The Pennsylvania State University

The Graduate School

CHEMICAL KINETIC INVESTIGATION OF THE THERMAL DECOMPOSITION OF ENERGETIC MATERIALS:
AMMONIA BORANE, AMMONIUM PERCHLORATE & HMX-TAGzT

A Dissertation in
Mechanical Engineering

by

Tanusree Chatterjee

© 2021 Tanusree Chatterjee

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2021
The dissertation of Tanusree Chatterjee was reviewed and approved by the following:

Stefan T. Thynell
Professor of Mechanical Engineering
Dissertation Advisor
Chair of Committee

Adri van Duin
Professor of Mechanical Engineering, Chemical Engineering, and Engineering Science and Mechanics

Jacqueline O’Connor
Assistant Professor of Mechanical and Nuclear Engineering Department

Joseph F. Horn
Professor of Aerospace Engineering

Daniel Haworth
Professor of Mechanical Engineering
Graduate Program Head of the Department of Mechanical Engineering
ABSTRACT

Energetic materials such as propellants which are burned to produce thrust, play a critical role in meeting the performance and safety requirements of applications such as munitions, rockets/space propulsion systems, automobile air bags and ejection seats of airplanes where generation of high pressure within a short duration of time is necessary. Propellants used in practical applications, generally consists of two or more energetic ingredients. The different ingredients are fuel, oxidizer, plasticizer, binder, burn rate enhancer and combustion instability suppressant. To ensure that the above-mentioned devices are well designed, it is critical to understand the thermal decomposition and combustion behavior of energetic ingredients that comprise the propellants. It is also of paramount importance to understand the chemistry involved during decomposition of these energetic ingredients which will enable a knowledge-based improvement and engineering of propellants. In this dissertation, thermal decomposition processes and the chemical kinetics involved decomposition of three different energetic materials and their intermediates are studied using synergistic application of experimental and computational methods. While experimental methods give information regarding stability of material, nature of reactions (exothermic/endothermic) involved along with the critical intermediates/products formed during decomposition, computational methods such as quantum mechanics (QM) calculations provide significant insight into the complex chemical kinetics involved during decomposition by explaining the reaction pathways for species (intermediates/products) formation. Three different energetic materials studied in this work are as follows:
i) Ammonia borane (AB): a hypergolic rocket fuel and a potential hydrogen storage medium

In this work, thermal decomposition behavior of ammonia borane is studied using thermolysis experiments at low heating rates (<50 K/min) in the temperature range of 300-520 K. In previous experimental studies, there was no consensus regarding release of NH$_3$ in the gaseous phase during thermal decomposition of AB. Experiments performed in this study using FTIR spectroscopy confirm the presence of NH$_3$ in gaseous phase during both steps of AB decomposition. Furthermore, we have also studied the effect of different heating rates on the trend of NH$_3$ evolution during AB decomposition, which has not been done previously. In addition to performing experiments, a detailed reaction mechanism for ammonia borane (AB) decomposition is developed using quantum mechanics (QM) calculations. The primary objective of this study is to provide comprehensive understanding regarding the chemical kinetics involved in the H$_2$ release process during AB dehydrogenation, to explore the pathways of oligomerization leading to ring formation during AB decomposition and to explain the experimental observations using the proposed mechanism. To identify reaction pathways based on QM studies, transition state theory (TST) is used in this work and the thermodynamic properties for both equilibrium species and transition states are calculated using the G4(MP2) compound method. Since AB melts before decomposition, a Solvation Model based on Density (SMD) is used with acetonitrile as the solvent to account for condensed-phase effect on calculations. The newly developed mechanism consisting of 63 reactions and 45 species is validated against experimental data by performing numerical simulations based on control-volume analysis. The comparison of simulation results and experimental data shows that the proposed mechanism captures all the key features of AB decomposition. The mechanism is also used to investigate chemical kinetics involved during the initial phase of AB decomposition (below 373 K) in glyme which is the common solution used to
study condensed-phase dehydrogenation. Reaction pathways proposed explain the formation of species observed during experiments in glyme, reconciling the existing conflicts regarding the initiation step, as well as the pathways of H₂ formation. The developed reaction mechanism not only explains the experimental observations, but also provides information which are difficult to obtain only by performing experiments. This additional information regarding the chemical kinetics of AB decomposition is essential to understand the hypergolic nature of AB as a rocket fuel and the thermal stability of AB as a hydrogen storage medium. It will also help in identifying improved catalysts according to specific needs.

ii) Ammonium perchlorate (AP): one of the most common oxidizers used in solid composite propellant

In this work, initiation reactions and important reaction pathways leading to the formation of decomposition products, such as O₂, during perchloric acid (HClO₄) decomposition are identified. Perchloric acid (HClO₄), which is one of the very strong mineral acids, is experimentally observed during the ignition and combustion of AP (NH₄ClO₄)-containing solid propellants in both gas and condensed phase. Hence, this work can be viewed as a first step towards development of detailed liquid-phase reaction mechanism for AP combustion modeling. To this end, we have performed quantum mechanics (QM) calculations using the Gaussian 09 program package to identify new reaction pathways and species formed during decomposition. The thermodynamic quantities of the species, such as Gibbs free energy and enthalpy, are calculated using a double-hybrid DFT method, B2PLYP with Jensen’s basis set, aug-pc2. For heavy atoms, such as chlorine, the basis set is augmented by adding 2 d functions with a stride factor of 2.5. To incorporate the solvation effect, the Conductor-like Polarizable Continuum Model (CPCM), which is an implicit solvation model, is used. Numerical simulations using a control-volume analysis akin to
experimental set up are also performed using the proposed mechanism. In these simulations, rates of the reactions are calculated using transition state theory (TST) incorporating diffusion effects on the rate constants. In order to consider the non-ideal behavior of concentrated HClO₄ solution, activity coefficients are used to calculate the effective concentration of acid in solution. The activity coefficient of HClO₄ plays a critical role in the calculation of induction period involved during HClO₄ decomposition. A comparison of numerically predicted O₂ evolution curve and the duration of induction period with that of experimental data shows that the numerical simulation using the proposed mechanism is able to well predict both the three-stage decomposition characteristics and the induction period observed during HClO₄ decomposition, thus validating the proposed mechanism.

iii) HMX-TAGzT: HMX is a high-explosive fuel and TAGzT is a burn rate enhancer for nitramine-based propellants

The thermal decomposition characteristics of HMX and TAGzT mixtures are studied using thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) coupled with FTIR spectroscopy. Three different heating rates (15, 20 and 25 KPM) are used to study the interaction between two energetic materials (HMX and TAGzT). Three weight ratios of TAGzT (10%, 20% and 30% of TAGzT by weight) are used to investigate the thermal decomposition behavior of the mixture. Based on thermolysis experiments, it is evident that although there exists significant difference between melting point of HMX and TAGzT (~70 K lower than HMX), decomposition products of TAGzT can react with HMX significantly even before it melts. FTIR spectra show that in addition to NH₃, N₂H₄, HCN and an azide, N₂O and other decomposition products of HMX are also formed during decomposition of TAGzT after it melts at ~480 K which indicates that condensed-phase TAGzT decomposition products react with solid-state HMX to significantly
accelerate the rate of HMX decomposition to form products which are observed only after HMX melts at 553 K in pure HMX sample. Along with thermolysis experiments, quantum mechanics (QM) calculations were performed to qualitatively identify the important reactions involving TAGzT and HMX decomposition products. These calculations show that the cyanide anion formed during condensed-phase TAGzT decomposition can quickly abstract an H\(^+\) ion from HMX forming a cyclic intermediate and NO\(_2^-\) anion in the process, which in subsequent reactions forms HONO, a critical intermediate required to initiate the process of HMX decomposition. Additionally, several new reactions involving decomposition products of TAGzT and HMX are studied which can form HONO during decomposition of the mixture.
# TABLE OF CONTENTS

**LIST OF FIGURES** ................................................................................................................................. x

**LIST OF TABLES** ................................................................................................................................. xv

**NOMENCLATURE** ............................................................................................................................... xvi

**ACKNOWLEDGEMENTS** ......................................................................................................................... xxi

**Chapter 1 INTRODUCTION** .................................................................................................................. 1

1.1 Background and motivation ............................................................................................................. 1
  1.1.1 Ammonia Borane (AB; BH₃NH₃) ......................................................................................... 4
  1.1.2 Ammonium Perchlorate (AP; NH₄ClO₄) ................................................................. 5
  1.1.3 HMX (C₄H₆N₆O₈) & Triaminoguanidinium azotetrazolate (TAGzT): .......... 6

1.2 Overview of dissertation .................................................................................................................. 8

1.3 References ................................................................................................................................... 9

**Chapter 2 QUANTUM MECHANICS INVESTIGATION ON INITIAL DECOMPOSITION OF AMMONIA BORANE IN GLYME** ............................................................................. 15

2.1 Introduction .................................................................................................................................. 15

2.2 Molecular modeling and numerical simulation ................................................................. 18
  2.2.1 Description of model used in QM calculations ......................................................... 18
  2.2.2 Details of rate constant calculation ........................................................................... 19
  2.2.3 Details of numerical simulation ................................................................................ 21

2.3 Results and discussion ............................................................................................................... 22
  2.3.1 Initiation of AB decomposition in glyme solution ..................................................... 26
  2.3.2 Formation of DADB and H₂ ....................................................................................... 33
  2.3.3 Formation of CDB, BCDB, CTB and Borazine ....................................................... 38

2.4 Conclusions ................................................................................................................................ 43

2.5 References ................................................................................................................................... 44

**Chapter 3 DEVELOPMENT AND VALIDATION OF DETAILED REACTION MECHANISM FOR LIQUID-PHASE DECOMPOSITION OF AMMONIA BORANE** ........................................ 53

3.1 Introduction .................................................................................................................................. 53

3.2 Details of experimental studies .................................................................................................. 57

3.3 Details of numerical simulation and molecular modeling ................................................ 58

3.4 Results and Discussion ............................................................................................................. 63
  3.4.1 Initiation and H₂ release pathways ............................................................................. 67
  3.4.2 Pathways for formation of ring-containing compounds ........................................ 71
FIGURE 1.1 Molecular structures of HMX, RDX and TAGzT ...................................................... 7

FIGURE 2.1 Molecular structures of intermediates and rings formed in the system .................. 24

FIGURE 2.2 Results from sensitivity calculations showing critical reactions to the
consumption of AB, formation of H₂, DADB and CDB for initial concentration of
AB in glyme solution [AB]₀=1M at T=368K. Naming convention: Ri represents the
i-th forward reaction and Ri_bwd represents the i-th backward reaction. ....................... 25

FIGURE 2.3 Results from sensitivity calculations showing critical reactions to the
formation of BCDB, BH₂NH₂, borazine and CTB for initial concentration of AB in
glyme solution [AB]₀=1M at T=368K. Naming convention: Ri represents the i-th
forward reaction and Ri_bwd represents the i-th backward reaction. ......................... 26

FIGURE 2.4 Molecular structure of transition state of reaction R3 and complex,
BH₄BH₂NH₃. (Distances between atoms are in Angstrom) ............................................. 32

FIGURE 2.5 Comparison of QM calculation with data for initial concentration of AB in
glyme solution [AB]₀=1M. Error bars are calculated based on temperature variation
(ΔT) of ±2K in numerical simulation ........................................................................... 33

FIGURE 2.6 Variation of mass fraction of AB and DADB with time for initial
concentration of AB in glyme solution [AB]₀=1M at T=368K .................................... 35

FIGURE 2.7 Potential energy surface for two pathways of H₂ formation based on QM
calculations ...................................................................................................................... 37

FIGURE 2.8 Hydrogen release from AB at different temperatures below 373K ([AB]₀=1M) .. 37

FIGURE 2.9 Reaction network for AB decomposition in glyme solution. Here, the use of a
solid thick line, ______ , indicates a dominant pathway and dashed, - - - - - - ,
indicates a minor pathway ............................................................................................ 39

FIGURE 2.10 Potential energy surface for DADB, CDB, BCDB, CTB and borazine
formation based on QM calculations ............................................................................ 40

FIGURE 2.11 Variation of mass fraction of BH₄NH₂ and AB with time for initial
concentration of AB in glyme solution [AB]₀=1M at T=348K and 368K ....................... 42

FIGURE 2.12 Variation of mass fraction of BH₄NH₂, CDB, BCDB, CTB and borazine with
time for initial concentration of AB in glyme solution [AB]₀=1M at T=348K and
368K ............................................................................................................................. 42
Figure 2.13 Mass fraction of DADB, CDB, BCDB, CTB and borazine during very early stage of AB decomposition in glyme solution [AB]_0=1M at T=348K and 368K. 

Fig. 3.1 Molecular structures of intermediates formed, and ring-containing species considered in the growth cycle. Species labeled RING10 and RING14 are assumed to be the final products.

Figure 3.2 Reaction network for initial phase of AB decomposition and H₂ release. Here, the use of a thick line, __________, indicates a dominant pathway and dashed, -----, indicates a minor pathway.

Figure 3.3 Reaction pathways for formation of borazine.

Figure 3.4 Reaction pathways for ring formation. NH₂BHNH₂ formed via reactions R61-R63.

Figure 3.5 TGA mass loss and DSC curves obtained for AB subject to 3 different heating rates in a nitrogen atmosphere.

Figure 3.6 FTIR absorbance spectra obtained for AB heated at 20K/min in a nitrogen atmosphere.

Figure 3.7 Comparison of simulation predicted mass loss curve with available TGA data at 20 K/min. *Mass loss profile predicted using modified mechanism (Error bars for both data and numerical simulation are added based on 95% confidence interval).

Figure 3.8 Mass loss curves predicted by numerical simulation at three different heating rates using modified mechanism (Error bars for numerical simulation are added based on 95% confidence interval).

Figure 3.9 Comparison of simulation predicted mass loss curve with TGA data at three different heating rates using modified mechanism (Error bars for both data and numerical simulation are added based on 95% confidence interval).

Figure 3.10 Wt% of gaseous species evolved during AB decomposition as predicted by numerical simulation for different heating rates using modified mechanism.

Figure 3.11 Temporal evolution of mass fraction of species (H₂, NH₃, BH₂NH₂, B₂H₆, and borazine) accumulated in gas phase as predicted by numerical simulation for heating rate of 20K/min using modified mechanism.

Figure 3.12 Mole fraction of NH₃ evolving during decomposition at different heating rates in a nitrogen atmosphere.
Figure 4.1 The transition state (TS) and molecular structures of reactants formed during initiation steps, R2 and R3. Red colored atoms are Oxygen, O; green colored atoms are Chlorine, Cl; grey atoms are hydrogen, H. .................................................................105

Figure 4.2 Dominant reaction pathway for formation of O3ClOClO3 to release O2 during initial phase of HClO4 decomposition........................................................................106

Figure 4.3 Mass fraction (y) of H2O, [H3O]+, [ClO4]-, O3ClOClO3 (plotted in log scale, base 10) and HClO4 over time (t) using the proposed mechanism. Decomposition temperature, T=353 K and initial mass fraction of anhydrous perchloric acid, yHClO4,0=1. ........................................................................................................109

Figure 4.4 Mass fraction (y) of HClO4 and O3ClOClO3 over time using the proposed mechanism showing the impact of barrier height of reaction R5. Decomposition temperature, T=353 K and initial mass fraction of anhydrous perchloric acid, yHClO4,0=1) ...........................................................................................................110

Figure 4.5 The PES diagram of new reaction pathway for O3ClOClO3 formation during decomposition. ........................................................................................................111

Figure 4.6 Dominant reaction pathway for formation of O2 during initial phase of HClO4 decomposition. ........................................................................................................115

Figure 4.7 Evolution of HClO4 and O2 (plotted in log scale, base 10) over time during the decomposition process at temperature, T=353 K and initial mass fraction of anhydrous perchloric acid, yHClO4,0=1. Volume of O2 is calculated at s.t.p; standard temperature (T) and pressure, (P) T=273.15 K, P=1 atm=101.325 kPa. .........................116

Figure 4.8 Comparison of numerical simulation with experimental data for O2 evolution and its rate of formation during anhydrous perchloric acid decomposition in the temperature range of 333-353 K. Initial mass of acid=1 gm; volume of O2 is measured at s.t.p; standard temperature (T) and pressure, (P) T=273.15 K, P=1 atm=101.325 kPa. ........................................................................123

Figure 4.9 Comparison of numerical simulation with experimental data for O2 evolution during anhydrous perchloric acid decomposition in the temperature range of 333-353K. Initial mass of acid=1 gm; volume of O2 is measured at s.t.p; standard temperature (T) and pressure, (P) T=273.15 K, P=1 atm=101.325 kPa. .........................124

Figure 4.10 Comparison of induction period (τ) predicted by numerical simulation with that of experimental data. Error bar shown in (a) is calculated based on ±15% variation in HClO4 activity coefficient .................................................................125
Figure 4.11 Comparison of $O_2$ evolution and its rate of liberation predicted by numerical simulation with that of experimental data at different initial concentrations of $HClO_4$ solution for $T=353$ K and initial mass of solution=1 gm (Volume of $O_2$ is measured at s.t.p; standard temperature (T) and pressure (P) $T=273.15$ K, $P=1$ atm=101.325 kPa) .................................................. 126

Figure 4.12 Comparison of $O_2$ evolution predicted by numerical simulation with that of experimental data at different initial concentrations of $HClO_4$ solution for $T=353$ K and initial mass of solution=1 gm. (Volume of $O_2$ is measured at s.t.p; standard temperature (T) and pressure.(P) $T=273.15$ K, $P=1$ atm=101.325 kPa) ........................................ 127

Figure 4.13 Comparison of induction period ($\tau$ in mins) predicted by numerical simulation with that of experimental data at different initial concentrations of $HClO_4$ solution in the temperature range of $T=333$-$353$ K (initial mass of solution=1 gm)...... 128

Figure 5.1 TGA and DSC results for HMX-TAGzT (90-10) mixture for three heating rates. .................................................................................................................. 141

Figure 5.2 Comparison of TGA and DSC results for HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT at three different heating rates (15, 20 and 25 K/min)...... 142

Figure 5.3 FTIR transmission spectra of evolved gases for HMX-TAGzT (90-10) mixture at different temperatures for 25K/min heating rate. .................................................. 146

Figure 5.4 Comparison of mole fractions of evolved IR-active species deduced from FTIR transmission spectra during decomposition of HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT. .................................................. 147

Figure 5.5 Mole fraction of evolved IR-active species released from HMX-TAGzT (90-10) mixture compared against pure HMX and pure TAGzT for a heating rate of 25K/min. ................................................................. 148

Figure 5.6 TGA and DSC results for HMX-TAGzT (80-20) mixture at different heating rates. .................................................................................................................. 150

Figure 5.7 Mole fraction of gaseous species released during decomposition of HMX-TAGzT (80-20) mixture.................................................................................. 151

Figure 5.8 Mole fraction of gaseous species released from pure HMX and two different mixture ratios of HMX-TAGzT (90-10 and 80-20) for a heating rate of 25K/min. ....... 152

Figure 5.9 TGA and DSC results for HMX-TAGzT (80-20) mixture at different heating rates. .................................................................................................................. 154

Figure 5.10 FTIR transmission spectra of evolved gases for HMX-TAGzT (70-30) mixture at different temperatures for 25K/min heating rate............................................. 155
Figure 5.11 Mole fraction of gaseous species released during decomposition of HMX-TAGzT (80-20) mixture. ................................................................. 156

Figure 5.12 Mole fraction of gaseous species released at 25 KPM for pure HMX and three different mixture ratios of HMX-TAGzT (90-10, 80-20 and 70-30). ................. 157

Figure 5.13 Molecular structure of INT249a ........................................................................ 159

Figure 5.14 Molecular structures of intermediates formed during decomposition of HMX-TAGzT mixtures .............................................................. 162
LIST OF TABLES

Table 2.1 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction (kJ/mol) of all the reactions involved in the developed reaction mechanism for initial decomposition of AB decomposition in glyme. ..........................30

Table 2.2 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction, as well as forward Arrhenius activation energy $E_a, f$ (kJ/mol, $T=400K$) of initiation step $R3$: $2AB \leftrightarrow BH_4BH_2NH_3+NH_3$ using different levels of theory with the SMD solvation model and acetonitrile as the solvent ......................31

Table 2.3 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction, as well as forward Arrhenius activation energy $E_a, f$ (kJ/mol, $T=400K$) of initiation step $R3$: $2AB \leftrightarrow BH_4BH_2NH_3+NH_3$ using different solvents and solvation models. The G4(MP2) compound method is used. ..............................31

Table 3.1 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction (kJ/mol) of several important reactions during initial phase of AB decomposition and $H_2$ release...............................................................65

Table 4.1 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction (kcal/mol) of important reactions governing the initial phase of $HClO_4$ decomposition in liquid phase below 373 K based on QM calculations .................103

Table 4.2 Comparison of induction period ($\tau$) calculated by numerical simulation with that of experimental data for anhydrous perchloric acid..............................................................119

Table 4.3 Induction period ($\tau$) calculated by numerical simulation at different initial concentrations of $HClO_4$ solution .....................................................................................122

Table 5.1 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction (kcal/mol) of all the reactions involved in the HONO formation during decomposition of HMX-TAGzT mixture. ..............................................160
## NOMENCLATURE

### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusivity coefficient</td>
</tr>
<tr>
<td>$G$</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$H$</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>$N$</td>
<td>Number</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$S$</td>
<td>Entropy</td>
</tr>
<tr>
<td>$S'$</td>
<td>Sensitivity coefficient</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$W$</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$y$</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Species generation rate</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
</tbody>
</table>
Abbreviations

TNT  Trinitrotoluene
HMX  Cyclotetramethylene tetranitramine
RDX  Cyclotrimethylene trinitramine
TAgzT Triaminoguanidinium azotetrazolate
AB   Ammonia borane
B₂H₆  Diborane
B₅H₉  Pentaborane
H₂   Hydrogen
DADB Diammoniate of diborane
PAB  Polyaminoborane
PIB  Polyiminoborane
CDB  Cyclodiborazane
BCDB B-(cyclodiborazanyl) aminoborohydride
CTB  Cyclotriborazane
AP   Ammonium perchlorate
NC   Nitrocellulose
NG    Nitroglycerin
TGA   Thermogravimetric analysis
DSC   Differential scanning calorimetry
FTIR  Fourier transform infrared (spectroscopy)
DTA   Differential thermal analysis
MS    Mass spectroscopy
QM    Quantum mechanical
TS    Transition states
SMD   Solvation Model based on Density
DFT   Density functional theory
IRC   Intrinsic reaction coordinate

**Subscript**

*i* or *j*  *i*th or *j*th species
*kin*     Kinetic
*diff*   Diffusion
*eff*    Effective
*evap*  Evaporation
*l*     Liquid
*g*     Gas
*ref*    Reference
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Stefan Thynell for the continuous support, with the required technical and emotional guidance these past five years. He has always been perceptive, forthcoming and considerate with me. His integrity, dedication and passion towards research and pushing the envelope have been inspiring.

I would also like to thank my dissertation committee members Dr. Adri van Duin, Dr. Jacqueline O’Connor and Dr. Joseph F. Horn for agreeing to provide their time and valued inputs to this research work. I would also like to take this opportunity to thank my previous dissertation committee member, late Dr. Michael Micci for his valuable inputs on dissertation during comprehensive exam.

I would like to thank my teacher, late Sameer Banerjee from my school years who not only shaped my young mind but also inculcated morals and principles to live by. He went above and beyond his duty to help me in my personal life and I will forever be grateful to him.

I would like to thank my parents who always have tried their best to shield me from adversities of life and to always ensure that I receive the best possible education irrespective of the financial condition of the family. I am thankful to my brother for always loving me and lending me support whenever I needed.

Last but most definitely not the least, I thank my husband, Bikramjit for his understanding and support through this journey and my son Rajarshi, a.k.a. Simba being a fount of joy and happiness these last three years.

