a reaction follows. Below follows a summary of the key results from the research.

(1) The hypergolic chemistry between the BMIM/DCA complex and HNO₃ oxidizer is initiated by the dicyanamide anion (C₂N₃⁻). The imidazolium cation is inert and does not participate in the reaction.

(2) Nitric Acid (HNO₃) is an oxidizer with superior performance compared to nitrogen tetroxide (N₂O₄). The ability of HNO₃ to promote hypergolic behavior with the BMIM/DCA class of ILs makes it the oxidizer of choice for use with potential ILs.

(3) The critical intermediate products that are formed during the reaction of BMIM/DCA with HNO₃ are HC₂N₃ and HC₂N₃NO₃. Besides these species, another transition/intermediate state species that has been regularly and widely formed in the course of the reaction is OHC₂N₃.
(4) BMIM/DCA has not been found to be hypergolic with nitrogen tetroxide (N₂O₄).

(5) The improved force field can be used to investigate reactions involving nitric acid, hydrazine, ILs comprised of primarily hydrogen, oxygen, nitrogen and to some extent, carbon.
Chapter 6

FUTURE WORK

Over the course of the research work, I have read and followed the progress of ionic liquids and their applications in diverse fields to some extent. There is a huge scope for working in this direction. Some areas where more research will prove beneficial is:

(1) The inherent advantage of ILs, viz., the ability to alter their property by changing the constituent cation/ anion/ functional group also creates a limitation in their physical manufacturing. The financial cost of preparing ILs is currently very high. So researching different cation/ anion combinations of IL for use as a hypergolic fuels is experimentally not viable. The use of ReaxFF should be extended for investigating the hypergolicity of other IL-oxidizer combinations (eg. ILs having the ethyl imidazolium cation/TMEDA salts mixed with oxidizers like N₂O₄, and anionic species such as HN₃).

(2) The influence of the cation size on the reaction chemistry needs to be studied in further detail. Though the cation here- BMIM, does not participate in the reaction, but other studies suggest that the presence of a function group on the primary cyclic ring can enable the cation to also participate in hypergolic ignition.
(3) The heat generated from initial combustion causes the liquids particles to evaporate into the gas phase. Research on understanding the combustion chemistry in the gas-phase should be done for identifying other intermediate and transition state species.

(4) The existing force field training set that has been developed for HNO₃ can be expanded to include other classes of ionic liquids that are being investigated elsewhere. For eg. amino triazolium salts, methyl-amino triazolium salts, tetrazolium family of ionic liquids [53] and also ILs developed with the N,N,N',N'-tetramethyl- ethane-1,2-diamine compound [54]. Further, ILs prepared using the 2,2-dialkyltriazanium cation have been found to be hypergolic with salts containing nitrate, chloride, nitrocyanamide, and dicyanamide anions [55]. Energetic ionic liquids that contain the 2-azido-N,N,N-trimethylethylammonium cation with nitrocyanamide, dicyanamide, dinitramide, or azide anion have been successfully synthesized in good yields by metathesis reactions [56].

(5) MD simulations at the atomistic level on a large system containing more than 3000-5000 atoms (current system contains around 2400 atoms) will provide more clarity into the analysis of gas phase products and identifying prominent transition states through which reaction progresses. Scaling up will allow simulating at lower initiation temperatures and lower impact velocities. Cluster size and selectivity of ILs (Eg. BMIM/DCA IL is hypergolic with HNO₃ and not with N₂O₄) should be studied.
REFERENCES