This work was supported by the Air Force Office of Scientific Research under grant number FA9550-13-1-0004 and the U. S. Army Research Laboratory and the U. S. Army Research Office under grant number W911NF-15-1-0202. This dissertation describes objective
technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the funding agencies or the United States Government.
This work is dedicated to my parents, Durgasis and Suvra Bhattacharya for all their sacrifices and hard work that went into making me who I am today.
Chapter 1
INTRODUCTION

1.1 Background and motivation

Energetic materials are a class of material, which, upon application of external stimulus such as heat, electrical current or shock, can release stored chemical energy in an exothermic, self-sustaining process. Energetic materials can be classified broadly into two types: 1) conventional hydrocarbon fuels such as diesel/gasoline used in automobiles, and 2) chemical explosives that include propellants used in munitions, rockets etc. to provide thrust or explosive power; they are commonly used in military as well as commercial applications for blasting/shattering. The primary distinction between conventional fuels and chemical explosives lies in the rapidity of the reactions involved and the rate at which heat is released during the process of decomposition/combustion. Although chemical explosives usually have less potential energy than fuels, their high rate of energy release produces a great blast pressure. Chemical explosives such as Trinitrotoluene (TNT) has a detonation velocity of 6,940 m/s compared to 1,680 m/s for the detonation of a pentane-air mixture, and the 0.34 m/s stoichiometric flame speed of gasoline combustion in air. Chemical explosives can further be subdivided into low explosive and high explosive. Low explosives such as black powder or smokeless gunpowder used as propellants, burn very rapidly, but at a subsonic speed, meaning that they “deflagrate.” High explosives are materials that burn or decompose quickly undergoing detonation, creating large quantities of gases, which take up much more space than the original materials. Although high explosives such as RDX and HMX are primarily used to create explosions, they are also often used in propellants as high-explosive fuel to provide
additional energy [1-3]. In this dissertation, the primary focus is on the energetic materials that constitute propellants used in applications such as gun, space propulsion systems or automobile air bags where high burning rate along with rapid generation of high pressure in a controlled manner is the requirement.

Black powder, developed in ancient China, can be considered as the earliest low explosives which were extensively used in firearms/canons before 1900. The first revolution in this field since the invention of black powder started with the use of nitrocellulose (NC, low explosive) and nitroglycerin (NG, high explosive) as propellants in the mid-19th century. Nitrocellulose-based propellants significantly reduced smoke, which was one of the biggest drawbacks of black powder-based propellants. Furthermore, propellants based on NC and NG, also known as double-base propellants, improved performance significantly. However, due to the presence of NG, the double-base propellants are unstable and highly prone to accidental ignition which makes them unsafe to handle [2]. Hence, double-base propellants were soon replaced with relatively solid composite propellants, especially in space applications. Unlike double-base propellants, composite propellants consist of crystalline particles made up of an oxidizer (ammonium perchlorate, a common oxidizer) and fuel (aluminum powder). Oxidizer and fuel are bound together in a polymeric matrix called binder [2]. In addition, burn rate enhancer and combustion instability suppressant are also often added as propellant ingredients. RDX/HMX are often added as burn rate enhancer to provide extra energy. In addition to the above-mentioned solid propellants, liquid propellants are also widely used in rockets. Liquid-fueled rockets have higher specific impulse than solid rockets and are capable of being throttled, shut down, and restarted. The most used oxidizer and fuel in liquid propellants are liquid oxygen and liquid hydrogen, respectively. However, liquid hydrogen require storage at extremely low temperatures (~253°C) to maintain it in a liquid state. To circumvent the storage problem with liquid H₂, non-cryogenic fuels such as hydrazine (N₂H₄) are often used in
rockets. However, these materials are highly toxic and carcinogenic. In recent years, ammonia borane has received significant attention as a potential next-generation rocket fuel that can replace hydrazine. A significant amount of research is currently going on to understand the hypergolic nature of ammonia borane which can reduce the ignition delay time significantly, thus further improving the performance of rocket propellants [4-8].

From the above discussion, it is evident that over the years, the development of propellants is primarily driven based on the performance and safety requirements. It is important to note that the definition of propellant performance depends largely on the purpose of the intended device. For instance, although double-base propellants typically provide higher specific impulse, solid composite propellants are preferred choice for the space shuttle launch where safe handling and storage of propellants is one of the primary requirements. The higher energy content of double-base propellants makes them ideal for use as ballistic missiles in submarines where space is limited [9]. Hence, to ensure that devices using propellants such as gun, rocket or automobile airbags are well designed, it is crucial to understand the combustion/decomposition behavior of energetic materials that comprise the propellants as well as the chemistry involved during decomposition. In this dissertation, intricate details of thermal decomposition processes of three energetic materials are studied using both experimental methods such as thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) coupled with Fourier transform infrared (FTIR) spectroscopy and theoretical methods such as newly developed quantum mechanical (QM) calculations. The details of three different energetic materials studied in this work are provided in the remainder of this section.
1.1.1 Ammonia Borane (AB; BH₃NH₃)

In recent years, ammonia borane (AB) has gained significant attention as a potential hydrogen storage medium. AB contains 19% of H₂ by weight, which corresponds to a significantly high volumetric (146 g H₂ per liter) and gravimetric (194 g H₂ per kilogram) density of hydrogen. In addition to being used as rocket fuel, AB finds application in several areas such as fuel cells, transportation devices etc. [10-14]. Over the past few years, significant contributions have been made by several researchers towards improving our understanding the thermal decomposition behavior of AB. Based on thermolysis experiments, Baitalow et al. [15] concluded that AB releases ~14% of H₂ by weight in two major exothermic mass loss steps. In addition to H₂, BH₂NH₂, B₂H₆ and borazine were also present in gaseous phase as impurities. Baitalow et al. [15] further observed that AB melts during decomposition before releasing first equivalent of H₂. Thus, to gain a detailed understanding of the thermal decomposition behavior of AB, one should focus such studies on the chemical kinetics in its condensed phase. In order to understand the condensed-phase AB dehydrogenation, several studies were performed using glyme as a solvent [16, 17]. Using NMR spectroscopy, researchers identified several cyclic intermediates during AB decomposition in glyme below 373 K. Based on the experimental observations, reaction pathways were also proposed. However, there exists no consensus regarding important pathways such as initiation and H₂ pathways. Hence, the chemical kinetics involved during condensed-phase AB dehydrogenation is still not understood. Computational efforts were also made to understand the chemical kinetics involved during thermal decomposition of AB [18]. However, only few early reactions involved during AB decomposition were studied using quantum mechanics (QM) calculations. Hence, it is evident that additional studies are required to unravel the intricate details of chemical kinetics involved during thermal decomposition of AB.
1.1.2 Ammonium Perchlorate (AP; $\text{NH}_4\text{ClO}_4$)

Ammonium perchlorate (AP) is one of the most common oxidizers used in composite propellants for propulsion of rockets. AP contains ~30% excess of oxygen, which allows combustion products of monopropellant AP to react readily with the fuel. Furthermore, it has been observed that the burn rate of propellants can be controlled by varying the particle size distribution of AP [9]. This unique ability of AP provides greater control of propellant burn rate and makes it even more desirable among the various oxidizers used today to propel rockets. To understand the complex chemical kinetics involved during the combustion of AP, numerous experimental and numerical studies have been undertaken. However, due to the extremely small scale of the AP flame structure, it has been a challenge to measure the species profiles in the premixed gas-phase flame. Hence, minimal amount of experimental data pertaining to species concentrations and temperature are available [9]. Therefore, numerical simulations of the flame can be utilized in order to understand the AP combustion characteristics. During the past decades, several numerical models were developed to study AP combustion. Among which the Beckstead-Derr-Price (BDP) model [19] developed in 1970 provides the most widely accepted theoretical picture of AP combustion. However, in this model Beckstead et al. [19] used one global reaction to model the kinetics involved. Gradually over the years in order to develop better theoretical understanding of AP combustion, models shifted to using detailed gas-phase mechanism. In 1982, based on experimental data Ermolin et al. [20] developed the first detailed AP gas-phase mechanism consisting of 80 reactions and 24 species. The Ermolin mechanism served as the basis for the development of more refined gas phase mechanism developed by Jing et al. in 1998 [21]. Although gas-phase mechanism was studied extensively, condensed-phase is still modeled using global/semi-global reactions. It is well known that during combustion of AP-based propellants, melt layer forms at the surface plays a critical role in controlling the heat feedback between gas and condensed-phase, thus controlling
the burn rate of the propellant [9]. Therefore, it is evident that the lack of a detailed AP condensed-phase reaction mechanism is the major drawback in modeling AP combustion and needs to be addressed to improve predictive capability of combustion models.

1.1.3 HMX (C₄H₈N₈O₈) & Triaminoguanidinium azotetrazolate (TAGzT)

HMX (C₄H₈N₈O₈, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine), also known as octogen, is a cyclic organic compound consisting of an eight-membered ring of alternating carbon and nitrogen atoms, with a nitro group (−NO₂) attached to each nitrogen atom in the cycle. HMX is one of the most common nitramine-based energetic materials containing −CH₂NNO₂− units into a loop and has similar molecular structure to that of RDX, which is a very well-known explosive. The molecular structures of HMX and RDX are shown in Fig. 1.1. In addition to being used as explosives, these high-density energy compounds are also used as ingredients in gun and rocket propellants [22]. In order to investigate the thermal decomposition and combustion behavior of explosives and propellants containing RDX and HMX as ingredients, several studies have been undertaken over the years [23-53]. While experimental studies were predominant till the end of 20th century, with the advancement of computational capability over the past few decades, theoretical studies have also become increasingly important for predictive modeling of the ignition, combustion and detonation behaviors of these energetic materials [48-53]. It is to be noted that these studies involve only one ingredient (RDX or HMX) to understand the combustion/decomposition characteristics of these nitramine-based propellants/explosives. However, in most practical applications, propellant/explosives are made up of two or more ingredients [3]. High-nitrogen energetic compounds having large positive heats of formation has gained significant attention in recent years for their ability to increase the burn rate of nitramine-
based propellants without producing undesirable smoke or soot. Furthermore, these high-nitrogen energetic ingredients have significant potential to reduce barrel erosion. Triaminoguanidinium azotetrazolate (TAGzT) is one of the commonly used high-nitrogen energetic materials [3]. The molecular structure of TAGzT is shown in Fig. 1.1. In this context, Hayden et al. [2] performed thermolysis experiments such as thermogravimetric analysis (TGA)/differential thermal analysis (DTA) coupled with mass spectroscopy (MS) to study the thermal decomposition behavior of RDX-TAGzT mixtures at low and moderate temperatures (below 573 K) using low heating rates (2.5 K/min). Although it is well known that the decomposition products of HMX and RDX are very similar, the melting point of RDX and HMX is significantly different (melting point of HMX is ~70 K higher than RDX). Therefore, it can be concluded that TAGzT will not alter the thermal decomposition characteristics of RDX and HMX in a similar way. Hence, although it is known from Hayden et al.’s [2] study how TAGzT interacts with RDX at low and moderate temperatures, similar study needs to be done for HMX-TAGzT mixtures as well. Furthermore, so far, no computational efforts were made to understand how the HMX decomposition pathway changes in the presence of TAGzT. Computational work plays a critical role in enhancing our understanding on chemical kinetics as it provides additional information which is not able to obtain only by performing experiments.

![Molecular structures of HMX, RDX and TAGzT](image)

Figure 1.1 Molecular structures of HMX, RDX and TAGzT
1.2 Overview of dissertation

Based on the above discussion, research goals of this dissertation are identified, and the research work are presented in six chapters of this dissertation. The outline of the dissertation is as follows:

Chapter 1 presents the background and motivation of the research performed in this work. Chapter 2 provides and 3 provide the details of the research work performed related to the thermal decomposition of AB. In Chapter 2, reaction pathways for initial phase of AB decomposition in glyme solution below 373 K are proposed. In Chapter 3, a detailed liquid-phase AB reaction mechanism is proposed which provides a comprehensive understanding regarding the initiation of AB decomposition and pathways of H\textsubscript{2} release during thermolysis experiments at different heating rates. Furthermore, the processes of cyclization to form borazine and other ring-containing species during the second phase of AB decomposition are also discussed in detail. Along with QM studies, experimental results obtained from thermolysis experiments (TGA/DSC coupled with FTIR) at different heating rates are also provided. Using the proposed mechanism, numerical simulations are performed at heating rates used during experiments. The comparison of simulated results with the acquired experimental data is shown in Chapter 3.

In Chapter 4, a reaction mechanism is proposed for solution of concentrated HClO\textsubscript{4} which is one of the primary decomposition products of AP in condensed-phase. The newly proposed HClO\textsubscript{4} mechanism is validated against available experimental data by performing numerical simulations. This work can be viewed as a first step towards the development of detailed condensed-phase reaction mechanism for AP combustion modeling.

In Chapter 5, thermal decomposition behavior of HMX and TAGzT was studied by performing thermolysis experiments. Quantum mechanical (QM) calculations were also performed
which provide insight on reaction pathway involved during initiation of HMX decomposition in the presence of TAGzT.

In Chapter 6, major findings of this work are summarized, and future work related to each energetic material studied in this work are discussed.

1.3 References


Chapter 2
QUANTUM MECHANICS INVESTIGATION ON INITIAL DECOMPOSITION OF AMMONIA BORANE IN GLYME

2.1 Introduction

With the ever-increasing consumption of fossil fuels, the search for alternatives is of paramount importance. Hydrogen is considered to be one of the most efficient and clean fuels whose only oxidation product is water [1]. However, one of the most significant hurdles regarding transition to the use of hydrogen is its storage, especially in transportation [2]. The obstacle of pure hydrogen storage can be circumvented by the development of efficient hydrogen storage materials [3,4]. Recently, ammonia borane (AB) has received significant attention as a potential medium of storing hydrogen due to high densities of hydrogen content. AB has a volumetric density of 146 g H$_2$ per liter and a gravimetric density of 194 g H$_2$ per kilogram. Furthermore, unlike other chemical hydrides, such as diborane (B$_2$H$_6$) and pentaborane (B$_5$H$_9$), AB does not pose significant safety and storage problems. As a result, AB is an attractive candidate for several practical applications, such as fuel cells, hydrogen powered transportation devices and propulsion systems [5-9]. A previous study by Weismiller et al. showed that AB as a fuel ingredient in propellants can increase the specific impulse of a hybrid rocket motor [9]. AB releases hydrogen at a relatively low temperature and at moderate pressures. The process is kinetically controlled rather than thermodynamically controlled which suggests that hydrogen release can be accelerated significantly in the presence of a catalyst [10-14]. In the presence of a solvent, the rate of AB dehydrogenation is enhanced and occurs at lower temperatures compared to pure AB. Furthermore, the rate of H$_2$ release and intermediates formed during the decomposition of AB in solid state and in solution are also significantly different [6,15–19]. In this work, we focus on the chemical kinetics of the initial
decomposition of AB in a glyme solution. Glyme is an organic solvent in which AB dissolves reasonably well, and it has a boiling temperature of 353K at atmospheric pressure. This temperature is also the minimum temperature at which an appreciable extent of decomposition of AB occurs [20].

In order to extract hydrogen from AB, as well as to consider regeneration of AB [21-23], many studies have been undertaken to study its thermal decomposition. Baitalow et al. [17] and Wolf et al. [24] showed that AB in a solid state decomposes to produce 12% of hydrogen by weight in two exothermic steps. In the first step, AB decomposes to produce polyaminoborane (PAB) which further decomposes to polyiminoborane (PIB) releasing hydrogen in the process. Using in-situ NMR spectroscopic studies, Stowe et al. [19] and Bowden et al. [25] concluded that the formation of diammoniate of diborane, \([\text{NH}_3\text{BH}_2\text{NH}_3]^+\text{[BH}_4^-\text{]}\) (DADB) is the key step in the formation of H\(_2\) from solid state AB. This was further validated by Heldebrant et al. [26] when they observed that the induction period of hydrogen release from solid state AB reduced significantly with the addition of DADB. DADB is also observed in ionic liquids and organic solvents during the initial decomposition stages of AB [6,18,15]. Mayer [27] observed that the addition of DADB in glyme also accelerates the formation of H\(_2\). These results suggest that DADB is an essential intermediate for hydrogen release from AB irrespective of its state.

However, when Wang and Geanangel [20] performed similar studies of AB decomposition at 80°C using several different solvents including glyme, they did not observe DADB as an intermediate. They concluded that AB decomposes only through a unimolecular reaction forming BH\(_2\text{NH}_2\) and H\(_2\). In a recent study by Al-Kukhun et al. [6], using NMR spectroscopy and DFT calculations of a few initial reactions, they concluded that the initiation of AB decomposition can be described by two possible ways: one through formation of BH\(_2\text{NH}_2\) and H\(_2\) in a unimolecular reaction and another through formation of DADB, which decomposes to produce cyclodiborazane
(CDB) and H₂. One of the very early studies on AB decomposition, Hu et al. [28] made a similar conclusion about the initiation of AB. This conclusion is in contrast to the common belief that DADB formation is the first key step in the process of AB dehydrogenation. Along with DADB, Al-Kukhun et al. [6] also observed CDB, B-(cyclodiborazanyl) aminoborohydride (BCDB) and cyclotriborazane (CTB) as intermediates. According to the reaction mechanism proposed by Al-Kukhun et al. [6], BH₂NH₂ formed during the initiation step plays an important role in the formation of above species. However, in another recent study done by Autrey and co-workers [29], BH₂NH₂ was not observed in NMR spectroscopic studies of AB in glyme. However, they detected other chemical species observed by Al-Kukhun et al. [6], including CDB, BCDB, CTB, and borazine. DADB was observed in a small amount only at the lower reaction temperature of 323K unlike Al-Kukhun et al. [6]. Based on experimental observation of above species, Shaw et al. [29] concluded that AB reacts in a bimolecular reaction to form DADB which decomposes to produce H₂ and CDB, which further reacts with AB to form BCDB. Although they observed CTB and borazine during later times, they could not identify the pathway of formation of CTB and borazine.

The literature survey presented above suggests that the details regarding the initiation of thermal decomposition of AB in solution is not fully understood, which is essential to determine the thermal stability of AB as a hydrogen storage medium and will also help in identifying improved catalysts according to specific needs. It is also evident that the reaction pathways developed so far are mainly based on the experimental observations of a limited set of chemical species. Herein we adopt recently developed methods of quantum mechanics (QM) to propose a detailed reaction mechanism of AB dehydrogenation in glyme solution during its initial phase of decomposition. This work explains the formation of species observed in above experiments, reconciling the existing conflicts regarding the initiation step, as well as the pathways of H₂ formation.
2.2 Molecular modeling and numerical simulation

2.2.1 Description of model used in QM calculations

QM calculations were used to identify the reaction pathways and also to provide additional information which otherwise is difficult to obtain experimentally. The Gaussian09 [30] suite of programs was utilized to this end. Various methods and basis sets were used, assuming that the condensed-phase reactions within the glyme solvent could be represented by the Solvation Model based on Density (SMD) solvation model with acetonitrile as the solvent. Searches for transition states (TS) were typically performed using density functional theory (DFT) and low-level basis sets, such as B3LYP/6-31G(d). Once a transition state was identified with its single negative frequency, intrinsic reaction coordinate (IRC) calculations were performed to link the reactants to the products [31,32]. Higher-level calculations were then performed using the G4(MP2) compound method for both the equilibrium species with only real vibrational frequencies, or transition state structures with a single negative frequency [33,34]. Here, the changes in the thermodynamic properties, such as enthalpy and free energy, were directly computed using the G4(MP2) output, rather than using Born-Haber cycles [35,36]. These latter cycle calculations would be important to use if a significant number of ionic species were identified in the calculations. The accuracy of the various calculations is in general about the same as the accuracy of calculations of the free energy of solvation. However, it is not known to the authors if there are experimental information of solvation free energies of boron-containing molecules and used in the training-set of parameters for the SMD solvation model. In addition, these calculations were performed for a temperature of 298.15 K. The free energy changes at higher temperatures are likely to be different, but would require the use of a solvation model parametrized to account for such effects. These computer
programs are not available for our use. We expect that the difference would amount to a few kJ/mol, since temperatures considered here are relatively low.

### 2.2.2 Details of rate constant calculation

It is well known that rate constant of reactions, especially barrier-less reactions, are significantly affected by diffusion effects. As a result, the effective rate constant \( k_{\text{eff}} \) is calculated taking into account both the kinetic and diffusion effects as follows [37]:

\[
\frac{1}{k_{\text{eff}}} = \frac{1}{k_{\text{kin}}} + \frac{1}{k_{\text{diff}}}
\]  

(1)

Here, \( k_{\text{kin}} \) and \( k_{\text{diff}} \) represent, respectively, the kinetic and diffusion rate constants. The kinetic rates of chemical reactions were computed using the thermodynamic formulation of the conventional transition state theory. As shown by Laidler and King [38] and by Fernandez-Ramos et al. [39], the kinetic rate constant, \( k_{\text{kin}} \) can be expressed by

\[
k_{\text{kin}} = \Gamma \sigma \frac{k_B T}{h c^{n-1}} \exp \left( -\frac{\Delta G}{R_u T} \right) = \Gamma \sigma \frac{k_B T}{h c^{n-1}} \exp \left( \frac{\Delta S}{R_u} \right) \exp \left( -\frac{\Delta H}{R_u T} \right)
\]  

(2)

where \( k_B, h, \Gamma, \sigma \) and \( \Delta G \) represent, respectively, Boltzmann’s constant, Planck’s constant, tunneling factor, symmetry factor and Gibbs free energy of activation which can be written in terms of entropy (\( \Delta S \)) and enthalpy barrier (\( \Delta H \)) since \( \Delta G = \Delta H - T \Delta S \). \( R_u \) is the universal gas constant, \( T \) is the temperature and \( n \) represents the order of reaction. Molecular symmetry and the degeneracy of reaction paths are taken into account by introduction of symmetry factor, \( \sigma \), into the rate expression. The units of \( k \) were appropriately determined for each reaction by dividing with a suitable conversion factor depending on the type of reaction for which it was calculated, \( c^{n-1} \). For evaluating
the solution-phase data, here we have adopted the standard state \( c \) of 1 mol L\(^{-1} \). To account for the tunneling effect, Wigner correction factor \([37,40]\) for each reaction was considered as follows:

\[
\Gamma(T) = 1 + \frac{1}{24} \left( \frac{h\nu}{k_BT} \right)^2
\]  

(3)

where \( \nu \) is the imaginary frequency of the transition state. A similar approach for development of condensed-phase chemical reaction mechanism and calculation of kinetic rate constants has been used previously by other research groups \([41, 42]\).

The diffusion rate constant, \( k_{\text{diff}} \) is approximated by \([37, 38, 43, 44]\):

\[
k_{\text{diff}} = 4\pi N R \left( D_A + D_B \right)
\]  

(4)

where \( N, R \) and \( D \) represent, respectively, Avogadro’s number, radius of molecular complex, and diffusion coefficient. Radius, \( R \), is the sum of radius of reactant molecules (\( r_A \) and \( r_B \)) and the diffusion coefficient, \( D \), is calculated using Stokes-Einstein relation \([44]\) assuming spherical particles using:

\[
D = \frac{k_BT}{6\pi \eta r}
\]  

(5)

where \( \eta \) and \( r \) represent, respectively, the viscosity and radius of reactant molecule. Radius of reactant molecules are calculated from Gaussian 09 package \([30]\) using keyword volume. The recommended radius printed in the gaussian output (which is 0.5 Å larger than the radius corresponding to the computed volume) is used as the radius of the molecules. The viscosity, \( \eta \) is the viscosity of glyme, which is 0.2-0.4 mPa-s in the temperature range of 323-368K \([45]\).
2.2.3 Details of numerical simulation

Assuming all reactions to be reversible, the mass fraction of species $i$, $y_i$, is calculated using a mass and species conservation model, which can be arranged into the form:

$$\frac{dy_i}{dt} = \dot{\omega}_i$$ (6)

where $\dot{\omega}_i$ represents the $i$-th species generation rate in terms of mass fraction. $\dot{\omega}_i$ is calculated using rate of reactions ($k$) and the chemical reaction mechanism, which is written in terms of species mass fraction rather than species concentration. In this study, species remain in the condensed-phase due to confinement. The above set of equations are solved using DVODE codes [46] written in Fortran.

Sensitivity analysis is being performed to gain detailed insight into the reaction mechanism. In performing sensitivity analysis, pre-exponential factor ($A_j$) of a reaction is changed by 10%. Since, reactions considered here are all reversible, sensitivity coefficients are calculated for both forward and backward reaction separately. Sensitivity coefficients are then calculated for AB, $H_2$, DADB, $BH_2NH_2$, CDB, BCDB, CTB and borazine as follows [42]

$$S_{ij} = \frac{A_j}{y_i} \frac{\Delta y_i}{\Delta A_j}$$ (7)

where $S_{ij}$, $\Delta A_j$ and $\Delta y_i$ represent, respectively, the sensitivity coefficient, change in pre-exponential factor of reaction $j$ and change in mass-fraction of species $i$. Based on results from sensitivity analysis coupled with experimental data and Gibbs free energy of activations, reaction pathways are identified for above mentioned species.
2.3 Results and discussion

Herein we aim to analyze the initial decomposition behavior of AB in glyme by explaining the formation of several chemical species, including H₂, DADB, CDB, BCDB, CTB and borazine, which are observed during experiment by several groups [6,29]. Reactions are formulated using experimental and theoretical results available in literature as a guide [13,47–54], and they include unimolecular decompositions, bimolecular, ion recombination and isomeric rearrangement reactions consisting of 21 reversible reactions and 19 species. During the decomposition of AB, it is believed that BH₃ could be produced by bond cleavage of B-N bond in AB [13,55,56], as well as from many other reactions. Since BH₃ is a very reactive species lacking a full octet, it can readily accept a pair of electrons and can bind easily to glyme, which is a Lewis base [6]. To account for this effect, all reactions that would involve BH₃ as a reactant or product are neglected in the mechanism. Figure 2.1 shows the molecular structures of intermediates and rings, which are included in the developed reaction mechanism provided in Table 2.1. As mentioned in the previous section, sensitivity analysis is preformed to gain detailed insight into the mechanism, and it also helps to identify the rate-determining steps. The details of the sensitivity analysis are provided in Figs. 2.2 and 2.3 for a temperature of T=368K and initial concentration of AB in glyme, [AB]₀=1M. Figure 2.2 shows the sensitivity coefficients of the three most sensitive reactions for consumption of AB and formation of H₂, DADB and CDB. Figure 2.3 shows the sensitivity coefficients of the three most sensitive reactions for formation of BCDB, BH₂NH₂, borazine and CTB. It is to be noted that since the sensitivity coefficient of a reaction changes over time, the relative roles of the sensitive reactions for a given species may also change with time. For example, during the initial period of AB decomposition, the three most sensitive reactions for H₂ are R3, R9 and R4. However,
as time increases, the sensitivity of reaction $R_4$ decreases significantly and simultaneously, the sensitivity coefficient of $R_{17\_bwd}$ increases sharply with time. Thus, for $t > 25$ min, the three most sensitive reactions for $H_2$ release are $R_3$, $R_9$ and $R_{17\_bwd}$. However, for intermediates such as DADB, CDB and BCDB, one is primarily interested when the specific intermediate species attain a peak value. Furthermore, it has been observed that $BH_2NH_2$ plays a critical role during the AB decomposition in glyme and its behavior will be further discussed in detail in subsequent sections. Hence, sensitivity analysis result for $BH_2NH_2$ is also provided in Fig. 2.3. Based on sensitivity analysis results and the Gibbs free energy of activations, dominant pathways are identified for all the above-mentioned chemical species; these pathways are discussed in detail in the following subsections. We describe in Section 2.3.2.1 pathways involved during the initiation of AB decomposition in glyme. In this section comparison between experimental and QM calculations regarding the rate of decomposition of AB at different temperatures is also provided. In the following Sections 2.3.2.2 and 2.3.2.3, pathways for the formation of species observed during experiment such as $H_2$, DADB, CDB, BCDB, CTB and borazine are discussed in detail.
Figure 2.1 Molecular structures of intermediates and rings formed in the system.
Figure 2.2 Results from sensitivity calculations showing critical reactions to the consumption of AB, formation of H₂, DADB and CDB for initial concentration of AB in glyme solution [AB]₀=1M at T=368K. Naming convention: Rᵢ represents the i-th forward reaction and Rᵢ_bwd represents the i-th backward reaction.
From Table 2.1, it is observed that based on QM calculations, three possible initiation steps are identified through which AB can decompose: \( R_1 \), \( R_2 \) and \( R_3 \). For unimolecular reaction \( R_1 \), the enthalpy \( (\Delta H_R) \) and free of energy \( (\Delta G_R) \) of reaction are 159 and 112.3 kJ/mol, respectively, which

2.3.1 Initiation of AB decomposition in glyme solution

Figure 2.3 Results from sensitivity calculations showing critical reactions to the formation of BCDB, \( \text{BH}_2\text{NH}_2 \), borazine and CTB for initial concentration of AB in glyme solution \( [\text{AB}]_0 = 1 \text{M} \) at \( T=368 \text{K} \). Naming convention: \( R_i \) represents the \( i \)-th forward reaction and \( R_i_{\text{bwd}} \) represents the \( i \)-th backward reaction.
signifies that R1 is a highly endothermic reaction. Furthermore, reaction R1 does not have a distinct TS. For such an endothermic bond-breaking process, the barrier is more accurately represented by the enthalpy of reaction ($\Delta H_a$) and is therefore used in R1; since this value is quite large, this reaction is not important for our considered temperature range. Therefore, from Table 2.1, it is evident that among the newly found initiation steps, R3 is the most kinetically favored reaction for AB decomposition since it has the lowest free energy barrier. Sensitivity analysis provided in Fig. 2.2(a) also shows that R3 has the highest sensitivity coefficients among all reactions regarding the decomposition of AB during the entire run period of simulation. Furthermore, Figs. 2.2 and 2.3 also show that the initiation step R3 is one of the most sensitive reactions for critical species such as $H_2$, DADB, $BH_2NH_2$ and CTB. This not only signifies the pivotal role played by the reaction R3 during the thermal decomposition of AB in glyme solution, but also places an emphasis on the fact that the output from the developed reaction mechanism is highly sensitive towards the energy barrier of reaction R3. Thus, we have calculated thermodynamic parameters, such as enthalpy and Gibbs free energy barriers of reaction R3 using different methods and basis sets which will provide us an estimation of variation involved in calculated thermodynamic parameters of R3. Here, B3LYP (Becke, 3-parameter, Lee-Yang-Parr), M05-2X (first family of Minnesota functionals) and ωB97X-D are DFT methods. B3LYP uses a hybrid functional to calculate the exchange and correlation energy terms [57,58]. M05-2X is a hybrid meta DFT method which uses approximate exchange-correlation energy functionals based on meta-GGA approximation [59]. ωB97X-D uses long-range-corrected functionals including dispersion [60]. MP2 is one of the post-Hartree–Fock ab initio methods which uses perturbation theory to improve on the Hartree-Fock methods by incorporating electron correlation effects [61]. Other than G4(MP2), which is a compound method involving several pre-defined calculations [33], each of the above mentioned methods are used along with two basis-sets, 6-311++G(d,p) and cc-pVTZ. 6-311++G(d,p) is Pople’s split-valence
triple-zeta basis set including diffuse functions for both hydrogen and non-hydrogen atoms along with d polarization functions on non-hydrogen atoms plus p polarization functions for hydrogen. cc-pVTZ is correlation-consistent triple-zeta basis set developed by Dunning and coworkers [62]. Compared to 6-311++G(d,p), cc-pVTZ basis set uses more functions per atom, hence is a much larger basis set relative to 6-311++G(d,p). Table 2.2 shows the results from the calculations using the previously mentioned levels of theory with the SMD solvation model and acetonitrile as solvent. An inspection of Table 2.2 reveals that the results differ by about 8-10 kJ/mol, which is relatively small and is not surprising since neutral species are involved.

Furthermore, we have also studied the impact of various solvents and solvation models on the calculation of barriers of reaction R3. Table 2.3 shows the results from calculations using the G4(MP2) compound method with different solvation models and solvents (both protic and aprotic) covering a wide range of dielectric constants and dipole moments. Two observations are made from an inspection of Table 2.3. First, changing the solvent for the SMD solvation model does not affect the results to a significant extent. Second, the SMD model predicts forward barriers that are quite different than the predictions from using the IEFPCM [63] and the CPCM [64, 65] solvation models. It is evident from the results in Tables 2.2 and 2.3 that the choice of theory and solvent does not significantly impact the results. Similar observations were also made previously by Kumbhakarna et al. [66] and Liu et al. [67]. However, it can be observed from the Table 2.3 that unlike solvents, solvation model has much greater impact on the calculation. In addition, we have also accessed the impact of hindered rotor corrections due to low frequency modes caused by internal rotations. Using B3LYP/6311++G(d,p) level of theory and the SMD/acetonitrile solvation model, it has been observed that the forward and backward free energy barriers of R3 change from 143.5 and 63.2 to 151.1 and 70.9 kJ/mol, respectively which is only ~8 kJ/mol or 2 kcal/mol change.
We also include results for an Arrhenius activation energy $E_{a,f}$, which is related to enthalpy barrier by [37]:

$$E_{a,f} = \Delta H_f + R_uT$$

Here we have assumed that the activation volume for a reaction in a solution phase is negligibly small. Such Arrhenius-type activation energy is the barrier one would determine from experimental data. If $T=400K$, then the difference is only 3.3 kJ/mol between the Arrhenius activation energy and the enthalpy barrier, as shown in Table 2.2.

From experiments [6], it has been observed that the experimentally determined activation energy of the initial step of AB decomposition is ~113 kJ/mol which matches closely with the activation energy calculated using the different levels of theory and solvents used along with SMD solvation model. Hence, the forward barrier of initiation step R3 is approximated as ~113 kJ/mol, in order to obtain an improved temperature dependence of the reaction rates, and the frequency of the transition state structure of R3 calculated using G4MP2 and SMD solvation model is ~331 cm$^{-1}$. The molecular structure of transition state and the complex, BH$_4$BH$_2$NH$_3$ formed during reaction R3 is provided below in Fig. 2.4. As can be observed from Fig. 2.4 (a) which shows the TS of reaction R3, the B-N bond length of one AB molecule increases by 1 Angstrom and one B-H bond of undissociated AB molecule is stretched towards dissociated BH$_3$ to form a shared H bond in the complex, BH$_4$BH$_2$NH$_3$.

Figure 2.5 shows a comparison between experimental data from Shaw et al. [26] with our QM calculations. It must be noted that in the comparison between experimental data and predictions in Fig. 2.5, even a small change of $\pm 2K$ ($\pm 0.57\%$) in the assumed temperature has a significant impact on the rate of AB decomposition at higher temperatures (353-368K). Furthermore, our model does not account for any non-isothermal effects, such as those that must occur when the sample
container’s initial temperature is increased to its final temperature. Since no uncertainty in
temperature measurements was provided by Shaw et al. [29], we use the temperature as indicated
in the experiments and make no attempt to alter the set temperature to match the data exactly. From
Fig. 2.5, it is evident that the results from QM calculations using TST theory can be incorporated
in a species conservation model to capture the observed second-order decomposition kinetics of
AB in glyme.

Table 2.1 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and
backward ($b$) direction (kJ/mol) of all the reactions involved in the developed reaction mechanism
for initial decomposition of AB decomposition in glyme.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta G_f$</th>
<th>$\Delta G_b$</th>
<th>$\Delta H_f$</th>
<th>$\Delta H_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>AB$\leftrightarrow$BH$_3$+NH$_3$</td>
<td>112.3</td>
<td>0.0</td>
<td>159.0</td>
<td>0.0</td>
</tr>
<tr>
<td>R2</td>
<td>AB$\leftrightarrow$BH$_2$NH$_2$+H$_2$</td>
<td>199.6</td>
<td>211.7</td>
<td>199.6</td>
<td>177.0</td>
</tr>
<tr>
<td>R3</td>
<td>2AB$\leftrightarrow$BH$_4$BH$_2$NH$_3$+NH$_3$</td>
<td>143.5</td>
<td>62.8</td>
<td>113.4</td>
<td>30.1</td>
</tr>
<tr>
<td>R4</td>
<td>BH$_4$BH$_2$NH$_3$+NH$_3$$\leftrightarrow$BH$_2$NH$_2$+[BH$_4$][NH$_4$]$^+$</td>
<td>58.2</td>
<td>66.1</td>
<td>17.6</td>
<td>15.9</td>
</tr>
<tr>
<td>R5</td>
<td>BH$_4$BH$_2$NH$_3$+NH$_3$$\leftrightarrow$DADB</td>
<td>83.7</td>
<td>131.8</td>
<td>46.9</td>
<td>136.4</td>
</tr>
<tr>
<td>R6</td>
<td>[BH$_4$][NH$_4$]$^+$$\leftrightarrow$AB+H$_2$</td>
<td>82.4</td>
<td>166.9</td>
<td>101.3</td>
<td>164.0</td>
</tr>
<tr>
<td>R7</td>
<td>BH$_2$NH$_2$+NH$_3$$\leftrightarrow$NH$_3$BH$_2$NH$_2$</td>
<td>41.0</td>
<td>29.3</td>
<td>4.2</td>
<td>39.3</td>
</tr>
<tr>
<td>R8</td>
<td>NH$_3$BH$_2$NH$_2$+[BH$_4$][NH$_4$]$^+$ $\leftrightarrow$ DADB+NH$_3$</td>
<td>0.0</td>
<td>51.0</td>
<td>0.0</td>
<td>56.5</td>
</tr>
<tr>
<td>R9</td>
<td>NH$_3$BH$_2$NH$_2$+ BH$_4$BH$_2$NH$_3$$\leftrightarrow$DADB+BH$_2$NH$_2$</td>
<td>31.4</td>
<td>90.0</td>
<td>-14.6</td>
<td>39.7</td>
</tr>
<tr>
<td>R10</td>
<td>BH$_2$NH$_2$+BH$_2$NH$_2$$\leftrightarrow$CDB</td>
<td>90.0</td>
<td>113.4</td>
<td>41.4</td>
<td>117.6</td>
</tr>
<tr>
<td>R11</td>
<td>BH$_2$NH$_2$+BH$_2$NH$_2$$\leftrightarrow$BH$_3$NH$_2$BHNH$_2$</td>
<td>79.9</td>
<td>96.2</td>
<td>32.2</td>
<td>95.4</td>
</tr>
<tr>
<td>R12</td>
<td>BH$_3$NH$_2$BHNH$_2$+BH$_2$NH$_2$$\leftrightarrow$BCDB</td>
<td>85.5</td>
<td>113.0</td>
<td>35.1</td>
<td>120.1</td>
</tr>
<tr>
<td>R13</td>
<td>BH$_3$NH$_2$BHNH$_2$+BH$_2$NH$_2$$\leftrightarrow$trans-BH$_2$NHBHNH$_2$+AB</td>
<td>82.8</td>
<td>107.1</td>
<td>31.4</td>
<td>56.9</td>
</tr>
<tr>
<td>R14</td>
<td>2BH$_3$NH$_2$BHNH$_2$$\leftrightarrow$trans-BH$_2$NHBHNH$_2$+BH$_3$NH$_2$BH$_2$NH$_3$</td>
<td>90.7</td>
<td>110.1</td>
<td>36.6</td>
<td>59.4</td>
</tr>
<tr>
<td>R15</td>
<td>trans-BH$_2$NHBHNH$_2$$\leftrightarrow$cis-BH$_2$NHBHNH$_2$</td>
<td>34.3</td>
<td>30.5</td>
<td>32.2</td>
<td>27.6</td>
</tr>
<tr>
<td>R16</td>
<td>cis-BH$_2$NHBHNH$_2$+BH$_2$NH$_2$$\leftrightarrow$INT1</td>
<td>68.2</td>
<td>100.0</td>
<td>18.0</td>
<td>110.0</td>
</tr>
</tbody>
</table>
Table 2.2 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction, as well as forward Arrhenius activation energy $E_{a,f}$ (kJ/mol, $T=400$K) of initiation step $R3$: $2\text{AB} \leftrightarrow \text{BH}_4\text{BH}_2\text{NH}_3+\text{NH}_3$ using different levels of theory with the SMD solvation model and acetonitrile as the solvent.

<table>
<thead>
<tr>
<th>QM Level of Theory</th>
<th>$\Delta G_f$</th>
<th>$\Delta G_b$</th>
<th>$\Delta H_f$</th>
<th>$\Delta H_b$</th>
<th>$E_{a,f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4(MP2)</td>
<td>143.5</td>
<td>63.2</td>
<td>113.4</td>
<td>30.1</td>
<td>116.7</td>
</tr>
<tr>
<td>B3LYP/6-311++G(d,p)</td>
<td>143.1</td>
<td>62.8</td>
<td>111.3</td>
<td>28.0</td>
<td>114.6</td>
</tr>
<tr>
<td>B3LYP/cc-pVTZ</td>
<td>143.9</td>
<td>63.6</td>
<td>112.5</td>
<td>29.3</td>
<td>115.9</td>
</tr>
<tr>
<td>M05-2X/6-311++G(d,p)</td>
<td>134.3</td>
<td>55.6</td>
<td>102.5</td>
<td>22.6</td>
<td>105.9</td>
</tr>
<tr>
<td>M05-2X/cc-pVTZ</td>
<td>134.7</td>
<td>50.2</td>
<td>104.2</td>
<td>18.0</td>
<td>107.5</td>
</tr>
<tr>
<td>oB97X-D/6-311++G(d,p)</td>
<td>138.1</td>
<td>56.9</td>
<td>107.5</td>
<td>24.3</td>
<td>110.9</td>
</tr>
<tr>
<td>oB97X-D/cc-pVTZ</td>
<td>140.2</td>
<td>57.7</td>
<td>109.6</td>
<td>25.5</td>
<td>113.0</td>
</tr>
<tr>
<td>MP2/6-311++G(d,p)</td>
<td>149.0</td>
<td>63.6</td>
<td>116.3</td>
<td>29.3</td>
<td>119.7</td>
</tr>
<tr>
<td>MP2/cc-pVTZ</td>
<td>150.2</td>
<td>59.8</td>
<td>116.3</td>
<td>24.3</td>
<td>119.7</td>
</tr>
</tbody>
</table>

Table 2.3 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction, as well as forward Arrhenius activation energy $E_{a,f}$ (kJ/mol, $T=400$K) of initiation step $R3$: $2\text{AB} \leftrightarrow \text{BH}_4\text{BH}_2\text{NH}_3+\text{NH}_3$ using different solvents and solvation models. The G4(MP2) compound method is used.

<table>
<thead>
<tr>
<th>Solvation model</th>
<th>Solvent</th>
<th>Type of solvent</th>
<th>Dielectric constant</th>
<th>$\Delta G_f$</th>
<th>$\Delta G_b$</th>
<th>$\Delta H_f$</th>
<th>$\Delta H_b$</th>
<th>$E_{a,f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMD</td>
<td>Acetonitrile</td>
<td>aprotic</td>
<td>37.5</td>
<td>143.5</td>
<td>63.2</td>
<td>113.4</td>
<td>30.1</td>
<td>116.7</td>
</tr>
<tr>
<td>SMD</td>
<td>THF</td>
<td>aprotic</td>
<td>7.5</td>
<td>134.7</td>
<td>61.0</td>
<td>104.5</td>
<td>26.9</td>
<td>107.9</td>
</tr>
<tr>
<td>Method</td>
<td>Solvent</td>
<td>Type</td>
<td>Index</td>
<td>C1-C2</td>
<td>C1-C3</td>
<td>C1-C4</td>
<td>C1-C5</td>
<td>C1-C6</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>---------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>SMD</td>
<td>Water</td>
<td>protic</td>
<td>80</td>
<td>145.9</td>
<td>69.1</td>
<td>112.1</td>
<td>32.9</td>
<td>115.4</td>
</tr>
<tr>
<td>SMD</td>
<td>Acetone</td>
<td>aprotic</td>
<td>21</td>
<td>143.0</td>
<td>63.9</td>
<td>111.7</td>
<td>29.5</td>
<td>115.1</td>
</tr>
<tr>
<td>SMD</td>
<td>Methanol</td>
<td>protic</td>
<td>33</td>
<td>144.5</td>
<td>64.3</td>
<td>113.3</td>
<td>30.1</td>
<td>116.6</td>
</tr>
<tr>
<td>SMD</td>
<td>Ethanol</td>
<td>protic</td>
<td>24.6</td>
<td>143.8</td>
<td>64.1</td>
<td>112.5</td>
<td>29.8</td>
<td>115.8</td>
</tr>
<tr>
<td>SMD</td>
<td>Nitro-methane</td>
<td>aprotic</td>
<td>35.9</td>
<td>145.0</td>
<td>64.5</td>
<td>112.9</td>
<td>29.6</td>
<td>116.3</td>
</tr>
<tr>
<td>SMD</td>
<td>DMSO</td>
<td>aprotic</td>
<td>46.7</td>
<td>145.5</td>
<td>64.7</td>
<td>113.1</td>
<td>29.5</td>
<td>116.5</td>
</tr>
<tr>
<td>IEFPCM</td>
<td>Acetonitrile</td>
<td>aprotic</td>
<td>37.5</td>
<td>126.6</td>
<td>60.4</td>
<td>98.8</td>
<td>29.0</td>
<td>102.2</td>
</tr>
<tr>
<td>CPCM</td>
<td>Acetonitrile</td>
<td>aprotic</td>
<td>37.5</td>
<td>126.9</td>
<td>60.6</td>
<td>99.1</td>
<td>29.2</td>
<td>102.4</td>
</tr>
</tbody>
</table>

![Molecular structure](image)

(a) TS of reaction R3
(b) BH₄BH₂NH₃

Figure 2.4 Molecular structure of transition state of reaction R3 and complex, BH₄BH₂NH₃.
(Distances between atoms are in Angstrom)
2.3.2 Formation of DADB and H₂

Hydrogen and DADB are formed very early during the process of AB decomposition in glyme. Here, important reactions are identified through which DADB and hydrogen are formed. These reactions are R4 through R9, as well as R18 in Table 2.1. QM calculations also identified other reactions through which H₂ can be released as well. However, those reactions do not play a significant role in formation of hydrogen since Gibbs free energies of activation in forward direction (ΔGᵢ) are too high; they are not included in Table 2.1.

From Table 2.1, it is observed that the products formed (BH₄NH₂NH₃ and NH₃) via initiation step R3 can undergo two possible reactions R4 and R5. Through R4, BH₂NH₂ and [BH₄][NH₄]⁺
are formed. The formed BH$_2$NH$_2$ further reacts with NH$_3$ via R7 to produce NH$_3$BH$_2$NH$_2$ which reacts further with BH$_4$BH$_2$NH$_3$ and [BH$_4$][NH$_4$]$^+$ to form DADB whereas through R5, DADB is directly formed. Since the forward barrier of R5 is higher than R4, R4 is more dominant or kinetically favored reaction. Thus, it is evident that the reaction pathway for DADB formation involves reactions R3, R4, R7, R8 and R9. However, it is to be noted that the backward free energy barrier of reaction R8 is quite low. As a result, DADB formed via R8 and R9 is then consumed rapidly via the reverse reaction of R8. Hence, reaction R9 is more dominant regarding formation of DADB during the initial decomposition of AB in glyme. The results of the sensitivity analysis shown in Fig. 2.2(c) also identify R9 as the most sensitive reaction for DADB formation. It is noteworthy that the forward barrier of reactions involved in the formation of DADB are relatively low (less than 42 kJ/mol), which suggests that diffusion effects become important in the formation of DADB. Figure 2.6 shows the normalized mass fractions of DADB and AB with time. Here, mass fraction of species AB and DADB are scaled with respect to initial mass fraction of AB, $y_{AB,0} = 0.036$ for [AB]$_0$=1M in glyme solution. From the Fig. 2.6, it is evident that mass fraction of DADB reaches a maximum very early. Also from NMR spectroscopic studies, DADB is detected very early which leads to the conclusion that AB decomposes rapidly to form DADB [6,29]. This QM-based study shows that rather than formed during an initiation step, DADB is possibly formed during subsequent reactions involving BH$_4$BH$_2$NH$_3$, BH$_2$NH$_2$ and NH$_3$ even though it is possible that DADB is the first species to be detected during NMR spectroscopic studies [6,29].
From Table 2.1, it can also be observed that there are two reactions releasing H$_2$, namely R6 and R18. The forward barrier of R18 is higher than R17 by ~42 kJ/mol. Hence, R18 does not play a significant role in the formation of hydrogen during AB decomposition. Thus, it is evident that reaction R6 is the only dominant hydrogen producing reaction which in the process regenerates AB as well. However, depending on the source of [BH$_4$][NH$_4$]$^+$, two major pathways are identified through which H$_2$ can be formed: **Pathway 1** involves reactions R3, R4, R6 and **Pathway 2** involves reactions R3, R4, R6, R7, R8, R9. In Pathway 1, [BH$_4$][NH$_4$]$^+$ is formed directly from BH$_4$BH$_2$NH$_3$ via R4, whereas in Pathway 2, [BH$_4$][NH$_4$]$^+$ is formed via reverse reaction of R8 from decomposition of DADB. The results from sensitivity analysis of H$_2$ shown in Fig. 1.2(b) also identify R3, R4 and R9 as the most sensitive reactions regarding formation of H$_2$. Furthermore, it is to be noted that if DADB is added to the system, the induction period of [BH$_4$][NH$_4$]$^+$ formation through **Pathway 2** is reduced, which leads to accelerated hydrogen release. A similar observation
was made by Heldebrant et al. [26] and Mayer [27] during their experiments, where they observed that the induction period for hydrogen release reduced with the addition of DADB. Thus, QM calculations validate that DADB plays a critical role in the formation of hydrogen during initial phase of AB decomposition. However, along with *Pathway 2* QM calculations also identify another pathway for hydrogen release involving reactions $\textbf{R3, R4}$ and $\textbf{R6}$ (*Pathway 1*). Thus, from QM calculations it can be concluded that $\text{H}_2$ can also possibly be formed in reaction pathways which do not involve DADB decomposition. Furthermore, it is also evident that along with DADB, another intermediate species $[\text{BH}_4][\text{NH}_4]^+$ also plays a significant role in the formation of hydrogen from AB in glyme solution. The potential energy surface for two pathways of $\text{H}_2$ formation is provided below in Fig. 2.7. In this figure, species name enclosed in parentheses represents one of the products of the preceding reaction; however, it does not become a reactant in the subsequent reaction. For instance in reaction $\textbf{R9}$, $\text{NH}_3\text{BH}_2\text{NH}_2$ and $\text{BH}_4\text{BH}_2\text{NH}_3$ react to form DADB and $\text{BH}_2\text{NH}_2$. However, in the subsequent reaction $\textbf{R8}$, only one of the products formed via $\textbf{R9}$, which is DADB, react with $\text{NH}_3$ to form $[\text{BH}_4][\text{NH}_4]^+$ and $\text{NH}_3\text{BH}_2\text{NH}_2$. From Fig. 2.7, it can be observed that the process of $\text{H}_2$ release during the initial phase of AB decomposition in glyme is exothermic. Figure 2.8 shows the evolution of $\text{H}_2$ for an initial concentration of AB in glyme solution $[\text{AB}]_0=1\text{M}$. From the figure, it is observed that for temperatures ranging from 333-368K, approximately 6-6.5% of hydrogen by weight is formed during isothermal decomposition of AB in glyme, although the rate of hydrogen release is slower at lower temperature due to slower kinetics. The similar trend of $\text{H}_2$ release from AB in glyme is observed by Al-Kukhun et al. as well [6].
Figure 2.7 Potential energy surface for two pathways of $\text{H}_2$ formation based on QM calculations.

Figure 2.8 Hydrogen release from AB at different temperatures below 373K ($[\text{AB}]_0=1\text{M}$).
2.3.3 Formation of CDB, BCDB, CTB and Borazine

From previous sections, it can be concluded that the initiation of AB decomposition starts via \( \text{R3} \). The products (\( \text{BH}_4\text{BH}_2\text{NH}_3 \) and \( \text{NH}_3 \)) formed undergo bimolecular reaction \( \text{R4} \) to produce \( \text{BH}_2\text{NH}_2 \) and \( [\text{BH}_4][\text{NH}_4]^+ \), the latter of which decomposes via \( \text{R6} \) to produce \( \text{H}_2 \). \( \text{R3} \) and \( \text{R4} \) are the primary sources of intermediate species, \( \text{BH}_4\text{BH}_2\text{NH}_3 \) and \( \text{BH}_2\text{NH}_2 \), respectively. \( \text{BH}_2\text{NH}_2 \) formed through \( \text{R4} \) then undergoes series of reactions to produce DADB. Along with DADB, other species observed during experiment are CDB, BCDB, CTB and borazine [6,29]. The important reactions leading to the formation of these four species are \( \text{R10} \) through \( \text{R19} \) in Table 2.1. Figure 2.9 shows the detailed reaction network explaining the formation of these four species and \( \text{H}_2 \) during initial phase of AB decomposition.

From Table 2.1 and Fig. 2.9, it is observed that \( \text{BH}_2\text{NH}_2 \), which forms via \( \text{R4} \), can participate in 3 competitive reactions: 1) \( \text{R10} \) producing CDB, 2) \( \text{R7} \) producing \( \text{NH}_3\text{BH}_2\text{NH}_2 \) which is critical in the formation of DADB and 3) \( \text{R11} \) producing \( \text{BH}_3\text{NH}_2\text{BHNNH}_2 \). \( \text{BH}_3\text{NH}_2\text{BHNNH}_2 \) then undergoes three competing reactions: \( \text{R12}, \text{R13} \) and \( \text{R14} \). \( \text{R12} \) produces BCDB and \( \text{R13} \) and \( \text{R14} \) produces trans-\( \text{BH}_2\text{NHBNHNNH}_2 \). However, the forward free energy barrier of reaction \( \text{R14} \) is higher than that of \( \text{R13} \), hence \( \text{R13} \) plays a dominant role in the formation of trans-\( \text{BH}_2\text{NHBNHNNH}_2 \). trans-\( \text{BH}_2\text{NHBNHNNH}_2 \) thus formed quickly undergoes transformation to its cis form via \( \text{R15} \) and then further participates in a series of reactions to produce CTB and borazine in competitive pathways. Figure 2.10 below shows the potential energy surface for DADB, CDB, BCDB, CTB and borazine. Similar to Fig. 2.7, species name enclosed in parentheses represents one of the products of preceding reaction; however, it does not contribute as reactant in the subsequent reaction.
Figure 2.9 Reaction network for AB decomposition in glyme solution. Here, the use of a solid thick line, ----, indicates a dominant pathway and dashed, - - - - - , indicates a minor pathway.
It is noteworthy from the above reaction network and the Gibbs free energy potential energy surface that contrary to the conclusion made in previous studies [9,10], QM calculations suggest that DADB, CDB and BCDB can possibly formed via competitive pathways involving BH$_2$NH$_2$. Furthermore, it is also observed that for both CTB and borazine formation, the key species is INT1 which is formed from reactions involving BH$_2$NBHNNH$_2$ and BH$_2$NH$_2$. INT1 then takes part in competitive reactions, R17 and R18 producing CTB and borazine, respectively, which leads to the conclusion that borazine might not be formed from CTB or BCDB. Rather CTB and borazine are possibly formed in competitive pathways involving BH$_2$NH$_2$ as the key species. Thus, from the above discussion, it is evident that QM calculations suggest BH$_2$NH$_2$ as a critical intermediate required in the formation of species observed in experiments.
Figures 2.11 and 2.12 show the evolution of BH$_2$NH$_2$, CDB, BCDB, CTB and borazine at temperatures of 368K and 348K for 1 mol of initial concentration of AB in glyme solution. In the figures, mass fractions of species ($y_i$) are scaled with respect to initial mass fraction of AB, $y_{AB,0} = 0.036$ for [AB]$_0$=1M. It can be observed that at both temperatures, trend of species evolution is very similar. In both cases similar to DADB, BH$_2$NH$_2$ forms very early and is very short-lived owing to its high reactivity. As BH$_2$NH$_2$ is consumed, concentration of species like CDB, BCDB, CTB and borazine continues to increase. However, it is to be noted that at the lower temperature of $T$=348K, due to slower chemical kinetics, CDB and BCDB peaks at much later time compared to the case with $T$=368K. It is also noted that for $T$=368K, the mass fraction of the intermediate species CDB and BCDB peak approximately at 10 mins, whereas for $T$=348K the peak occurs after ~50-60 mins. The similar observation was made by Al-Kukhun et al. [6] as well during NMR spectroscopy. Another important observation made by Al-Kukhun et al. [6] and Shaw et al. [29] regarding the initial decomposition of AB in glyme is the sequence of species appearance during NMR spectroscopy. Both of these research groups observed that after DADB, CDB appears which is followed by BCDB and then finally CTB and borazine. To investigate the sequence of above-mentioned species formation, in Fig. 2.13 mass fraction of above-mentioned species are plotted during the very early stage of AB decomposition in glyme. From the figure, it can be observed that QM calculations also predict the similar sequence of species formation, which provides further validation of the proposed reaction mechanism for initial decomposition of AB in glyme. Hence, from the above discussion it is evident that the results from QM calculations follow the trends observed in experiments conducted made by previous researchers [6,29] and also provide detailed insight into the chemical kinetics involved during the initial phase of AB decomposition in glyme, which is otherwise not obtainable only by performing experiments.
Figure 2.11 Variation of mass fraction of BH$_2$NH$_2$ and AB with time for initial concentration of AB in glyme solution [AB]$_0$=1M at $T$=348K and 368K.

Figure 2.12 Variation of mass fraction of BH$_2$NH$_2$, CDB, BCDB, CTB and borazine with time for initial concentration of AB in glyme solution [AB]$_0$=1M at $T$=348K and 368K.
Using QM calculations, various initiation steps are proposed, among which the most dominant pathway during lower reaction temperature of 323-368K is identified. The results from this study capture the second-order decomposition kinetics of AB observed in previous experiments [6,29]. Contrary to the previous belief that AB initiates decomposition by forming DADB [6,11,29], the results from this study suggest that the initiation step possibly involves formation of BH$_4$BH$_2$NH$_3$ and NH$_3$, which react further with BH$_2$NH$_2$ to form DADB. Based on comparisons with experimental results from literature, QM calculations enable an improved understanding of the initiation step of AB dehydrogenation and possible pathways of DADB formation.

Furthermore, QM calculations validate the common belief that DADB is a key intermediate required in the formation of hydrogen during AB decomposition. It is also concluded that in addition to DADB, another key intermediate required in the formation of H$_2$ is an ionic species, [BH$_4$][NH$_4$]$^+$. In addition, QM calculations predict that under isothermal conditions, AB in glyme
releases approximately 6-6.5% of hydrogen by weight during the lower reaction temperature ranging from 323-368K, which is in close agreement with the experimental observations [29]. Reaction pathways which explain the formation of species observed in previous experiments are also provided. These pathways show that DADB, CDB, BCDB, CTB and borazine are formed via several competing reactions involving BH$_2$NH$_2$ as the key intermediate species.

2.5 References


[8] C. W. Hamilton, R. T. Baker, A. Staubitz, and I. Manners, “B-N compounds for chemical


[50] V. S. Nguyen, M. H. Matus, D. J. Grant, M. T. Nguyen, and D. A. Dixon, “Computational study of the release of H₂ from ammonia borane dimer (BH₃NH₃)₂ and its ion pair isomers,”


[59] Y. Zhao, N. E. Schultz, and D. G. Truhlar, “Design of density functionals by combining the


monomethylhydrazine with mixtures of NO$_2$ and N$_2$O$_4$;"*Combust. Flame*, vol. 160, no. 5, pp. 970-981, 2013.
Chapter 3

DEVELOPMENT AND VALIDATION OF DETAILED REACTION MECHANISM FOR LIQUID-PHASE DECOMPOSITION OF AMMONIA BORANE

3.1 Introduction

Hydrogen is a clean alternate fuel that produces water as the only oxidation product. However, hydrogen is very difficult to store, especially in transportation systems, which leads researchers to focus on hydrogen-containing materials, such as chemical hydrides, which have high density of hydrogen content [1-3]. In recent years, ammonia borane, BH$_3$NH$_3$ (AB) has gained significant attention as a potential hydrogen storage medium. AB contains 19.6% of H$_2$ by weight, which corresponds to a significantly high volumetric (146 g H$_2$ per liter) and gravimetric (194 g H$_2$ per kilogram) density of hydrogen. The process of hydrogen release from AB is exothermic and kinetically controlled, which indicates that the presence of a catalyst can significantly accelerate the hydrogen release rate [4-8]. Using chemical additives or solvent, AB can be used to release hydrogen at temperatures below 373K [9-12]. Furthermore, previous studies have shown that other than being a hydrogen storage medium, AB can also be used as a rocket fuel for propulsion due to its high hydrogen content [13]. Recently, the hypergolic nature of AB as a rocket fuel has also been reported by several researchers which makes it an attractive candidate to replace existing toxic hypergolic fuels based on hydrazine and its derivatives [14, 15]. Hence, from the above discussion it is evident that AB finds application in several areas such as fuel cells, transportation devices and rocket propulsion.

To understand the chemical kinetics of hydrogen release from and the potential for regeneration of AB, many studies have been undertaken to elucidate the decomposition of AB both in a solid
state as well as in a solution phase [16, 17]. These studies show that in the presence of a solvent, the rate of hydrogen release from AB is enhanced and the intermediates formed are also significantly different compared to a solid state. Thus, it can be concluded that depending on its state, AB decomposition follows different reaction pathways [11, 18–21]. In a previous study [22] which is discussed in Chapter 2, we proposed reaction pathways explaining the chemical kinetics involved during the initial decomposition of AB in a glyme solution. In this work, we focus on the development of a detailed reaction mechanism for liquid-phase decomposition of pure AB.

Over the past few years, significant contributions have been made by several researchers towards improving our understanding the thermal decomposition behavior of AB. Wolf et al. [23] showed that upon heating, solid state AB releases 12% of H$_2$ by weight producing polyaminoborane (PAB) and polyiminoborane (PIB) in the process. It is also observed that H$_2$ is released in two steps, both of which are exothermic. A similar conclusion was also made in one of the early studies by Sit et al. [24]. Based on differential scanning calorimetry (DSC) experiments, Sit et al. [24] further concluded that AB melts before releasing the first equivalent of hydrogen. In the process, it forms BH$_2$NH$_2$. The formed BH$_2$NH$_2$ then polymerizes to form PAB, which decomposes to release second equivalent of hydrogen. Further reactions produce borazine and other species in the process. Similar conclusions were made by Baitalow et al. [19] using thermogravimetric analysis (TGA)/DSC coupled with Fourier transform infrared (FTIR) spectroscopy, mass spectroscopy (MS) and volumetric measurements. Baitalow et al. [19] further observed that the total mass loss of AB is significantly higher than the amount of hydrogen released. From an analysis of data acquired by FTIR spectroscopy, they concluded that BH$_2$NH$_2$, B$_2$H$_6$ and borazine were also present in gaseous phase. However, borazine and B$_2$H$_6$ were observed only in a very small amount. Therefore, they concluded that BH$_2$NH$_2$ is the major species released in addition to hydrogen. Baitalow et al. [19]
further concluded that although amount of H₂ release remains same (14% by weight, i.e., ~2.2 mol/mol of AB) as heating rate increases, release of BH₂NH₂ into the gaseous phase increases significantly leading to higher mass loss of AB. In a recent study by Al-Kukhun et al. [7], they also observed similar gaseous species during TGA/MS experiments using a 1 K/min heating rate. However, they also detected NH₃, which was not observed by Baitalow et al. [19]. In another recent study by Weismiller et al. [13] using heating rates in the range of 1-50 K/min, they also concluded that as heating rate increases so does mass loss of AB. Weismiller et al. [13] also observed several condensed-phase products, composed mainly of PAB and PIB, which corroborates the conclusion made by Sit et al. [24] and Baitalow et al. [19] previously that AB melts during decomposition. Thus, to gain a detailed understanding of the thermal decomposition behavior of AB, one should focus such studies on the chemical kinetics in its condensed phase.

Along with experiments, several computational efforts have also been made to unravel the complex chemical kinetics involved during AB dehydrogenation. Based on quantum chemical calculations, several studies have been undertaken to identify reaction pathways for AB dehydrogenation, especially during the initial phase of decomposition [6,7,25,26]. These computational studies provide information which is not easily accessible from experiments and hence significantly improve our understanding regarding the kinetics involved during the process of H₂ release from AB. However, the above studies are done based on gas-phase calculations. Zimmerman et al. [18] concluded that reaction pathways differ if calculations are done in solution phase. They concluded that in contrast to gas-phase calculations, solution-phase calculations suggest that homolytic B-N cleavage of AB is not favored since the B-N bond is significantly stronger due to solvent interaction with AB’s dipole. Thus, in solution phase the initiation of AB decomposition occurs with the formation of an AB dimer since the barrier of unimolecular decomposition of AB is also significantly higher. Furthermore, they also concluded that
diammoniate of diborane, $[\text{NH}_3\text{BH}_2\text{NH}_3]^+[\text{BH}_4]^-$ (DADB) is not the only pathway through which dehydrogenation of AB takes place. However, in either pathway decomposition products are similar ($\text{BH}_2\text{NH}_2$, $\text{H}_2$, $\text{NH}_3$ and $\text{BH}_3$). They further concluded that $\text{BH}_2\text{NH}_2$ is a key intermediate required to produce experimentally observed species such as borazine. However, the details of the pathway of borazine formation are not discussed in their study. In an experimental and computational investigation, Al-Kukhun et al. [7] proposed an overall reaction mechanism of AB decomposition. Their conclusion regarding the initiation of AB decomposition is very similar to that of solution-phase calculations done by Zimmerman et al. [18]. They further concluded that $\text{BH}_2\text{NH}_2$, DADB, $\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2$ and $\text{BH}_3\text{NH}_2\text{BHNH}_2$ are formed during the initial phase of AB decomposition. The latter two species undergo competing reactions to form acyclic-PAB-like species, which undergo further reactions to form borazine and other heavier molecular weight rings during the second phase of AB decomposition.

It is evident from the preceding discussion that AB decomposition has been extensively studied. However, very few studies have been done to investigate the reaction pathways describing the polymerization and cyclization steps forming PAB and higher molecular weight species, such as ring-containing species which comprise the latter stages of the AB decomposition. Even the overall mechanism proposed by Al-Kukhun et al. [7] does not provide the details of the ring-forming reactions during the latter stages of AB decomposition and additional release of $\text{H}_2$. It is also to be noted that there is no consensus regarding release of $\text{NH}_3$ in gaseous phase during AB decomposition. Although Al-Kukhun et al. [7] observed $\text{NH}_3$ using MS for 1K/min heating rate, they did not quantify the amount of $\text{NH}_3$ released and also did not study the effect of different heating rates on the amount of $\text{NH}_3$ released in gaseous phase. Moreover, although species information from experiments are used to device reaction pathways in QM calculations, validation
of such developed reaction mechanisms is lacking. Validation could include a comparison with experimental data obtained from TGA studies, using species evolution obtained from time-of-flight mass spectrometry (ToF-MS). Such a comparison is essential to confirm the validity of the proposed mechanism. Therefore, it is evident from the above discussion that additional studies are required to understand the details of the thermal decomposition of condensed-phase AB.

Here in this study, we perform TGA/FTIR experiments for different heating rates in the range of 1-20K/min and propose a detailed reaction mechanism of liquid-phase decomposition of AB using QM calculations. The proposed mechanism will provide a comprehensive understanding regarding the initiation of AB decomposition and pathways of H₂ release. Furthermore, the processes of cyclization to form borazine and other ring-containing species during the second phase of AB decomposition are also discussed in detail. In this study using the proposed mechanism, numerical simulations are also performed at different heating rates. The simulated results are compared against the acquired experimental data in order to validate the proposed mechanism.

3.2 Details of experimental studies

We performed thermal analysis of AB decomposition using TGA/DSC combined with FTIR spectroscopy. The TGA/DSC apparatus used in the experiment is an STA449 F5 Jupiter manufactured by NETZSCH, coupled with a Bruker Vertex 80 FTIR spectrometer. The source to and purity of the AB sample used are described in Ref. 13. For each experiment, samples were placed in open lid aluminum crucibles and the amount used that is the initial amount of sample \( m_{\text{sample,0}} \) was approximately 2.5 mg for each test. The sample chamber was purged with N₂. To measure heat flow from the sample, two S-type thermocouples are attached to the sample carrier, which holds both a reference and sample crucible. Prior to each experiment, a baseline
measurement is made to compensate for buoyancy and specific heat effects in the TGA and DSC measurements, respectively. The evolved gases from the TGA apparatus are transferred to an isothermal transmission cell with two ports, and each port has a pair of wedged ZnSe/KBr windows. The modulated beam of the FTIR spectrometer propagates through the cell to allow spectral transmission measurements. The spectral transmittance data are then analyzed following previously used procedures [27].

3.3 Details of numerical simulation and molecular modeling

In order to validate the proposed mechanism, numerical simulations were performed of a model considering mass loss from and chemical reactions within the sample during the TGA experiment. The results predicted by the simulations are compared against experimental data obtained in this work as well as by Weismiller et al. [13] and Baitalow et al. [19]. In order to compare with the experimental data, we considered similar heating rates and amount of AB sample (2.5 mg) as used during experiments. No reactions are assumed to take place in the gas phase among species emanating from the sample. The transfer line and FTIR transmission cell, where gaseous species are collected, are constantly diluted by a purge gas and are maintained at a relatively low temperature of 353 K so that no reactions take place among gaseous species. One of the primary objectives in this simulation is to predict the mass loss of AB sample over time using our proposed condensed-phase reaction mechanism for AB. The predicted mass loss curve is then compared with the experimentally obtained TGA data. The following conservation equations are used to predict the chemical kinetic behavior of condensed-phase AB:

\[
\text{Rate of change of mass of liquid phase (} m_l \text{):}
\]
\[
\frac{dm_l}{dt} = -m_l \sum_{j=1}^{N_l} y_{l,j} k_{\text{evap},j}
\]

Rate of change of mass fraction of \( j \)-th liquid species (\( y_{l,j} \)):

\[
\frac{dy_{l,j}}{dt} = \dot{w}_j - y_{l,j} k_{\text{evap},j} + y_{l,j} \sum_{k=1}^{N_g} y_{l,k} k_{\text{evap},k}, \quad j = 1, \ldots, N_l
\]

where \( m_l, y_{l,j}, k_{\text{evap},j}, \dot{w}_j, N_l \) and \( N_g \) represent the total mass of liquid phase, mass fraction of species \( j \) in liquid phase, rate of evaporation of species \( j \) from liquid to gas phase, rate of generation of species \( j \) due to chemical reactions in liquid phase, total number of species involved in mechanism and total number of species evaporating from liquid to gaseous phase respectively. \( m_l \) and \( y_{l,j} \) are functions of time. The initial conditions of the above variables are as follows: \( m_{l,0} = m_{\text{sample},0} = 0.0025 \text{ g} \); \( y_{AB,0} = 1 \); \( y_{j,0} = 0 \) for all species except AB. Based on experimental observations, we assumed 5 species (\( \text{H}_2, \text{NH}_3, \text{BH}_2\text{NH}_2, \text{B}_2\text{H}_6 \) and borazine) evaporate from liquid to gas phase. The evaporation rate is approximated using the kinetic approach to the evaporation of liquids as follows [28]:

\[
k_{\text{evap},j} = A_j \exp(-E_{a,\text{evap},j} / RT)
\]

where \( A_j \) and \( E_{a,\text{evap},j} \), respectively, represent pre-exponential factor and barrier associated with the evaporation of \( j \)-th species. Using the above kinetic model for evaporation, here in this study we have assigned a specific rate constant \((k_{\text{evap},j}) \) for each species evaporating from liquid to gaseous phase, rather than assuming infinitely fast evaporation which would result in significantly high erroneous mass loss. It has been reported that \( E_{a,\text{evap},j} \) is analogous to the enthalpy of vaporization of the species [28]. Hence, the values of the evaporation rate parameters
are initially chosen in such a way that lower molecular weight species evaporate fast and vice-versa. Thus, while $E_{a,\text{evap},j}$ of gaseous species such as H$_2$ and NH$_3$ is considered to be quite low (~4.2 kJ/mol), borazine has the highest $E_{a,\text{evap},j}$ (~62 kJ/mol) among all the gaseous species observed during experiment [28]. Since the molecular weight of BH$_2$NH$_2$ and B$_2$H$_6$ are in the range of ~30 g/mol, which is higher than H$_2$ and NH$_3$ but much lower than that of borazine, these two species can be assumed to have the value of $E_{a,\text{evap},j}$ between 4.2 and 62 kJ/mol. However, since it is difficult to measure the parameter experimentally, the value of $E_{a,\text{evap},j}$ for BH$_2$NH$_2$ and B$_2$H$_6$ is not well known. Hence, in this study we performed sensitivity studies of $E_{a,\text{evap},j}$ for gaseous species to obtain better match with the experimental data obtained in this study. The average value of $E_{a,\text{evap},j}$ used in our numerical simulation for the temperature range of 373-523K is ~17 kJ/mol for both BH$_2$NH$_2$ and B$_2$H$_6$. The pre-exponential factor, $A_j$ is assumed to be similar for the above-mentioned gaseous species. These assumptions are assessed in Sect. 3.3.

By solving the above-mentioned conservation equations, we obtain a temporal variation of liquid phase mass ($m_l$) which is compared to the evolution of AB sample mass ($m_{\text{sample}}$) during experiments to validate our condensed-phase reaction mechanism. Other than mass loss curve, the IR-active species are revealed in the FTIR spectra. Regarding the FTIR transmission cell, species enter at a certain rate from the TGA with the purge gas and simultaneously leave at a certain rate. In our numerical simulation, this evolution of species in gaseous phase is governed by following conservation equations:

Rate of change of mass fraction of $i$-th gaseous species ($y_{g,i}$):
\[ \frac{dy_{g,i}}{dt} = \frac{m_i y_i, k_{evap,i} - y N_{out} - y_m}{m_g}, \quad i = 1, \ldots, N_g \]

Rate of change of mass fraction of purge gas, \(N_2\) (\(y_{N_2}\)):

\[ \frac{dy_{N_2}}{dt} = \frac{\dot{m}_{N_2} - y_{N_2} \dot{m}_{out} - y_{N_2} \dot{m}_m}{m_g} \]

Rate of change of mass of gaseous phase (\(m_g\)):

\[ \frac{dm_g}{dt} = \sum_{i=1}^{N_g} m_i y_i, k_{evap,i} + \dot{m}_{N_2} - \dot{m}_{out} \]

Rate at which mass leaving the gas-phase control volume (\(\dot{m}_{out}\)):

\[ \dot{m}_{out} = \frac{1}{N_g + N_{out}} \left( \sum_{i=1}^{N_g} \frac{m_i y_i, k_{evap,i}}{W_i} + \frac{\dot{m}_{N_2}}{W_{N_2}} \right) \]

where, \(y_{g,i}, y_{N_2}, \dot{m}_{N_2}, \dot{m}_{out}, m_g\) and \(W_i\) represent the mass fraction of species, \(i\) in gaseous phase, the mass fraction of purge gas (\(N_2\)), the mass flow rate of purge gas, the rate at which mass is leaving the gas-phase control volume, the total mass of gaseous species including purge gas and the molecular weight of species, respectively. The above expression for \(\dot{m}_{out}\) assumes that the number of moles of mixture inside the transmission cell is constant at any given time. The initial conditions of the mass fraction of species in gaseous phase are as follows: \(y_{g,i} = 0\) \((i = 1, \ldots, N_g)\), \(y_{N_2} = 1\). The quantity, \(\dot{m}_{N_2}\) is known from measurements. In our experiment, the volume flow rate of \(N_2\) gas used for purging is 70 ml/min which translates to a mass flow rate of 0.00134 g/s of \(N_2\).
Another important piece of information obtained from experiments [19] is the wt% of H₂ released during AB decomposition which is given by total mass of H₂ released \( (m_{H_2}) \) relative to mass of AB sample used, i.e., wt% of H₂ = \( m_{H_2} / m_{\text{sample,0}} \). In our numerical simulation, \( m_{H_2} \) is calculated by assuming \( \dot{m}_{\text{out}} = 0 \). Hence, in our numerical simulation the total mass of hydrogen accumulated in gas-phase control volume is equivalent to the total amount of H₂ released during experiment. In a similar way using numerical simulation, we also calculated wt% of other species (NH₃, BH₂NH₂, B₂H₆ and borazine) released in gaseous phase which are not easily available from experiments. The above set of equations are solved using DVODE codes [29] written in Fortran. A similar approach has been used previously [30, 31].

Assuming all reactions to be reversible, \( \dot{W}_j \) is calculated based on the rates of reactions and the mass fractions of species involved in the generation and consumption of species \( j \). This information is taken from the developed reaction mechanism. The rates of reactions are calculated using results from QM calculations with the Gaussian program package [32] in a similar way as in Chapter 2 [22]. To identify reaction pathways, density functional theory (DFT) and low-level basis sets were used to search transition states of the reaction. Intrinsic reaction coordinate (IRC) calculations were then performed to link the reactants to the products. Finally, thermodynamic properties such as enthalpy and free energies were computed using G4(MP2) compound method for both the equilibrium species and transition states using SMD solvation model with acetonitrile as the solvent. The effect of solvation model/solvent on calculations is shown in Chapter 2 [22]. It was observed that the choice of solvent does not impact the result significantly. Using various solvent, the differences in energy barriers did not exceed by more than 9 kJ/mol compared to the results obtained by using acetonitrile. Similar observations were also made previously by Kumbhakarna et al. [30] and Liu et al. [33]. However, solvation model did impact the result to a
greater extent. It was noted that the activation energy of initiation step R2 calculated using SMD solvation model with acetonitrile as solvent matches closely with the experimentally determined activation energy of the initial step of AB decomposition in glyme [22], whereas the IEPCM and CPCM underpredict the barrier by about 10.5 kJ/mol. Hence, SMD is our choice for solvation model in this study.

Unlike in Chapter 2 [22], where viscosity was known, here the viscosity of the liquid phase is unknown and changes with time as new species are formed continuously. To account for such changes, we assume that the bulk viscosity can be estimated from computed, individual values of viscosity for AB, BH$_2$NH$_2$ and borazine. To obtain such individual values of viscosity at different temperatures, we used molecular dynamics simulations [34]. The obtained viscosity data are then fitted in the form equivalent to Vogel-Tammann-Fulcher (VTF) equation given by:

$$\eta = A \exp\left[\frac{B}{T - T_{ref}}\right]$$

where $A$ and $B$ are constants. $T_{ref}$ is the reference temperature of 273 K. The bulk viscosity is then calculated based on the weighting of mole fractions of the above-mentioned species. We have also performed calculations of the bulk viscosity with a weighting based on mass fraction, but such a calculation of the viscosity did not seem to significantly impact the simulation results.

### 3.4 Results and Discussion

In order to effectively use QM calculations to elucidate reaction pathways, it is imperative to incorporate results from experiments, in particular results that include temporal variations of species, as well as from previous theoretical calculations. By using such results as a guide [6, 7, 9, 18, 35–40], 63 reactions involving 45 species were formulated. However, many more reactions
and species were identified, but comparison with the experimental results and by performing sensitivity studies, the number of reactions and species were reduced considerably. The details of the reduced mechanism consisting of 63 reactions are listed in Table 3.1 below. The molecular structures of intermediates and ring structures formed during decomposition are shown in Fig. 3.1.

Based on the developed mechanism, we describe in Section 3.1 the pathways involved during initiation and H₂ release during decomposition of AB in condensed phase. In the following section 3.2, the pathways for the continued growth among the product species, such as borazine and larger-molecular weight species containing rings, are discussed in greater detail. A comparison of numerical simulation with the experimental data is provided in Sect. 3.4.3 along with brief discussion on experimental results obtained in this study.

In any reaction mechanism, rate-determining steps play a critical role and sensitivity analyses are a very powerful tool in identifying those reactions and thus, help to gain detailed insight into the reaction mechanism. In performing sensitivity analysis, pre-exponential factor \( A_i \) of \( i \)-th reaction is changed by 10%. Sensitivity coefficients are then calculated for gaseous species H₂, NH₃, BH₂NH₂, B₂H₆ and borazine as follows [30]

\[
S_{ij} = \frac{A_i \Delta y_j}{y_j \Delta A_i}
\]

where \( S_{ij} \), \( A_i \) and \( \Delta y_j \) represent, respectively, the sensitivity coefficient, change in pre-exponential factor of \( i \)-th reaction and change mass-fraction of \( j \)-th species.
Table 3.1: Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction (kJ/mol) of several important reactions during initial phase of AB decomposition and H$_2$ release.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta G_f$</th>
<th>$\Delta G_b$</th>
<th>$\Delta H_f$</th>
<th>$\Delta H_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$\text{AB} \leftrightarrow \text{BH}_2\text{NH}_3+\text{H}_2$</td>
<td>199.6</td>
<td>211.7</td>
<td>199.6</td>
<td>177.0</td>
</tr>
<tr>
<td>R2</td>
<td>$2\text{AB} \leftrightarrow \text{BH}_2\text{BH}_2\text{NH}_3+\text{NH}_3$</td>
<td>113.4</td>
<td>62.8</td>
<td>113.4</td>
<td>30.1</td>
</tr>
<tr>
<td>R3</td>
<td>$\text{AB} \leftrightarrow \text{BH}_3+\text{NH}_3$</td>
<td>159.0</td>
<td>0.0</td>
<td>159.0</td>
<td>0.0</td>
</tr>
<tr>
<td>R4</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_3 \leftrightarrow \text{BH}_3+\text{AB}$</td>
<td>31.8</td>
<td>0.0</td>
<td>75.7</td>
<td>0.0</td>
</tr>
<tr>
<td>R5</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_3+\text{NH}_3 \leftrightarrow \text{BH}_2\text{NH}_2+[\text{BH}_4][\text{NH}_4]^+$</td>
<td>58.2</td>
<td>66.1</td>
<td>17.6</td>
<td>15.9</td>
</tr>
<tr>
<td>R6</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_3+\text{NH}_3 \leftrightarrow \text{DADB}$</td>
<td>83.7</td>
<td>131.8</td>
<td>46.9</td>
<td>136.4</td>
</tr>
<tr>
<td>R7</td>
<td>$\text{DADB} \leftrightarrow \text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3+\text{H}_2$</td>
<td>141.0</td>
<td>197.5</td>
<td>158.2</td>
<td>190.0</td>
</tr>
<tr>
<td>R8</td>
<td>$[\text{BH}_4][\text{NH}_4]^+ \leftrightarrow \text{AB}+\text{H}_2$</td>
<td>82.4</td>
<td>166.9</td>
<td>101.3</td>
<td>164.0</td>
</tr>
<tr>
<td>R9</td>
<td>$\text{BH}_2+\text{AB} \leftrightarrow \text{BH}_2\text{NH}_2+\text{BH}_3+\text{H}_2$</td>
<td>93.7</td>
<td>105.9</td>
<td>53.1</td>
<td>30.5</td>
</tr>
<tr>
<td>R10</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{AB}+\text{B}_2\text{H}_6$</td>
<td>0.0</td>
<td>83.7</td>
<td>0.0</td>
<td>90.4</td>
</tr>
<tr>
<td>R11</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2+\text{BH}_3+\text{H}_2$</td>
<td>52.3</td>
<td>69.9</td>
<td>9.2</td>
<td>-5.0</td>
</tr>
<tr>
<td>R12</td>
<td>$\text{BH}_2\text{NH}_2+\text{BH}_3 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2$</td>
<td>0.0</td>
<td>87.4</td>
<td>0.0</td>
<td>139.3</td>
</tr>
<tr>
<td>R13</td>
<td>$\text{BH}_2\text{NH}_2+\text{BH}_3 \leftrightarrow \text{NH}_2\text{BH}_2\text{NH}_2$</td>
<td>41.0</td>
<td>29.7</td>
<td>4.2</td>
<td>39.3</td>
</tr>
<tr>
<td>R14</td>
<td>$\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_2\text{NH}_2 \leftrightarrow \text{DADB}+\text{BH}_2\text{NH}_2$</td>
<td>31.4</td>
<td>90.0</td>
<td>-14.6</td>
<td>39.7</td>
</tr>
<tr>
<td>R15</td>
<td>$\text{DADB}+\text{NH}_3 \leftrightarrow \text{NH}_2\text{BH}_2\text{NH}_2+[\text{BH}_4][\text{NH}_4]^+$</td>
<td>51.0</td>
<td>0.0</td>
<td>56.5</td>
<td>0.0</td>
</tr>
<tr>
<td>R16</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_3$</td>
<td>66.9</td>
<td>102.9</td>
<td>29.3</td>
<td>109.6</td>
</tr>
<tr>
<td>R17</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_2+\text{BH}_3+\text{H}_2$</td>
<td>87.4</td>
<td>93.7</td>
<td>47.3</td>
<td>17.6</td>
</tr>
<tr>
<td>R18</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_3+\text{H}_2$</td>
<td>81.2</td>
<td>98.7</td>
<td>42.3</td>
<td>22.6</td>
</tr>
<tr>
<td>R19</td>
<td>$\text{NH}_2\text{BH}_2\text{NH}_3 \leftrightarrow \text{cis-}\text{H}_3\text{O}_2\text{B}_2\text{N}_2$</td>
<td>13.0</td>
<td>14.6</td>
<td>8.8</td>
<td>10.5</td>
</tr>
<tr>
<td>R20</td>
<td>$\text{cis-}\text{H}_3\text{O}_2\text{B}_2\text{N}_2+\text{BH}_3 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_3+\text{H}_2$</td>
<td>86.2</td>
<td>103.3</td>
<td>44.4</td>
<td>24.7</td>
</tr>
<tr>
<td>R21</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{AB}+\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2$</td>
<td>99.2</td>
<td>104.2</td>
<td>47.3</td>
<td>49.8</td>
</tr>
<tr>
<td>R22</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_2+\text{BH}_3 \leftrightarrow \text{BH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3$</td>
<td>0.0</td>
<td>41.4</td>
<td>0.0</td>
<td>86.2</td>
</tr>
<tr>
<td>R23</td>
<td>$\text{BH}_2\text{BH}_2\text{NH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2+[\text{BH}_4]^+$</td>
<td>58.6</td>
<td>61.9</td>
<td>18.4</td>
<td>9.2</td>
</tr>
<tr>
<td>R24</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3+\text{BH}_3 \leftrightarrow \text{NH}_3\text{BH}_2\text{NB}_2\text{BH}_2+\text{AB}$</td>
<td>104.6</td>
<td>98.3</td>
<td>54.4</td>
<td>47.3</td>
</tr>
<tr>
<td>R25</td>
<td>$2\text{BH}_2\text{NH}_2 \leftrightarrow \text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2$</td>
<td>79.5</td>
<td>96.2</td>
<td>32.2</td>
<td>95.4</td>
</tr>
<tr>
<td>R26</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_3 \leftrightarrow \text{trans-}\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2+\text{AB}$</td>
<td>82.8</td>
<td>107.1</td>
<td>31.4</td>
<td>56.9</td>
</tr>
<tr>
<td>R27</td>
<td>$\text{trans-}\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_3\text{NB}_2\text{BH}_2\text{NH}_3$</td>
<td>90.8</td>
<td>110.0</td>
<td>36.4</td>
<td>59.4</td>
</tr>
<tr>
<td>R28</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_3 \leftrightarrow \text{BH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2$</td>
<td>0.0</td>
<td>32.2</td>
<td>0.0</td>
<td>76.1</td>
</tr>
<tr>
<td>R29</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2+\text{BH}_3 \leftrightarrow \text{BH}_3\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2$</td>
<td>38.5</td>
<td>71.1</td>
<td>-5.4</td>
<td>18.8</td>
</tr>
<tr>
<td>R30</td>
<td>$\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2+\text{AB} \leftrightarrow \text{cis-}\text{H}_3\text{O}_2\text{B}_2\text{N}_2+\text{BH}_2\text{NH}_2$</td>
<td>100.4</td>
<td>97.1</td>
<td>46.0</td>
<td>45.2</td>
</tr>
</tbody>
</table>
R31  cis-H_{10}B_2N_2+BH_2NH_2\leftrightarrow NH_3BH_2NHBBH_2+AB  
98.7  90.8  50.2  41.0
R32  NH_3BH_2NHBBH_2\leftrightarrow BH_2NHBBH_2+NH_3  
47.3 0.0 95.0  0.0
R33  BH_3NH_2BNNH_2+BH_2NH_2\leftrightarrow BCDB  
85.5 112.8 35.1 119.9
R34  BH_3NHBBH_2+BH_2NHBBH_2\leftrightarrow INTI  
51.0 105.4  2.1 109.2
R35  INTI+AB\leftrightarrow BH_2NHBBNHBBH_2+BH_2BH_2NH_3  
116.3 79.5  84.9  40.6
R36  BH_2NHBBNHBBH_2+NH_3\leftrightarrow BH_2NHBBNHBBH_2NH_3  
  0.0  31.8  0.0  79.1
R37  BH_3NHBBNHBBH_2NH_3+BH_3\leftrightarrow BH_2NHBBNHBBH_2H_2  
+BH_3+H_2  
25.9  66.1 -14.6  -7.9
R38  BH_2NHBBH_2+BNH_2\leftrightarrow BH_3NH_2BHBBH_2  
47.3  95.0  0.8 100.4
R39  trans-BH_2NHBBH_2+BNH_2\leftrightarrow BH_3NH_2BHBBH_2  
  0.0  53.6  0.0 105.4
R40  BH_3NH_2BHBBH_2+NH_3\leftrightarrow BH_3NH_2BHBBH_2NH_3  
36.8  81.6  2.1  89.1
R41  BH_3NH_2BHBBH_2NH_3+BH_3\leftrightarrow 
BH_3NH_2BHBBH_2NH_3+BH_3H_2  
37.2  78.7 -1.7  5.4
R42  BH_3NH_2BHBBH_2NH_3+BH_2NH_2\leftrightarrow 
BH_3NH_2BHBBH_2NH_2+AB  
77.8  95.8  27.2  47.3
R43  BH_3NHBBNHBBH_2\leftrightarrow RING1  
43.1  54.4 35.6  56.1
R44  trans-BH_2NHBBH_2\leftrightarrow cis-BH_2NHBBH_2  
34.7  30.5 32.2  27.6
R45  cis-BH_2NHBBH_2\leftrightarrow BH_2NHBBH_2  
35.6  21.3  -9.2  25.9
RING2  
R46  BH_3NHBBH_2NH_2BHBBH_2\leftrightarrow RING2  
23.8  92.0 12.6  97.1
R47  RING2+NH_3\leftrightarrow RING1+AB  
107.5 143.9 78.2 107.9
R48  RING1+BH_2NH_2\leftrightarrow B_3N_3H_6+AB  
60.7 172.8 10.9 123.4
R50  RING3+BH_2NH_2\leftrightarrow AB+RING4  
64.9 155.2 14.2 105.0
R51  RING4+BH_2NHBBH_2\leftrightarrow RING5  
48.5 102.9 -1.7 105.0
R52  RING5+AB\leftrightarrow RING6+BH_4BH_2NH_3  
115.5  77.8 84.9 38.9
R53  RING6+NH_3\leftrightarrow RING7  
  0.0  31.4  0.0  77.8
R54  RING7+BH_2NH_2\leftrightarrow RING8+AB  
87.0 108.4 33.9  57.7
R55  RING8\leftrightarrow RING9  
41.8  24.7 33.1  24.7
R56  RING9+BH_2NH_2\leftrightarrow RING10+AB  
60.7 202.1 10.9 152.7
R57  RING6+NH_2BHBBH_2\leftrightarrow RING11  
9.2  0.0  0.0  41.8
R58  RING11+BH_2NH_2\leftrightarrow RING12+AB  
72.4 123.0 23.4  72.4
R59  RING12\leftrightarrow RING13  
39.3  35.6 28.5 37.2
R60  RING13+BH_2NH_2\leftrightarrow RING14+AB  
60.7 184.9  9.2 134.3
R61  BH_3BH_2NHBBH_2\leftrightarrow NH_3BHBBH_2+B_3H_6  
63.2  78.7 62.3 32.6
R62  NH_3BNNH_2+[BH_4]_n[NH_4]_n\leftrightarrow NH_3BNNH_2BH_4+NH_3  
19.7  58.6 -22.6  12.1
R63  NH_3BNNH_2BH_4\leftrightarrow NH_3BNNH_2BH_4+H_2  
59.8  70.3  56.1 -5.4
3.4.1 Initiation and $H_2$ release pathways

The pathways for hydrogen release are shown by the reaction network in Fig. 3.2 below. Based on the Gibbs free energy of activation and sensitivity analysis, the dominant reactions are identified, and they are highlighted using solid arrows in Fig. 3.2. Table 3.1 shows the reactions, including free energy and enthalpic barriers.

Figure 3.1 Reaction network for initial phase of AB decomposition and $H_2$ release. Here, the use of a thick line, ————, indicates a dominant pathway and dashed, - - - - - -, indicates a minor pathway.
In our previous work on the initiation of AB decomposition in glyme [22], we identified that initiation of AB decomposition occurs via 3 different pathways: 1) R1, which involves intramolecular hydrogen transfer to form \( \text{BH}_2\text{NH}_2 \) and \( \text{H}_2 \), 2) R2, which is a bimolecular reaction forming \( \text{BH}_4\text{BH}_2\text{NH}_3 \) and \( \text{NH}_3 \), and 3) R3, which is the homolytic B-N bond cleavage producing \( \text{BH}_3 \) and \( \text{NH}_3 \). However, since both reactions R1 and R3 have significantly high forward Gibbs free energy barriers in the range of ~160-200 kJ/mol, we conclude that R2 is the key initiation step in the process of AB decomposition, in agreement with conclusion made by Zimmerman et al. [18] regarding the initiation of solvent phase AB dehydrogenation. It is also noteworthy that in Chapter 2, in order to consider the reactivity of \( \text{BH}_3 \) with glyme, which is a Lewis base, all reactions that would involve \( \text{BH}_3 \) as a reactant or product were neglected in the mechanism. However, in the current work those reactions will play a critical role. For instance, it is to be noted that the backward reaction of R3 which involves \( \text{BH}_3 \) is barrierless. This indicates that although the forward reaction of R3 does not play significant role in the initiation of AB decomposition, the backward reaction involving \( \text{BH}_3 \) plays a major role in the mechanism.

From Fig. 3.2, it can be observed that the formed \( \text{BH}_4\text{BH}_2\text{NH}_3 \) during initiation step, R2, can undergo three possible reactions: 1) R4, which is a unimolecular decomposition reaction forming a critical intermediate species, \( \text{BH}_3 \), and reform AB in the process, 2) R5, in which \( \text{BH}_4\text{BH}_2\text{NH}_3 \) reacts with \( \text{NH}_3 \) to form \( \text{BH}_2\text{NH}_2 \) and the ammonium borohydride salt ([\( \text{BH}_4 \)][\( \text{NH}_4 \]^+), and 3) R6 producing DADB, which undergoes unimolecular decomposition to release \( \text{H}_2 \) via R7. However, since R4 is a unimolecular reaction and has the lowest forward Gibbs free energy barrier among all, it can be assumed to be the dominant pathway for the consumption of \( \text{BH}_4\text{BH}_2\text{NH}_3 \). Furthermore, R4 plays a critical role as it is the only reaction producing \( \text{BH}_3 \) during the initial phase.
of AB decomposition. Sensitivity analysis also identifies R4 as one of the most important reactions for formation of gaseous species (H₂, NH₃, BH₂NH₂, B₂H₆ and borazine) observed during experiment. Since BH₃ lacks a full octet, it can readily accept a pair of electrons, which makes it a very reactive species. Thus, it plays a major role in the H₂ release process, which will be discussed further in this section. Furthermore, the forward free energy barrier of R4 is quite low (31.8 kJ/mol), which indicates that diffusion has significant effect on the formation of BH₃. Nonetheless, this reaction occurs very fast and BH₃ is formed. Once BH₃ is formed, it undergoes bimolecular reactions with AB and BH₄BH₂NH₃ to release H₂ via R9 and R11. In the process, another critical intermediate species is formed, namely aminoborane, BH₂NH₂. B₂H₆ is also formed via R10. The formed BH₂NH₂ then produces BH₃NH₂BH₂ and NH₃BH₂NH₂ via R12 and R13, respectively. Both BH₃NH₂BH₂ and NH₃BH₂NH₂ play critical roles in the process of H₂ release during initial phase of condensed phase AB dehydrogenation. While NH₃BH₂NH₂ reacts further with BH₄BH₂NH₃ to form DADB which reacts with NH₃ to form an ionic species ([BH₃][NH₄⁺]) releasing H₂, BH₃NH₂BH₂ undergoes bimolecular reaction (R16) with NH₃ to form BH₃NH₂BH₂NH₃, a key intermediate for H₂ release. BH₃NH₂BH₂NH₃ thus formed then undergoes 3 reactions: 1) R19 which is merely a trans to cis formation reaction to form cis-H₁₀B₂N₂, and 2) autocatalytic reactions with BH₃ to release H₂ via R17 and R18. Here, cis-H₁₀B₂N₂ is the cis form of BH₃NH₂BH₂NH₃. The cis-H₁₀B₂N₂ then decomposes autocatalytically with BH₃ to release H₂ via R20. Therefore, it is evident from Fig. 3.2 that, similar to the conclusion made by Zimmerman et al. [18], there exists pathways of AB dehydrogenation which do not involve DADB formation. However, there exist differences in the reaction pathways of H₂ release. Zimmerman et al. [18] reported two pathways of H₂ release from AB in solution phase: unimolecular decomposition of AB dimer and DADB.
having energy barrier of ~ 140.6 kJ/mol and ~ 105.9 kJ/mol, respectively. In this study, we observe two pathways of hydrogen release from DADB: 1) unimolecular decomposition of DADB via $\text{R7}$ ($\Delta G_f = 141$ kJ/mol); 2) $\text{R8}$, unimolecular decomposition of $[\text{BH}_4^-][\text{NH}_4]^+$ formed from DADB via $\text{R15}$ ($\Delta G_f = 82.4$ and $51$ kJ/mol, respectively). However, since reaction $\text{R7}$ has a significantly high Gibbs free energy barrier (141 kJ/mol), the only dominant pathway of $\text{H}_2$ release from DADB involves the formation of an ionic species, $[\text{BH}_4^-][\text{NH}_4]^+$ via $\text{R15}$. Thus, from the above discussion it is evident that two other species, $\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_3$ and $[\text{BH}_4^-][\text{NH}_4]^+$ also play an important role in the process of hydrogen release, in addition to DADB. Sensitivity analysis also identifies reactions involving $\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_3$ ($\text{R17}$ and $\text{R18}$) as important reactions for release of $\text{H}_2$ during initial phase of AB dehydrogenation. Hence from the above discussion it is evident that mainly four pathways exist through which $\text{H}_2$ is released during AB decomposition in liquid phase. One of them involves DADB and the other three pathways involve $\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_3$.

The autocatalytic role that $\text{BH}_3$ plays in the process of hydrogen release via $\text{R9}$, $\text{R11}$, $\text{R17}$, $\text{R18}$ and $\text{R20}$ is also to be noted. A similar observation was previously made by Nguyen et al. [6]. Furthermore, it is to be noted that if DADB is added to the mixture, $[\text{BH}_4^-][\text{NH}_4]^+$ will be formed quickly since $\text{R15}$ has a relatively low Gibbs free energy barrier of ~51 kJ/mol. The formed $[\text{BH}_4^-][\text{NH}_4]^+$ then quickly decomposes via $\text{R8}$ thus reducing induction period of $\text{H}_2$ release. A similar observation was made by Heldebrant et al. [9] during their experiment where they observed that the induction period of hydrogen release was reduced with the addition of DADB. It is also noteworthy that the Gibbs free energy of reaction ($\Delta G_R = \Delta G_f - \Delta G_b$) is negative for most of the reactions listed in Table 1. This signifies that the forward rates of reactions are faster than the reverse reactions. It is also noted in Table 1 that these reactions are exothermic during the initial
phase of AB decomposition and H\textsubscript{2} release. A similar observation was made during DSC experiments in this study as well as in previous studies [13, 19].

QM calculations also identified three other reactions responsible for releasing hydrogen in the process, namely reactions describing formation of borazine and larger molecular weight rings during the second phase of AB decomposition. This is discussed in following Sect. 3.4.2.

### 3.4.2 Pathways for formation of ring-containing compounds

TGA experiments revealed that mass loss of AB takes place in two steps. During the second phase of decomposition beyond \( \sim T=423 \) K, in addition to H\textsubscript{2} and BH\textsubscript{2}NH\textsubscript{2}, borazine is also released into the gas phase. Simultaneously, it is generally expected that larger molecular weight species are formed via polymerization and cyclization containing two or more rings of the B\textsubscript{3}N\textsubscript{3}H\textsubscript{6} moiety. From our QM calculations, an attempt has been made to identify the reaction pathways for these species, including formation of borazine. In addition, reactions that could be responsible for the second phase of hydrogen release are also discussed in this section.

In the previous section, it was recognized that BH\textsubscript{3}NH\textsubscript{2}BH\textsubscript{2}NH\textsubscript{3} is a key intermediate required for formation of H\textsubscript{2}. In this section, the role of BH\textsubscript{3}NH\textsubscript{2}BH\textsubscript{2}NH\textsubscript{3} in the formation of borazine and other larger molecular weight species will be explored. From Table 1, it can be observed that other than H\textsubscript{2}, two new intermediate species (BH\textsubscript{3}NH\textsubscript{2}BHNH\textsubscript{2} and NH\textsubscript{3}BH\textsubscript{2}NHBH\textsubscript{2}) are also formed from BH\textsubscript{3}NH\textsubscript{2}BH\textsubscript{2}NH\textsubscript{3} via several competing reactions. Once BH\textsubscript{3}NH\textsubscript{2}BHNH\textsubscript{2} is formed, it undergoes series of reactions to form critical intermediates such as BH\textsubscript{2}NH\textsubscript{2}, trans-BH\textsubscript{2}NHBH\textsubscript{2}NH\textsubscript{2} and a cyclic compound NH\textsubscript{2}BH\textsubscript{2}NH\textsubscript{2}BH-NH\textsubscript{2}BH\textsubscript{3}, which is also known as B-(cyclodiborazanyl) aminoborohydride (BCDB). Simultaneously, NH\textsubscript{3}BH\textsubscript{2}NHBH\textsubscript{2} is formed in the system via R17,
R24 and R31, and it quickly undergoes unimolecular decomposition via R32 to form another critical intermediate species, BH$_2$NHBNH$_2$. These four intermediate species (BH$_2$NH$_2$, BCDB, trans-BH$_2$NHBNH$_2$, and BH$_2$NHBNH$_2$) play a very important role in the ring formation during the second phase of AB decomposition. Al-Kukhun et al. [7] also concluded that during the initial phase of AB decomposition in solvent phase, BH$_3$NH$_2$BHBNH$_2$ and NH$_3$BH$_2$NHBNH$_2$ are formed which undergo competitive reactions to produce borazine and other larger molecular weight rings during the second phase of AB decomposition. However, they have not provided any further details on reaction pathways of cyclization process to form borazine and rings. In this study, three major reaction pathways are identified through which borazine is formed. Figure 3.3 below shows the three reaction pathways involved in the formation of borazine. From Fig. 3.3, it can be observed that all three pathways involve R48 as the sole reaction producing borazine. However, the intermediate species, RING1 involved in R48 can be formed through 3 different pathways involving BH$_2$NHBNH$_2$ and trans-BH$_2$NHBNH$_2$ as the critical intermediates. From sensitivity analysis, it has been observed that reactions R38, R39 and R40 play a critical role in the formation of borazine. Therefore, it can be concluded that the dominant pathway for the formation of borazine is pathway 2. Furthermore, it is to be noted that during the process of borazine formation, a second equivalent of H$_2$ is released via R41 and R37 in the presence of BH$_3$ as an autocatalyst.
Figure 3.2 Reaction pathways for formation of borazine.
During this second phase of AB decomposition, several larger molecular weight species containing rings, in addition to borazine, can also be formed in the liquid phase. Figure 4 below show the reaction pathways of these ring formations. It is to be noted that ring formation is a growth process, resulting in very large molecular weight species. However, in this mechanism we have considered a limited number of reactions and species that can explain the behavior observed during experiments. Hence, we have considered RING10 and RING14 as final products, which may be representative of the polymers observed in the experiments. It is to be noted that using this mechanism, the amount of calculated hydrogen release will be less than the observed amount in experiment (~14% by mass). However, the difference will be not be very significant since the amount of hydrogen release during these growth processes is generally quite small. From Fig. 3.3, it can be observed that BH$_2$NH$_2$ plays a major role in the ring formation, and in the process, AB is reformed. From sensitivity analysis, it has been observed that during the second phase of AB decomposition reaction R33 plays a critical role in the formation of BH$_2$NH$_2$. During this phase, BCDB formed from BH$_3$NH$_2$BHNH$_2$ decomposes to release BH$_2$NH$_2$. Moreover, during this phase R33 has the highest sensitivity coefficient ($S_{ij}$) for BH$_2$NH$_2$ (~0.85 for 20K/min of heating rate at $T=453$K). This signifies that R33 is not only an important reaction for BH$_2$NH$_2$ formation, it is also one of the most sensitive or rate determining reactions for species BH$_2$NH$_2$ during the second phase of AB decomposition. Furthermore, it is noted from sensitivity analysis, that similar to BH$_2$NH$_2$, reaction R33 is the most sensitive reaction for other gaseous species such as H$_2$ and borazine as well. Furthermore, it is noteworthy that reaction R52 reforms BH$_4$BH$_2$NH$_3$, which is the major source of a critical intermediate, BH$_3$, required in both H$_2$ release and borazine formation. Thus, it is evident from the above discussion that ring formation is essential to H$_2$ release during the second phase of AB decomposition. It is also noteworthy that similar to the first step of AB decomposition,
the free energy of reaction ($\Delta G_R$) is negative for most of the reactions involved in cyclization and polymerization process during the second phase of decomposition are exergonic, which is corroborated by the experimental observation made in this study as well as by Baitalow et al. [19] during DSC experiments.

$$\text{RING2} \xrightarrow{R49} \text{RING3} \xrightarrow{R50} \text{RING4} \xrightarrow{R51} \text{RING5} \xrightarrow{R52} \text{RING6} + \text{BH}_4\text{BH}_2\text{NH}_3$$

$$\text{RING6} \xrightarrow{R53} \text{RING7} \xrightarrow{R54} \text{RING8} \xrightarrow{R55} \text{RING9} \xrightarrow{R56} \text{RING10} + \text{AB}$$

$$\text{RING6} \xrightarrow{R57} \text{RING11} \xrightarrow{R58} \text{RING12} \xrightarrow{R59} \text{RING13} \xrightarrow{R60} \text{RING14} + \text{AB}$$

Figure 3.3 Reaction pathways for ring formation. $\text{NH}_2\text{BH}_2\text{NH}_2$ formed via reactions $\text{R61-63}$.

### 3.4.3 Experimental results and validation of proposed reaction mechanism

Figure 3.5 shows the TGA and DSC data for three heating rates. Similar to previous studies, our DSC data also show that just before the first exothermic event, which begins the first step of AB decomposition, there exists an endothermic step. This endothermic step starts from a temperature of $\sim 380 \text{ K}$ and ends $\sim 383 \text{ K}$. Since melting of AB occurs approximately at $380 \text{ K}$, the experimentally observed endothermic step is attributed to the melting of AB. It is to be noted from DSC data that as the heating rate increases, the melting point of AB also slightly increases. The similar observation has also been made by Baitalow et al. [19]. However, this increase in melting point of AB due to increased heating rate is not significant and for all three heating rates decomposition starts approximately at the same temperature. Hence, in our numerical simulation...
for condensed phase AB, we used a constant melting temperature for all three heating rates (380 K). It is also to be noted that there exists a small endothermic peak at \( T = 373 \) K. This peak can be attributed to the evaporation of water present in the sample. But since the amount is very small as none is detected in the FTIR spectra, we made no attempt to quantify the water content. Along with capturing TGA/DSC data, we have also performed FTIR transmission measurements of the evolved gases during decomposition. Unlike previous studies, we observed \( \text{NH}_3 \) in the FTIR spectra during both decomposition steps for all three heating rates used in our experiment. Figure 3.6(a) shows FTIR absorbance data in the range of 900-980 cm\(^{-1}\) for a heating rate of 20 K/min, which contains several spectral lines of \( \text{NH}_3 \) [13]. As can be observed from the figure, the two strong lines at \( \sim 930 \) cm\(^{-1}\) and 965 cm\(^{-1}\) first appear at \( \sim 383 \) K. The intensity of these two spectral lines continues to rise till a temperature of about 403 K and then starts to decrease towards the end of first phase of AB decomposition. However, during the second phase of AB decomposition starting from \( \sim 423 \) K, intensity of \( \text{NH}_3 \) spectral lines at \( \sim 930 \) cm\(^{-1}\) and 965 cm\(^{-1}\) again start to increase indicating the formation of \( \text{NH}_3 \) during the second step of AB decomposition as well. The absorbance data for wavenumbers 930 cm\(^{-1}\) and 965 cm\(^{-1}\) are plotted as function of temperature in Fig. 6(b). The similar observation has been made for other two heating rates.
Figure 3.4 TGA mass loss and DSC curves obtained for AB subject to 3 different heating rates in a nitrogen atmosphere.
(a) Absorbance spectra for wavelength ranging from 900-980 cm\(^{-1}\)

(b) Absorbance data for wavelength 930 and 965 cm\(^{-1}\) as function of temperature

Figure 3.5 FTIR absorbance spectra obtained for AB heated at 20K/min in a nitrogen atmosphere.
In this section, we also provide the validation of the proposed mechanism by comparing the result predicted by numerical simulation with the experimental data. To assess the effect of changes in evaporation rate parameters on the mass loss, we alter one such value at a time by a factor of ten for a given heating rate to obtain a corresponding mass loss. By considering $A$-factors of 5 gaseous species ($\text{H}_2$, $\text{NH}_3$, $\text{BH}_2\text{NH}_2$, $\text{B}_2\text{H}_6$ and borazine), as well as the nominal value of $A$-factors and viscosity, we obtain 11 different mass losses. These values then have a range and an uncertainty can be evaluated. Based on a 95% confidence interval, error bars are calculated for net mass loss at different heating rates. The error bars from such changes are small and range from $\sim 1.5\%$ to $3.5\%$. It is to be noted, however, that there are significant uncertainties in the measurements themselves [8], and these uncertainties are larger than the uncertainties caused by varying the parameters for the evaporation rates. It has been observed that if the forward barrier of one of the most sensitive reactions in the mechanism (R2) is increased by $\sim 4.2$ kJ/mol, which is a relatively small amount and most likely less than the uncertainty associated with the calculations using the G4(MP2)/SMD method, a better agreement with the first phase of mass loss data is obtained. Figure 3.7 below shows the comparison of original and modified mechanism with experimental data for 20 K/min heating rate.
As it can be observed from Fig. 3.7, both original and modified mechanisms capture the two-step decomposition of AB and the predicted net mass losses are within the uncertainties of the experimental data. Hence for our study we have used the modified mechanism in which the forward free energy barrier of reaction R2 is increased by ~4.2 kJ/mol. Figure 3.8 and 3.9 below show the simulation predicted mass loss curves and comparison with experimental data, respectively, for three different heating rates. It can be observed from above figures that the proposed mechanism predicts both the net mass loss and two-step decomposition of AB at all the heating rates. It is also to be noted that although net mass loss increases with heating rate, simulation predicts approximately similar amount of mass loss during the first step of decomposition at all heating rates. Similar conclusion can be made from the TGA experimental data in Fig. 3.5(a). The simulation predicted mass loss during the first phase closely matches the experimental data.

Figure 3.6 Comparison of simulation predicted mass loss curve with available TGA data at 20 K/min. aMass loss profile predicted using modified mechanism (Error bars for both data and numerical simulation are added based on 95% confidence interval).
Furthermore, it is to be noted that the rate of decomposition during the first phase reduces as heating rate increases. However, once second phase of decomposition starts, the reverse occurs resulting in an increased net mass loss as heating rate increases. TGA experimental data in Fig. 5(a) also show the similar trend. This is due to increased amount of BH₂NH₂ released in gaseous phase along with H₂ as heating rate increases [19]. A similar conclusion can also be made from numerical simulation performed in this study. Figure 10 below shows the wt% of species (H₂, NH₃, BH₂NH₂, B₂H₆ and borazine) accumulated in gaseous phase at different heating rates. It can be observed from the figure that the amount of H₂ release remains approximately 12 wt% irrespective of heating rate. This is one of the key observations made by several researchers during experiments performed at different heating rates [13,19,23,25]. It is also to be noted that the amounts of NH₃, B₂H₆ and borazine present in gaseous phase are relatively small in comparison to BH₂NH₂, especially at heating rates beyond 5 K/min. Furthermore, it can be observed from Fig. 3.10 that with increasing heating rate, the change in mass of NH₃, B₂H₆ and borazine is negligible compared to that of BH₂NH₂. Hence, it is evident that our numerical simulation also predicts that the main contributor to the mass loss as heating rate increases is BH₂NH₂. Figure 3.11 shows the temporal evolution of the mass fraction of above-mentioned species (\( y_{g,i} \frac{m_g}{m_{t,0}} \)) accumulated in gas phase for the heating rate of 20 K/min. As can be observed from Fig. 3.11, similar to FTIR absorbance spectra, mechanism also predicts that during the first half of AB decomposition below ~413 K, major gaseous species released are H₂ and NH₃. During the second phase of decomposition, BH₂NH₂, B₂H₆ and borazine are also released along with H₂ and NH₃. It is to be noted that the predicted amount of hydrogen released is less than that of experimental data (~14 wt%). As discussed in previous section, the second half of AB decomposition is dominated by continuous growth process releasing H₂, while
in our mechanism we have considered limited number of larger molecular weight ring-containing species, which gives rise to a slight reduction of $\text{H}_2$ release by $\sim$2%.

By performing data reduction [31] using a high-resolution transmission molecular absorption database (HITRAN) [41], another important information obtained from experiments performed in this study is the mole fraction of $\text{NH}_3$ evolved in gas phase during AB decomposition. Figures 3.12(a) and 3.12(b) show the experimentally measured and simulation predicted mole fractions of $\text{NH}_3$ released during decomposition, respectively. From these figures, it can be observed that simulation predicts both the trend and the amount of $\text{NH}_3$ evolved beyond 373 K reasonably well. Below $\sim$373 K which is the melting point of AB, amount of $\text{NH}_3$ evolving due to sublimation or slid phase reactions are not taken into account in this condensed-phase study. Furthermore, it is to be noted that simulation also predicts the overall behavior of $\text{NH}_3$ evolution at different heating rates reasonably well. Thus, it can be concluded from the above discussion that although the predicted amount of $\text{H}_2$ release is slightly less, the overall decomposition behavior of AB is generally captured by the proposed mechanism. The differences observed in Fig. 3.12 for the lower temperatures are believed to be caused by a neglect of solid-phase reactions.
Figure 3.7 Mass loss curves predicted by numerical simulation at three different heating rates using modified mechanism (Error bars for numerical simulation are added based on 95% confidence interval).
Figure 3.8 Comparison of simulation predicted mass loss curve with TGA data at three different heating rates using modified mechanism (Error bars for both data and numerical simulation are added based on 95% confidence interval).
Figure 3.9 Wt% of gaseous species evolved during AB decomposition as predicted by numerical simulation for different heating rates using modified mechanism.

Figure 3.10 Temporal evolution of mass fraction of species (H$_2$, NH$_3$, BH$_2$NH$_2$, B$_2$H$_6$, and borazine) accumulated in gas phase as predicted by numerical simulation for heating rate of 20K/min using modified mechanism.
3.5 Conclusions

Using QM calculations and thermo-analytical methods such as TGA/DSC combined with FTIR spectroscopy, reaction pathways during the initiation of AB decomposition are identified. Our calculations suggest that initiation of AB decomposition most likely begins via a bimolecular reaction producing BH$_4$BH$_2$NH$_3$. The formed BH$_4$BH$_2$NH$_3$ quickly undergoes unimolecular decomposition to form BH$_3$, which plays an auto catalytic role in the process of H$_2$ release from AB. It is also evident that the initiation step, R2, is the primary source of NH$_3$ evolved into the gaseous phase. Furthermore, this study also identifies critical intermediate species required for the formation of H$_2$, BH$_2$NH$_2$, borazine and other ring-containing species during the process of AB decomposition. It is also observed that [BH$_4$]$^+$/[NH$_4$]$^-$ and BH$_3$NH$_2$BH$_2$NH$_3$ are two important sources for the formation of H$_2$, among which BH$_3$NH$_2$BH$_2$NH$_3$ plays a major role in the process.

Figure 3.11 Mole fraction of NH$_3$ evolving during decomposition at different heating rates in a nitrogen atmosphere.
Furthermore, three pathways are identified for formation of borazine, and it can be deduced from the reaction mechanism that BH$_2$NH$_2$, BH$_2$NHBH$_2$ and trans-BH$_2$NHBH$_2$ formed via several competing reactions from BH$_3$NH$_2$B$_2$NH$_3$ play a critical role in the process of ring formation during the second phase of AB decomposition. Based on the results shown in this work, further details have been provided on the initiation of decomposition of AB, as well as identification of intermediates and reactions responsible for the growth to borazine and larger molecular weight ring-containing compounds. Simulated results match quite well with the experimental findings which confirms the validity of the proposed mechanism.

### 3.6 References


[36] M. L. McKee, “Ab initio study of the formation of H₂BNH₂ from NH₃ and B₂H₆,”


Chapter 4

QUANTUM MECHANICS INVESTIGATION OF PERCHLORIC ACID DECOMPOSITION RELEASING OXYGEN

4.1 Introduction

Perchloric acid (HClO₄), which is one of the very strong mineral acids, is experimentally observed during the ignition and combustion of AP (NH₄C1O₄)-containing solid propellants. Using the T-jump/FTIR experiment at 440K and 11 atm on AP, Brill et al. [1] studied the sequence of gaseous species leaving a simulated burning surface of AP. They identified HClO₄ and water as early products during AP decomposition followed by HNO₃, NO₂ and N₂O. Near the end of the experiment, a highly exothermic event occurred releasing HCl, NOCl and NO. In one of the earlier works on characterizing the AP flame, Ermolin et al. [2] also reported similar species leaving an actual burning surface. In addition, Ermolin et al. [2] also observed homonuclear diatomic decomposition products of NH₃ and HClO₄ such as O₂, N₂ and Cl₂ which could not be detected by Brill et al. [1] in their FTIR diagnostics. Based on the FTIR results and the presence of AP aerosol in the gas phase, Brill [1] concluded that one of the initiation steps of AP decomposition involves formation of NH₃ and HClO₄. Behrens and Minier [3] also made similar conclusion based on their experimental data. Based on computational studies using higher level quantum mechanics (QM) based QM methods, Zhu and Lin [4–6] also concluded that AP forms NH₃ and HClO₄ during the initial steps of its decomposition in both gas and condensed phase. Based on the above studies and several others, it has been concluded that perchloric acid and its reactive decomposition products play a critical role during the process of AP oxidation [7–10]. Since AP is one of the most common oxidizers for solid-rocket propellants, there has been a considerable amount of work done to unravel
the kinetics involved during the thermal decomposition of perchloric acid in both gas and liquid phases in order to better understand the combustion behavior of AP. Although significant efforts have been made to explain the reaction mechanism for HClO₄ decomposition, there remains several contradictions [9, 11]. Furthermore, while considerable effort has been made to study gas-phase decomposition, very few studies have been done on the corresponding liquid-phase decomposition for both AP and HClO₄ [9, 10, 12–18]. In order to identify the decomposition pathways, we use QM calculations to identify the important reactions for HClO₄ decomposition in condensed phase.

A numerical model is formulated of the experiment in order to predict the evolution of diatomic oxygen during decomposition using the developed reaction mechanism. Since the experiments were conducted at temperatures below 373K, it is clear that HClO₄ is a very reactive species in the liquid phase.

In order to understand the thermal stability and thermal decomposition behavior of the anhydrous perchloric acid, several studies were undertaken in the last century. One of the very early works on liquid-phase decomposition of anhydrous perchloric acid was done in 1959 by Tsentsiper et al. [15]. He proposed that the perchloric acid decomposition is initiated by the fission of the H-O-Cl bond, followed by a chain reaction. However, the above hypothesis was questioned by Zinov’ev and Babaeva [16]. Their numerous studies on perchloric acid decomposition provided invaluable information on the corresponding chemical kinetics. They observed that perchloric acid undergoes decomposition to release O₂, Cl₂ and H₂O in the temperature range of 333-353 K. Along with these species, they also observed chlorine oxides as intermediate products. Based on measurements of O₂ evolved during decomposition, they concluded that the liquid-phase decomposition of perchloric acid takes place in three stages: i) an induction period during which no appreciable amount of O₂ is evolved, ii) an active period during which reaction rate sharply rises
to a maximum in a very short time, and iii) a final period when reactions cease to take place. Based on the observed induction period, Zinov’ev and Babaeva [16] also determined the activation energy of the HClO₄ decomposition, which was found to be very close to that of gas-phase decomposition of chlorine heptoxide (Cl₂O₇), ~125.5 kJ/mol. Furthermore, they observed that when ~35 wt.% of Cl₂O₇ was added to the anhydrous perchloric acid solution, the induction period decreased but the activation energy remained unchanged. Babaeva and Zinov’ev [17] also studied in detail the effect of initial acid concentration and inhibitors (trichloroacetic acid and carbon tetrachloride) on rate of decomposition. They observed that as acid concentration in the solution decreased, the length of the induction period increased significantly. However, the activation energy of induction period was found to be independent of the concentration of the acid and the presence of inhibitors. Based on the above observations, Zinov’ev and Babaeva [16] argued that since the activation energy remained unchanged irrespective of the composition of the acid solution, the chemical kinetics involved during the decomposition process must be dependent on the same substance for all acid mixtures. They further argued that since the decomposition characteristics of mixture containing appreciable amount of Cl₂O₇ (~35 wt.%) should be determined by Cl₂O₇, the common substance involved during all acid mixtures must be Cl₂O₇. The above assumption was further validated based on the previous finding of Cl₂O₇ in highly concentrated perchloric acid [11]. Based on the above hypothesis, Zinov’ev and Babaeva [16] rejected the previous hypothesis regarding initiation and concluded that the decomposition rate of HClO₄ solution was determined by formation and subsequent decomposition of Cl₂O₇. The initiation reaction is:

\[
2\text{HClO}_4 \leftrightarrow \text{Cl}_2\text{O}_7 + \text{H}_2\text{O}
\]  

(1)

Furthermore, they mentioned that the above-mentioned initiation step is facilitated by the formation of a crystalline solid perchloric acid monohydrate, \([\text{H}_3\text{O}]^+[\text{ClO}_4]^-\) via reaction of \(\text{H}_2\text{O}\)
with HClO₄. The above hypothesis aligns very well with one of the very early works on thermal stability of perchloric acid done by Van Wyk in 1906, who suggested that perchloric acid is always associated with the formation of perchloric acid anhydride (Cl₂O₇) and monohydrate via the equilibrium reaction given by [18]

$$3\text{HClO}_4 \leftrightarrow \text{Cl}_2\text{O}_7 + [\text{H}_3\text{O}]^+[[\text{ClO}_4]]^-$$

The above hypothesis was further validated based on the observation of $[\text{H}_3\text{O}]^+[[\text{ClO}_4]]^-$ in the residue, and the amount of monohydrate formed corresponded to the above mentioned reaction, that is, for every 3 moles of HClO₄ used, 1 mole of $[\text{H}_3\text{O}]^+[[\text{ClO}_4]]^-$ is formed (i.e., ~39% of monohydrate by weight is formed during decomposition). Zinov’ev and Babaeva [16] further reported that Cl₂O₇ thus formed during initiation is the primary intermediate which decomposes in subsequent reactions to release O₂ during decomposition process. No additional details regarding pathways of O₂ formation from Cl₂O₇ were provided by Zinov’ev and Babaeva [16].

The above hypothesis of Zinov’ev and Babaeva [16] regarding initiation step given by (1) and the rate of HClO₄ decomposition being determined by formation of Cl₂O₇ was contested by Pearson [11] and Solymosi [9] in their review papers on perchloric acid decomposition. It is to be noted from previous discussion that the hypothesis made by Zinov’ev and Babaeva [16] is primarily based on three observations: 1) the calculated activation energy of induction period during HClO₄ decomposition is similar to that of gas-phase Cl₂O₇ decomposition, ~125.5 kJ/mol; 2) the induction period reduces when 35 wt% of Cl₂O₇ is added to HClO₄ solution but activation energy remains unchanged, ~125.5 kJ/mol; 3) detection of Cl₂O₇ in highly concentrated HClO₄ solution. Pearson [11] contended that the above mentioned 2nd observation can be better explained by Tsentsiper’s theory on initiation along with the equilibrium hypothesis (2) proposed by Van Wyk in 1906 [18]
as follows: due to addition of Cl$_2$O$_7$ in the mixture, the equilibrium of reaction given by (2) will shift towards left, thus more HClO$_4$ will remain undissociated to undergo unimolecular dissociation thus reducing induction period. Pearson [11] further mentioned that it is well known that concentrated perchloric acid, when not purified properly, will contain Cl$_2$O$_7$ [19]. Thus, the conclusion made by Zinov’ev and Babaeva [15] based on observation no. (3) does not have enough credibility. In the review paper, both Pearson [11] and Solymosi [9] also provided details regarding subsequent study on liquid-phase decomposition of Cl$_2$O$_7$ by Zinov’ev and Babaeva, which does not lend support to the above conclusion. In this study, Zinov’ev and Babaeva observed that inhibitors, which increase the induction period during HClO$_4$ decomposition, do not have any influence on Cl$_2$O$_7$ decomposition. However, they observed that if 1% of perchloric acid is added to Cl$_2$O$_7$, the decomposition characteristics changes dramatically. Thus, it is evident that the previous conclusion of Babaeva and Zinov’ev [17] that the kinetics of perchloric acid decomposition remains unchanged by addition of Cl$_2$O$_7$ in the acid solution cannot be explained by their subsequent work on Cl$_2$O$_7$ decomposition. Hence, from the above discussion, it is apparent that the only evidence in support of perchloric acid decomposition via Cl$_2$O$_7$ was that the activation energy based on length of induction period is similar to that of gas-phase decomposition of Cl$_2$O$_7$. Thus, the conclusion of Zinov’ev and Babaeva [16] regarding pathways of perchloric acid decomposition was highly debated.

From the above discussion, it is evident that although significant efforts have been made for studying and explaining the initial reactions involved during thermal decomposition of perchloric acid in the liquid phase, there appears to be no consensus on the important reaction pathways. Moreover, the mechanistic details of O$_2$ evolution during decomposition have not been the subject
of in-depth studies. Hence, in this study we use theoretical calculations to investigate the chemical kinetics involved during early stage of liquid-phase HClO₄ decomposition releasing O₂ below 373 K. The identified reactions are incorporated in a numerical simulation of the experiments that captured the O₂ evolution from perchloric acid decomposition, thus validating the proposed reaction mechanism. The primary objective of this study is to identify initiation reactions and important reaction pathways leading to the formation of decomposition products, such as O₂, during decomposition. This study aims to theoretically explain all the observations made during previous experiments and also to provide additional details thus reconciling the exciting differences in opinion regarding condensed-phase HClO₄ decomposition pathways.

4.2 Molecular modeling and numerical simulation

4.2.1 Description of model used in QM calculations

In this study, QM calculations are performed using the gaussian 09 program package to identify new reaction pathways [20]. Searches for transition state (TS) structures of the reaction are performed using density functional theory (DFT) and low-level basis sets, such as B3LYP/6-31G(d). After identification of TS structures having a single negative frequency, intrinsic reaction coordinate (IRC) calculations were performed to ensure that the TS structure connects the reactants to the expected products [21, 22]. Following IRC calculations, thermodynamic properties, such as Gibbs free energy and enthalpy, are calculated using higher-order QM methods for both the equilibrium species and TS structures. Specifically, we used the double-hybrid DFT method, B2PLYP in which exact HF exchange is combined with an MP2-like correlation to a DFT calculation [23]. Thus, B2PLYP method has an accuracy comparable to that of MP2 computations.
Furthermore, unlike hybrid-GGA and meta GGA DFT functionals, the double hybrid DFT methods such as B2PLYP offer unique capability of calculating both main-group thermochemistry and barrier heights within 5-10 kJ/mol [24, 25]. The combination of high accuracy with reasonable computational cost makes B2PLYP and similar, recently developed methods attractive for various thermochemistry calculations as discussed by Martin and Santra [26]. Along with B2PLYP, we used a polarization consistent basis set, aug-pc2 along with addition of 2 high-exponent d functions with a stride factor of 2.5 for the chlorine atom. Based on highly accurate atomization energy calculations, this basis set has been recommended by Martin et al. [27, 28] for molecules with extreme case of inner polarization such as HClO$_4$ and Cl$_2$O$_7$. The effect of solvation is calculated using CPCM model [29], which provides some advantages over other solvation models in the case of HClO$_4$ solution having high permittivity (~100) [30]. QM calculations are performed at 298 K and 1 atm.

### 4.2.2 Details of numerical simulation

Furthermore, we have also performed a numerical simulation in order to validate our proposed mechanism by comparing predicted results with that of experimental data reported by Babaeva and Zinov’ev [16, 17]. During experiments, Babaeva and Zinov’ev [16] observed that gaseous O$_2$ is released during HClO$_4$ decomposition below 373 K. Along with O$_2$, they also observed traces of HClO$_4$ and chlorine-oxides (Cl$_x$O$_y$) in the gaseous phase, which evaporated during the decomposition process. It is to be noted that due to the release of O$_2$ and evaporation of species during decomposition, the mass of the condensed phase ($m_j$) is a function of time. In order to simulate experimental set-up and conditions, in our simulations we used control volume approach.
similar to one of our earlier works to develop mass-conservation equations for the mass of the condensed phase as well as mass-fraction of species in liquid phase $\left( y_{l,j} \right)$, where $N$ is the number of species [31]. The mass of oxygen released is calculated by solving the following equation for the rate of change of mass of $O_2$ in gaseous phase:

$$\frac{dm_{O_2}}{dt} = m_l y_{l,O_2} k_{O_2}$$

where $m_l = \text{total mass of liquid phase or solution}$,

- $m_{O_2} = \text{mass of gaseous } O_2 \text{ released during decomposition}$,
- $y_{l,O_2} = \text{mass fraction of } O_2 \text{ in liquid phase}$,
- $k_{O_2} = \text{rate at which } O_2 \text{ is released from the liquid to gaseous phase after formation}$

A solution to the above set of nonlinear differential equations are obtained using the DVODE solver developed by Brown et al. [32].

The species generation term $\left( \dot{w}_j \right)$, which is used in the mass-conservation equations for liquid phase species, is a function of reaction rate constants and mass fractions of species. In the rate constants calculation, both the kinetic and diffusive effects are considered as described in one of our previous works [33]. The effective viscosity of the liquid phase is calculated based on mass fraction of $\text{HClO}_4$ and $\text{H}_2\text{O}$ present in liquid phase. The viscosity value of $\text{HClO}_4$ solution is taken from the experimental work done by Brickweede [34] and for water, viscosity is taken to be ~0.35 mPa-s in the temperature range of 333-353 K used to perform the simulations. Other than $\dot{w}_j$, mass-fractions of species in liquid phase $\left( y_{l,j} \right)$ are also a function of the rate at which liquid phase species evaporate, which is calculated using the kinetic approach similar to our previous work [31]. In this approach, the rate of evaporation follows an Arrhenius type of relation involving $A_j = \text{pre-exponential factor}$ and $E_{a,j} = \text{barrier involved in evaporating from liquid phase to gaseous phase}$,
which is analogous to the enthalpy of evaporation. Based on our previous studies [31] and data available in literature [35], we have used following values of evaporation parameters for the species: For oxygen which can readily release from liquid to gas phase, $E_{a,O_2} = \sim 5 \text{ kJ/mol}$; higher molecular weight species such as HClO$_4$ and chlorine-oxide compounds formed during decomposition can have $E_a$ values in the range of 42-63 kJ/mol. In this study, we have used average value of $E_a \sim 50 \text{ kJ/mol}$. Evaporation of water present in the solution or formed during decomposition is also taken into account. The value of $E_{a,H_2O} \sim 40 \text{ kJ/mol}$ in the temperature range used to perform experiments (333-353 K). The value of $A_j$ is assumed to be same for all the species ($\sim 1000$). The effect of the evaporation parameters on simulation results are further examined in Section 4.3.3. by calculating error bars. In these calculations, pre-exponential factor, $A_j$ for each species is varied by a factor of 10, corresponding to an increase or decrease of $E_a$ by $\sim 7 \text{ kJ/mol}$, thus encompassing the entire range of possible values of $E_a$ for higher molecular weight species ($\sim 42$-63 kJ/mol).

From previous studies, it is known that HClO$_4$ solutions are highly non-ideal [36]. This non-ideality has been taken into account by incorporating the activity coefficient of HClO$_4$ in calculating $\dot{w}_j$ in our simulation. The activity coefficients are used as reported by Karelin and Tarasenko [36]. The uncertainty involved in the reported values is $\sim 5$-$15\%$ which has been used to calculate the error bars in our simulation.

Sensitivity analysis is also performed to identify sensitive and critical reactions in the proposed mechanism by changing pre-exponential factor, $A_i$ of $i$-th reaction by 10%. Sensitivity coefficients are then calculated as follows [31]

$$S_{ik} = \frac{A_i \Delta y_k}{y_k \Delta A_i}$$
where \( S_{ik}, \Delta A_i \) and \( \Delta y_k \) represent, respectively, the sensitivity coefficient, change in pre-
exponential factor of \( i \)-th reaction and change in mass-fraction of \( k \)-th species.

4.3 Results and Discussion

In order to study the chemical kinetics as well as to explain the experimental observations
during decomposition releasing \( \text{O}_2 \), a reaction mechanism is proposed consisting of 14 species and
15 reactions. The details of these reactions are provided in Table 4.1. In addition to these reactions,
we also identified many other reactions. However, based on sensitivity analysis and thermodynamic
quantities, such as barrier heights of the reaction, those additional reactions are not considered to
be important during the initial phase of \( \text{HClO}_4 \) decomposition below 373 K.

It is to be noted that since our proposed mechanism has reactions involving \( \text{O}_2 \) whose ground
state is a triplet, reactions such as \( \text{R9}, \text{R11}, \text{R12}, \text{R14} \) and \( \text{R15} \) undergoes a change in the total
electronic spin state from reactants to products. In quantum mechanics calculations, such changes
in spin state are not allowed [37, 38]. Harvey et al. provided extensive details on different methods
that can be used to calculate barriers for spin-forbidden reactions [38, 39]. One of the most common
methods used to deal reactions involving change in total-spin state requires knowledge of the
potential energy surface for every spin state involved for all structures along with the coupling
between different spin states. However, this method is extremely demanding and computationally
expensive. One of the easier methods proposed by Harvey et al. [39] to deal with spin-forbidden
reactions is to calculate TS of the reaction based on relativistic chemistry methods using spin-orbit
Hamiltonian, which includes the relativistic effects of spin-orbit coupling. This method is also
computationally extensive but much less tasking than the former method. Their study revealed that
the inclusion of spin-orbit coupling lowers the activation energy by \( \sim 13-21 \text{ kJ/mol} \) for heavy
metals, such as gold, where the relativistic effects are significant. In this study, we have accessed the effects of spin-orbit coupling for above-mentioned spin-forbidden reactions by lowering their barriers by the same amount reported by Harvey et al. for heavy metals [39]. Although it is a very crude way of incorporating the effect of total spin-change across the reactions, this approach has helped us to qualitatively examine the effect of spin-forbidden reactions on the results of our numerical simulation without performing computationally extensive relativistic calculations. Results from numerical simulations performed by lowering barriers of above-mentioned spin-forbidden reactions in our mechanism show that these reactions are not very sensitive to their barrier height. Thus, it is evident that the change of spin state in reactions involving O₂ does not have any significant impact on the results of our simulation. Hence, in this study we made no further effort to examine the impact of spin-orbit coupling in spin-forbidden reactions.

Based on the proposed reaction mechanism, we discuss in Section 4.3.1 regarding the chemical kinetics involved during initiation and the formation of perchloric acid anhydride, one of the most common intermediates observed during experiments involving HClO₄. In the following section 4.3.2, we discuss reaction pathways for O₂ release during decomposition. The validation of the proposed mechanism is provided in Section 4.3.3.

Table 4.1 Gibbs free energy barrier ($\Delta G$) and enthalpy barrier ($\Delta H$) in forward ($f$) and backward ($b$) direction (kJ/mol) of important reactions governing the initial phase of HClO₄ decomposition in liquid phase below 373 K based on QM calculations

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta G_f$</th>
<th>$\Delta G_b$</th>
<th>$\Delta H_f$</th>
<th>$\Delta H_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>HClO₄ → OH + ClO₃</td>
<td>216.0</td>
<td>0</td>
<td>265.0</td>
<td>0</td>
</tr>
<tr>
<td>R2</td>
<td>2HClO₄ → O₃ClOClO₃ + H₂O</td>
<td>196.0</td>
<td>157.3</td>
<td>156.9</td>
<td>119.4</td>
</tr>
<tr>
<td>R3</td>
<td>2HClO₄ → ClOCl₀₂ClO₂ + H₂O</td>
<td>177.5</td>
<td>160.7</td>
<td>143.9</td>
<td>117.2</td>
</tr>
<tr>
<td>R4</td>
<td>HClO₄ + H₂O ↔ [ClO₄]⁺ + [H₃O]⁺</td>
<td>0</td>
<td>57.0</td>
<td>0</td>
<td>57.0</td>
</tr>
<tr>
<td>R5</td>
<td>HClO₄ + [H₃O]⁺ ↔ [ClO₃]⁺ + 2H₂O</td>
<td>111.8</td>
<td>0</td>
<td>161.0</td>
<td>0</td>
</tr>
<tr>
<td>R6</td>
<td>[ClO₄]⁻ + [ClO₃]⁺ ↔ O₃ClOClO₃</td>
<td>0</td>
<td>125.5</td>
<td>0</td>
<td>174.4</td>
</tr>
<tr>
<td>Reaction</td>
<td>Energy (kJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R7 $\text{O}_3\text{ClOClO}_3 + [\text{ClO}_4^-] \leftrightarrow \text{O}_2\text{ClOOOCIO}_2 + [\text{ClO}_4^-]$</td>
<td>111.4 244.4 74.0 201.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R8 $\text{O}_3\text{ClOClO}_3 \leftrightarrow \text{O}_2\text{ClOOOCIO}_2$</td>
<td>134.0 154.8 135.3 133.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R9 $\text{O}_2\text{ClOOOCIO}_2 \leftrightarrow \text{O}_2\text{ClOClO}_2 + \text{O}_2$</td>
<td>91.8 243.9 92.6 196.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R10 $\text{O}_2\text{ClOClO}_2 \leftrightarrow \text{OCIOOOClO}$</td>
<td>96.7 145.6 94.5 186.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R11 $\text{OCIOOOClO} \leftrightarrow \text{ClOClO}_2 + \text{O}_2$</td>
<td>98.1 223.4 123.8 174.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12 $\text{ClOClO}_2 \leftrightarrow \text{ClOCl} + \text{O}_2$</td>
<td>81.4 189.5 84.6 148.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R13 $\text{ClOCl} + \text{ClOCl} \leftrightarrow \text{ClOOCl} + \text{Cl}_2$</td>
<td>138.6 153.8 90.2 112.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R14 $\text{ClOOCl} \leftrightarrow \text{Cl}_2 + \text{O}_2$</td>
<td>121.5 297.8 121.5 260.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R15 $\text{ClOOCl} + \text{ClOOCl} \leftrightarrow 2\text{Cl}_2 + 2\text{O}_2$</td>
<td>138.7 491.2 89.4 366.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Enthalpy and Gibbs free energy of the acid-base reaction, **R4** is calculated based on experimentally obtained pKa value of HClO\(_4\) ~ -10 [30]

### 4.3.1 Initiation of HClO\(_4\) decomposition and formation of perchloric acid anhydride

In earlier works on liquid-phase decomposition of perchloric acid, two different initiation steps were reported based on experimental observations [9, 11, 16]. Using QM calculations, we theoretically studied those earlier reported initiation steps (**R1** and **R2**) and identified an additional initiation step (**R3**), which has comparable barrier heights to that of **R2**. While **R1** is a unimolecular reaction involving the bond breaking of HO-ClO\(_3\) to form OH and ClO\(_3\), **R2** is a bimolecular reaction forming H\(_2\)O and perchloric acid anhydride, O\(_3\)ClOClO\(_3\) reported by Zinov’ev and Babaeva [16]. QM calculations suggest that HClO\(_4\) decomposition can also be initiated via another bimolecular reaction **R3**, forming H\(_2\)O and a newly found intermediate, O\(_2\)ClOOOCIO\(_2\) which is an isomer of O\(_3\)ClOClO\(_3\). The transition state and molecular structures of anhydrides formed during initiation steps **R2** and **R3** are provided in Fig. 4.1. As can be observed from Fig. 4.1, two HClO\(_4\) molecules can approach each other in two different ways. While in reaction **R2**, oxygen from one HClO\(_4\) molecule approaches the chlorine atom of other HClO\(_4\) molecule to form...
O$_3$ClOClO$_3$ and H$_2$O, in reaction **R3** oxygen atoms from two HClO$_4$ molecules approaches each other to form O$_2$ClOOOCIO$_2$ and H$_2$O.

From Table 4.1, it can be observed that **R1** is highly endothermic and hence, it is not expected to play significant role during initiation below 373 K in a solution phase. Based on QM calculations, it can then be concluded that initiation of HClO$_4$ decomposition proceeds via formation of H$_2$O, O$_3$ClOClO$_3$ and O$_2$ClOOOCIO$_2$. This study thus validates the conclusion made by Zinov’ev and his coworkers [16] regarding initiation. However, it is to be noted that the Gibbs
free energy barriers of both initiation steps, R2 and R3 are significantly high (~175-197 kJ/mol). Hence unlike previously made conclusions by Zinov’ev et al. [16], QM calculations suggest that the initiation step is not likely to be a rate determining step in the HClO₄ decomposition and formation of perchloric acid anhydride during decomposition below 373 K. Instead, we have identified a new reaction pathway as shown in Fig. 4.2 through which perchloric acid anhydride, O₃ClOClO₃ can be formed.

![Reaction Pathway Diagram]

Figure 4.2 Dominant reaction pathway for formation of O₃ClOClO₃ to release O₂ during initial phase of HClO₄ decomposition.

It is well known that acids in the presence of H₂O undergo acid-ionization or acid-base reaction as follows: HA + H₂O ⇌ A⁻ + [H₃O]⁺, where HA is the acid that loses a proton to form a conjugate base (A⁻). The proton is transferred to the base, H₂O creating a conjugate acid, [H₃O]⁺. Perchloric
acid being a very strong acid, having a pKₐ ~ -10 [28], its corresponding acid-base reaction (R4) is highly exergonic with ΔG_rxn = pKₐRTln(10) = -57 kJ/mol at a temperature of T=298 K. Hence, a very small concentration of H₂O produced during initiation step (R2/R3) is enough to start the reaction R4, producing ions [H₃O]⁺ and [ClO₄]⁻. The acid-base reaction R4 is similar to the reaction producing monohydrate as mentioned by Babaeva and Zinov’ev [16] in their study. Once [H₃O]⁺ is formed, it can react with HClO₄ to form H₂O and [ClO₃]⁺ ion via R5, whose Gibbs free energy barrier is approximately 84 kJ/mol lower than that of the initiation step. Therefore, once [H₃O]⁺ ions are formed via R4, H₂O concentration increases primarily by R5, and the water concentration is being concomitantly reduced by R4 to produce more ions, making the decomposition process become self-sustaining. The process continues until HClO₄ is completely consumed. Simultaneously, [ClO₄]⁻ and [ClO₃]⁺ ions formed via R4 and R5, respectively, can react among themselves to form Cl₂O₇ via a barrierless reaction, R6. From the above discussion, it is worth noting that H₂O and [H₃O]⁺ act as chain carriers in the proposed mechanism, and while R4 is a chain-propagation reaction, R5 is a chain-branching reaction in which the number of chain carriers increases in each propagation step. Thus, concentration of chain carrier, H₂O, increases after every cycle which further increase the concentration of ions ([H₃O]⁺, [ClO₄]⁻, [ClO₃]⁺) formed during the next cycle. In this way, process tends to grow exponentially, leading to a rapid acceleration of the reaction. Furthermore, it is to be noted that summation of reactions R4, R5 and R6 gives the initiation step R2, which was reported earlier as the key step determining the rate of formation of O₃ClOCIO₃ during decomposition based on experimental observations [17]. Therefore, our study based on QM calculations validate the previously made hypothesis and further provide additional details on chemical kinetics involved during decomposition.
Numerical simulations are performed using the proposed mechanism listed in Table 4.1, which further elucidate the role of ions and ionic reactions during decomposition. The results are shown in Figs. 4.3, 4.4 and 4.5 below. From an inspection of Fig. 4.3, it is observed that an induction period exists before HClO₄ decomposition is initiated. However, it decomposes very rapidly thereafter. Babaeva and Zinov’ev [17] also reported the existence of an induction period followed by sharp rise in reaction rate during HClO₄ decomposition. As can be observed from Fig. 4.3, the induction period is characterized by growth of the ion pool of [H₃O]⁺ and [ClO₄]⁻, along with H₂O and O₃ClOClO₃, approximately according to exponential law (ln \( y \approx C t \); where \( C \) is a constant) as explained earlier. Based on previous discussion, it is evident that H₂O and ion pools are formed during decomposition via chain reactions R4 and R5. Results from numerical simulation also show that without R5, ions pools and H₂O are not formed to any extent and HClO₄ decomposition does not occur. Since R4 is barrierless and highly spontaneous, R5 is the rate-determining reaction in the chain. Thus, the rate at which species [H₃O]⁺, [ClO₄]⁻, [ClO₃]⁺, and H₂O are formed during the induction period is highly sensitive to the barrier height of R5. Therefore, the duration of the induction period as well as the rate at which HClO₄ decomposes and O₃ClOClO₃ forms during decomposition is a function of barrier height of reaction R5. Numerical simulations show that even a small change of Gibbs free energy barrier (± 2 kJ/mol) drastically changes the rate of species formation/decomposition and the duration of induction period making it one of the most sensitive reactions in the mechanism. The results of the simulation are shown in Fig. 4.4, from which it can be observed that the results are changed to a slightly more significant extent when the barrier is increased compared to when it is reduced by the same amount of Gibbs free energy. Hence from the above discussion, it is evident that ions play a critical role during initial phase of perchloric acid decomposition and are indispensable for O₃ClOClO₃ formation and HClO₄ decomposition to occur.
The potential energy surface (PES) of O₃ClOClO₃ formation during decomposition is provided in Fig. 4.5. In this figure, species mentioned within parentheses represent one of the products of the previous reaction; however, it does not take part in the subsequent reaction. For instance, in reaction R4, both [H₃O]⁺ and [ClO₄]⁻ are formed. However, in the subsequent reaction R5, only [H₃O]⁺ react with HClO₄ to form [ClO₃]⁺ and H₂O. From the figure and Table 4.1, it can be observed that once H₂O is formed, the newly proposed reaction pathway for O₃ClOClO₃ formation is highly spontaneous and exothermic.

Figure 4.3 Mass fraction (y_i) of H₂O, [H₃O]⁺, [ClO₄]⁻, O₃ClOClO₃ (plotted in log scale, base 10) and HClO₄ over time (t) using the proposed mechanism. Decomposition temperature, T=353 K and initial mass fraction of anhydrous perchloric acid, y_{HClO₄,0}=1.
Figure 4.4 Mass fraction ($y_i$) of HClO$_4$ and O$_3$ClOClO$_3$ over time using the proposed mechanism showing the impact of barrier height of reaction R5. Decomposition temperature, $T$=353 K and initial mass fraction of anhydrous perchloric acid, $y_{\text{HClO}_4,0}=1$)
4.3.2 Reaction pathways for $O_2$ evolution during initial phase of perchloric acid decomposition

In earlier studies on liquid-phase decomposition of HClO$_4$, significant efforts were expended to explore decomposition characteristics of the perchloric acid solution at different temperatures and concentrations [16, 17]. In these studies, primary objectives were to investigate the initiation step and the characteristics of decomposition product, $O_2$ evolution over time during decomposition. These studies provided invaluable information about the decomposition characteristics of perchloric acid in the condensed phase. One of these characteristics is that the $O_2$ evolution curve consists of three phases resembling an S-shaped curve. However, reaction pathways of $O_2$ evolution and the chemical kinetics involved during the decomposition process.
explaining the S-shaped decomposition curve were never studied in detail. Using QM calculations, we have proposed a reaction pathway for O$_2$ formation during decomposition, which explains the experimentally observed phenomena as well as provide additional details of the decomposition process. The newly proposed reaction pathway for O$_2$ formation is provided in Fig. 4.6 below. The TS structures of the reactions are also shown in Fig. 6, and the details of the reactions involved are provided in Table 4.1. From QM calculations, we observed that O$_3$ClOClO$_3$ formed via R6 can undergo decomposition to release O$_2$ and in the process forms lower molecular weight Cl$_x$O$_y$ compounds, which undergo similar decomposition steps to release more O$_2$. As can be observed from TS of R7/R8 in Fig. 4.6, oxygen on the chlorine atoms in O$_3$ClOClO$_3$ can approach each other in an attempt to release O$_2$. However, before releasing first molecule of O$_2$, O$_3$ClOClO$_3$ first undergoes isomerization to form O$_2$ClOOOCIO$_2$. From the molecular structure of O$_2$ClOOOCIO$_2$, it can be observed that O$_2$ is loosely bonded to other atoms in the molecule. Hence, once O$_2$ClOOOCIO$_2$ is formed, O$_2$ is released promptly via R9 having barrier height of ~92 kJ/mol. Similar to O$_3$ClOClO$_3$, O$_2$ClOClO$_2$ formed in R9 from O$_2$ClOOOCIO$_2$ further releases O$_2$ in two steps via R10 and R11. In the process, a new lower molecular weight Cl$_x$O$_y$ intermediate, ClOClO$_2$ is formed which releases O$_2$ via R12 producing ClOCl in the process. Using additional TS searches, we observed that ClOCl can further react to form O$_2$ and Cl$_2$. However, barriers of these reactions are in the range of ~147 kJ/mol. Hence, these reactions do not play a critical role in O$_2$ release during initial phase of perchloric acid decomposition below 373 K. It is to be noted that both the enthalpy ($\Delta H_{rxn} = \Delta H_f - \Delta H_b$) and Gibbs free energy ($\Delta G_{rxn} = \Delta G_f - \Delta G_b$) of the reactions (R8-R12) involved in the O$_2$ reaction pathway are negative, which indicates that the O$_2$ releasing process during perchloric acid decomposition is exothermic as well as spontaneous.
Figure 4.7 below shows the numerical simulation result for \( \text{O}_2 \) evolution during decomposition using the proposed mechanism provided in Table 4.1. Similar to the experimental observations made by Babaeva and Zinov’ev [17], the \( \text{O}_2 \) evolution curve predicted by numerical simulation is also S-shaped and comprised of three stages: 1) initial phase of decomposition defined as the induction period, 2) active stage when bulk of \( \text{O}_2 \) is released in a short period of time, and 3) reaction-cessation phase when rate of \( \text{O}_2 \) release is negligibly small. As mentioned in Sect. 4.3.1, the early phase of decomposition is characterized by the growth of ion pools, \( \text{H}_2\text{O} \) and \( \text{O}_3\text{ClOClO}_3 \) via reaction pathways shown in Fig. 4.2. During this phase, rates of reactions involved during decomposition are low due to small concentrations of \( \text{H}_2\text{O} \) and ions in the solution. As a result, no appreciable amount of \( \text{HClO}_4 \) decomposition occurs via R4 and R5. However, since \( \text{H}_2\text{O} \) and ions are formed in an exponential manner, reaction rates of R4 and R5 also increase exponentially. At a certain point depending on the forward barrier of R5, when \( \text{HClO}_4 \) consumption accelerates rapidly via R4 and R5, the rate of \( \text{O}_2 \) formation increases steeply thereby marking the beginning of the second phase of decomposition and the end of the induction period. It is to be noted from Fig. 4.7 that the second, active phase of decomposition lasts for a short period of time and the rate of \( \text{O}_2 \) release becomes almost negligible as soon as \( \text{HClO}_4 \) concentration in the solution approaches zero.

From our sensitivity analysis, it is observed that the duration of this active stage depends on the forward free energy barrier of reaction R5, as well the backward free energy barrier of reaction R4, which is determined by the pKₐ value of perchloric acid. The higher the forward barrier of reaction R5, longer is the duration of the active stage and vice-versa. The third phase of decomposition starts when the concentration of \( \text{HClO}_4 \) in the solution becomes negligibly small, which implies that R4 and R5 are no longer relevant. Hence, ion pools and \( \text{O}_3\text{ClOClO}_3 \) are depleted, which are
required to release O₂ during HClO₄ decomposition. From the above discussion, it is noteworthy that the S-shape of O₂ evolution curve is attributed to the exponential growth of critical intermediates [H₃O]^+, [ClO₄]⁻, H₂O, and Cl₂O₇ in the solution via ionic reactions R₄, R₅ and R₆ until HClO₄ concentration becomes negligibly small.
Figure 4.6 Dominant reaction pathway for formation of O₂ during initial phase of HClO₄ decomposition.
In this section, we provide validation of the proposed mechanism by comparing numerical simulation results with that of experimental data available in literature [17]. Babaeva and Zinov’ev performed experiments using anhydrous perchloric acid (100% concentration) at temperatures in the range of $T = 333$-$353$ K. In these experiments, authors monitored the amount of $O_2$ released during decomposition over time, based on which they reported the induction period and the reaction rate of the decomposition at different decomposition temperatures. They observed that as temperature increases, the induction period ($\tau$) decreases associated with higher reaction rate and increased amount of $O_2$ release during decomposition. They further reported that there exists a

Figure 4.7 Evolution of $HClO_4$ and $O_2$ (plotted in log scale, base 10) over time during the decomposition process at temperature, $T=353$ K and initial mass fraction of anhydrous perchloric acid, $y_{HClO_4,0} = 1$. Volume of $O_2$ is calculated at s.t.p; standard temperature ($T$) and pressure, ($P$) $T = 273.15$ K, $P = 1$ atm=$101.325$ kPa.
logarithmic relation between the induction period and decomposition temperature, $T$ (ln $\tau \sim T$). Using our proposed mechanism, numerical simulations were performed to capture all the above mentioned experimentally observed phenomena. The simulation results and the comparison with the experimental data are provided in Fig. 4.8. Since the duration of induction period is highly sensitive to the barrier height of reaction $R5$ for these simulations, we have calculated the Gibbs free energy barrier of $R5$ at higher temperatures used during experiments. Although solvation models are parametrized at $T = 298$ K, these calculations at higher temperature provide a qualitative estimation of how barrier of $R5$ changes with temperature. From calculations performed at higher temperature, we observed that in the temperature range of 333-353 K, Gibbs free energy barrier of $R5$ is $\sim 103$ kJ/mol which is $\sim 9$ kJ/mol lower than the barrier height calculated at $T = 298$ K in Table 4.1. This approach has provided an improved temperature dependence of reaction rates during simulation. From Fig. 4.8, it is evident that our proposed mechanism is able to predict all the key features of anhydrous perchloric acid decomposition below 373 K. Figures 4.9 (a) to 4.9 (d) show comparison of numerically predicted O$_2$ evolution with that obtained experimentally for four different temperatures. The zoomed view of early stage of decomposition is provided in the inset for each figure to provide closer examination of the induction period. It is to be noted that during a few experiments, some amount of O$_2$ release was observed within $\sim 1$-$2$ min of heating during the induction period. These small amounts were attributed to the release of dissolved O$_2$ upon heating. In our numerical simulations, however, no consideration was given to any initially, dissolved oxygen. Apart from such initial effect, numerical simulations match very well with the experimentally observed O$_2$ evolution curves in all stages of decomposition process. To assess the effect of species evaporation parameters, viscosity and activity coefficient of HClO$_4$ on simulation results, here-in we calculated error bars based on 95% confidence level by varying each evaporation parameter and viscosity by 10-fold and activity coefficient by $\pm 15\%$, which is the uncertainty
involved in activity coefficient reported by Karelin and Tarasenko [36]. Based on 24 data points, the calculated error bars range within 7-8% of total amount of $O_2$ evolved at a given decomposition temperature. It can further be observed from Fig. 4.8 (d) that the numerical error bar is well within the experimental uncertainty involved in measuring $O_2$ evolved during decomposition. A comparison of the experimentally observed induction period with that of numerical simulations is provided in Fig. 4.10 and Table 4.2. It is to be noted that the duration of the induction period observed during experiment will depend significantly on the sensitivity of $O_2$ measuring apparatus; higher the sensitivity of apparatus, lower will be the reported induction period and vice-versa. Since the sensitivity of the $O_2$ measurements was not indicated, we have defined the induction period for $O_2$ evolution based on the definition used by Zinov’ev and Babaeva [15] in calculating the activation energy of the induction period. The induction period for $O_2$ evolution is the duration during which ≥ 90% of HClO$_4$ is consumed to produce ~1 mL of $O_2$. By examining the $O_2$ evolution data, we also noticed that in most of the cases, the reported induction period was the time when ~1-2 ml of $O_2$ had evolved. This further validates our definition of the induction period for comparison purposes. From Fig. 4.10, it can be observed that similar to experimental observations made by Zinov’ev and Babaeva [16], numerical simulations also predict that the duration of induction period varies logarithmically with that of decomposition temperature. During calculations of uncertainty of induction period based on 24 data points mentioned earlier, it was observed that the induction period is most sensitive to the variation of HClO$_4$ activity coefficient than any other parameters involved in error bar calculations. Furthermore, it was noted that the sensitivity increases as decomposition temperature decreases. At a decomposition temperature of $T = 353$ K, the error bar associated with induction period calculation due to ±15% variation in activity coefficient is less than 1 min (±0.7 mins). However, at $T = 333$ K error bar increases to ~6.5 mins for same ±15%
variation in activity coefficient. Nevertheless, it is to be noted from Fig. 4.9 that the calculated induction period matches very closely with that of the experimental data, and the predicted uncertainty associated with the induction period lies within the experimental uncertainty of ~1-5 mins.

Table 4.2 Comparison of induction period (τ) calculated by numerical simulation with that of experimental data for anhydrous perchloric acid

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>353 K</td>
<td></td>
<td>5.3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>343 K</td>
<td></td>
<td>15.6</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>338 K</td>
<td></td>
<td>27.5</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>333 K</td>
<td></td>
<td>48.2</td>
<td>53</td>
<td>50</td>
</tr>
</tbody>
</table>

Based on the duration of the induction period observed at different temperatures, Zinov’ev and Babaeva [16, 17] also calculated the activation energy (E_a) of the decomposition process from the equation

\[
\log(\tau) = \log(b) + \frac{E_a}{2.303RT}
\]

Since τ varies in a logarithmic manner with that of temperature, the above equation signifies that the activation energy, E_a of the decomposition process during induction period can be determined by the slope of the straight line obtained by plotting log(τ) vs. 1/T which is a constant in the temperature range of 333-353 K. Zinov’ev and Babaeva [16] reported the activation energy to be
The activation energy was found to be 138 kJ/mol. It is noteworthy that due to very steep gradient of logarithmic functions, $E_a$ is found to be highly sensitive to the value of induction period ($\tau$), especially for $\tau$ in the range of ~1-20. We noticed that if $\tau_{353}$ is reduced by even a small amount of 1 min, $E_a$ increases by ~13 kJ/mol and vice-versa. As can be observed from the reported data, uncertainty in induction period predictions can range from minimum of 1 min to ~5 mins which leads to 12 kJ/mol variation in $E_a$ among the experiments. One of the possible reasons for uncertainty could be the release of dissolved oxygen during early stage of heating, which makes it difficult to identify the end of induction period accurately. Furthermore, we observed from the reported data that the value of $E_a$ can vary significantly depending on the choice of temperatures and their corresponding induction periods used to calculate $E_a$. For instance, if $\tau_{343}$ and $\tau_{338}$ are used to calculate the value of $E_a$, we obtain the value of 117 kJ/mol while based on $\tau_{338}$ and $\tau_{343}$, the value calculated is 171.5 kJ/mol. For each experimental data set, we calculated six different activation energies by using all possible combinations of temperature and their corresponding induction periods. Based on above calculations, we observed that experimentally obtained $E_a$ has an average value of 125 kJ/mol, which is reported by Zinov’ev and Babaeva [16]. However, the error bar associated with experimental prediction of $E_a$ based on induction period is observed to be significantly high, ~±12.5 kJ/mol. Thus, it is evident from the above discussion that there exists uncertainty in the calculation of induction periods during experiment which leads to an approximate value of $E_a$. Here-in by performing numerical simulations, we found activation energy of anhydrous perchloric acid decomposition during induction period to be $\sim109\pm4.2$ kJ/mol. It is to be noted that the activation energy found in this study is very close to that reported by Zinov’ev and Babaeva.
[16]; variation is within the experimental uncertainty involved in calculating $E_a$ as mentioned earlier. Furthermore, it is noteworthy that $E_a$ calculated by performing numerical simulations is very close to the Gibbs free energy barrier of reaction, \textbf{R5}, which plays a critical role in the formation of ions and critical species such as H$_2$O and O$_3$ClOClO$_3$ during the induction period.

In a subsequent study, Babaeva and Zinov’ev [17] also examined the effect of HClO$_4$ concentration on the decomposition process. They observed that as the initial concentration of HClO$_4$ in the solution is reduced, the induction period for O$_2$ release is increased considerably along with reduction in amount of O$_2$ evolved during decomposition below 373 K. However, activation energy of the decomposition process at all concentrations was observed to remain same as that of anhydrous perchloric acid solution. During these experiments, authors observed that added water in the solution reacts with HClO$_4$ to produce solid monohydrate ([$\text{H}_3\text{O}^+\text{[ClO}_4^-]$), which is stable below 373 K thus reducing effective concentration of perchloric acid in the solution.

Furthermore, we performed numerical simulations to study the effect of initial concentration of HClO$_4$ in the solution on the decomposition process. Unlike anhydrous perchloric acid solution (100% concentration) where activity coefficient is very close to 1 (~0.93-0.94) [34], activity of HClO$_4$ reduces significantly as the initial concentration of HClO$_4$ in the solution reduces. In these simulations, we used activity coefficients reported by Karelin and Tarasenko [34]. Figures 4.10 and 4.11 show the comparison of numerical simulation results with that of experimental data. Errors bars are also calculated following the similar procedure mentioned earlier. It has been noticed during error bar calculations that at a given decomposition temperature, as concentration of HClO$_4$ in the solution reduces, the sensitivity towards the evaporation parameter and the activity coefficient of HClO$_4$ increases for both the duration of induction period and the amount of O$_2$
evolved during decomposition. We believe that use of more accurate values of activity coefficient and evaporation parameter for HClO₄ will reduce the range of error bars obtained during simulation. Nevertheless, it can be observed from Figs. 4.11 and 4.12 that all the experimentally observed phenomena are very well predicted by the performed numerical simulations. In order to calculate the activation energy of the decomposition process at different HClO₄ concentrations, we calculated induction periods in the temperature range of 333-353 K for each concentration, the details of which is provided in Table 4.3. Similar to conclusion made by Babaeva and Zinov’ev [17], numerical simulation also predicts that the activation energy of the decomposition process during induction period remains same at all concentrations, ~109 kJ/mol. The comparison of numerically predicted induction period with that of experimental data is shown in Fig. 4.13 for different HClO₄ concentrations over the temperature range of 333-353 K.

Table 4.3 Induction period (τ) calculated by numerical simulation at different initial concentrations of HClO₄ solution

<table>
<thead>
<tr>
<th>Decomposition temperature (T in K)</th>
<th>100% (anhydrous perchloric acid)</th>
<th>98.5%</th>
<th>95.8%</th>
<th>94.29%</th>
<th>91.77%</th>
</tr>
</thead>
<tbody>
<tr>
<td>353 K</td>
<td>5.3</td>
<td>6.2</td>
<td>13.9</td>
<td>20.7</td>
<td>54.9</td>
</tr>
<tr>
<td>343 K</td>
<td>15.6</td>
<td>18.4</td>
<td>41.4</td>
<td>62.1</td>
<td>162.4</td>
</tr>
<tr>
<td>338 K</td>
<td>27.5</td>
<td>32.4</td>
<td>72.8</td>
<td>109.3</td>
<td>284.2</td>
</tr>
<tr>
<td>333 K</td>
<td>48.2</td>
<td>57.6</td>
<td>125.1</td>
<td>185.8</td>
<td>491.3</td>
</tr>
</tbody>
</table>
Figure 4.8 Comparison of numerical simulation with experimental data for O$_2$ evolution and its rate of formation during anhydrous perchloric acid decomposition in the temperature range of 333-353 K. Initial mass of acid=1 gm; volume of O$_2$ is measured at s.t.p; standard temperature ($T$) and pressure, ($P$) $T=273.15$ K, $P=1$ atm=101.325 kPa.
Figure 4.9 Comparison of numerical simulation with experimental data for O₂ evolution during anhydrous perchloric acid decomposition in the temperature range of 333-353K. Initial mass of acid=1 gm; volume of O₂ is measured at s.t.p; standard temperature (T) and pressure, (P) 
T=273.15 K, P=1 atm=101.325 kPa.
Figure 4.10 Comparison of induction period ($\tau$) predicted by numerical simulation with that of experimental data. Error bar shown in (a) is calculated based on $\pm 15\%$ variation in HClO$_4$ activity coefficient.
Figure 4.11 Comparison of O₂ evolution and its rate of liberation predicted by numerical simulation with that of experimental data at different initial concentrations of HClO₄ solution for T=353 K and initial mass of solution=1 gm (Volume of O₂ is measured at s.t.p; standard temperature (T) and pressure (P) T=273.15 K, P=1 atm=101.325 kPa)
Figure 4.12 Comparison of O\textsubscript{2} evolution predicted by numerical simulation with that of experimental data at different initial concentrations of HClO\textsubscript{4} solution for T=353 K and initial mass of solution=1 gm. (Volume of O\textsubscript{2} is measured at s.t.p; standard temperature (T) and pressure,(P) T=273.15 K, P=1 atm=101.325 kPa)
Figure 4.13 Comparison of induction period (\(\tau\) in mins) predicted by numerical simulation with that of experimental data at different initial concentrations of \(\text{HClO}_4\) solution in the temperature range of \(T = 333-353\) K (initial mass of solution=1 gm)
4.4 Conclusions

Using QM calculations, we arrived at a detailed reaction mechanism that explains the chemical kinetics involved during the thermal decomposition of perchloric acid solutions below 373 K releasing O$_2$. Furthermore, we identified the initiation steps and reaction pathways of O$_2$ formation during decomposition, which has not been studied previously in significant detail. Similar to conclusion made by earlier researchers [16], our study also shows that the initiation step during HClO$_4$ decomposition involves a bi-molecular reaction forming perchloric acid anhydride, O$_3$ClOClO$_3$ and H$_2$O. In addition to this initiation step, QM calculations suggest that there exists another initiation step which is also bimolecular forming an isomer of perchloric acid anhydride, O$_2$ClOOOClO$_2$ and H$_2$O. However, unlike previously made conclusions regarding role of initiation step in perchloric acid anhydride formation, we have concluded that the rate of HClO$_4$ decomposition and Cl$_2$O$_7$ formation is not determined by the initiation step. QM suggests that perchloric acid anhydride is primarily formed during decomposition via ionic reactions, R4, R5 and R6 where R4 is the rate-determining step in the mechanism. These ionic reactions make the decomposition process self-sustaining by forming H$_2$O, which is a critical species required to form ions during decomposition. This is one of the important findings of this study on HClO$_4$ decomposition. By performing numerical simulations, we observed that H$_2$O and ions are formed in the HClO$_4$ solution in an exponential manner, which reveals itself as an S-shaped curve in the O$_2$ evolution. For the first time, here-in we have provided a detailed reaction pathway for O$_2$ formation during decomposition. QM calculations show that O$_2$ is possibly formed via three unimolecular steps (R9, R10, R11) involving isomer of O$_3$ClOClO$_3$ and lower molecular weight Cl$_x$O$_y$ compounds formed during decomposition. Furthermore, by performing numerical
simulations, our study shows that the newly proposed reaction mechanism is able to predict all the experimentally observed phenomena which confirms the validity of the proposed mechanism.

4.5 References


[28] J. M. L. Martin, “Heats of formation of perchloric acid, HClO₄, and perchloric anhydride,


[38] J. N. Harvey, “Spin-forbidden reactions: computational insight into mechanisms and

Chapter 5

INVESTIGATION OF THERMAL DECOMPOSITION PROCESSES OF HMX AND TAGZT MIXTURES

5.1 Introduction

HMX (C₄H₈N₈O₈, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine), also known as octogen, is a cyclic organic compound consisting of an eight-membered ring of alternating carbon and nitrogen atoms, with a nitro group (−NO₂) attached to each nitrogen atom in the cycle. HMX is one of the most common nitramine-based energetic materials containing −CH₂NNO₂− units into a loop and has similar molecular structure to that of RDX, which is a very well-known explosive. Both RDX and HMX rapidly release large amounts of heat and gas during thermal decomposition or combustion and with the presence of one additional −CH₂NNO₂− unit, HMX has a higher energetic performance than RDX. Moreover, their decomposition/combustion products are relatively non-toxic and non-corrosive leading to their widespread use as explosives in both military and commercial applications such as detonators, primers, mines and plastic explosives. In addition to being used as explosives, these high-density energy compounds are also used as ingredients in gun and rocket propellants [1].

In order to investigate the thermal decomposition and combustion behavior of explosives and propellants containing RDX and HMX as ingredients, several studies have been undertaken over the years [2-26]. While experimental studies were predominant until the end of the twentieth century, with the advancement of computational capability over the past few decades, theoretical studies have also become increasingly important for predictive modeling of the ignition, combustion and detonation behaviors of these energetic materials [27-31]. It is to be noted that
these studies involve only one ingredient (RDX or HMX) to understand the combustion/decomposition characteristics of these nitramine-based propellants/explosives. However, in most practical applications, propellant/explosives are made up of two or more ingredients. In addition to fuel and oxidizer, plasticizer, binder, burn-rate enhancer and/or combustion instability suppressant can also be added [32]. These ingredients often play multiple roles. For example, RDX in the propellant can act both as fuel and oxidizer; commonly used binders such as glycidyl azide polymer (GAP), nitrocellulose, and nitroglycerine also act as burn-rate enhancers owing to their high density of energy content. The choice of ingredients to be used in propellant depends on various factors such as desired flame temperature and burn rate among many others. It has been observed that although GAP has a higher burning rate than RDX, addition of GAP to RDX leads to reduction in burn rate owing to inert gas formation reducing gas-phase heat feedback. However, addition of butanetriol trinitrate (BTTN) has been observed to increase the burn rates considerably. High-nitrogen energetic compounds having large positive heats of formation has gained significant attention in recent years for their ability to increase the burn rate of nitramine-based propellants without producing undesirable smoke or soot. Furthermore, these high-nitrogen energetic ingredients have significant potential to reduce barrel erosion [33]. Triaminoguanidinium azotetrazolate (TAGzT) is one of the commonly used high-nitrogen energetic materials. Few studies have been done to understand the decomposition and burning behavior of TAGzT [33,34]. However, these studies were primarily focused on decomposition behavior of TAGzT as a monopropellant. Thus, these studies do not explain how the decomposition behavior of RDX/HMX changes in the presence of TAGzT and why high-nitrogen energetic compounds such as TAGzT are capable of enhancing the burning rate of RDX/HMX-based nitramine propellants. In this context, Hayden et al. [33] performed thermolysis experiments such as thermogravimetric analysis (TGA)/differential thermal analysis (DTA) coupled with MS to
study the thermal decomposition behavior of RDX-TAGzT mixtures at low and moderate temperatures (below 573 K) using low heating rates (2.5 K/min). Hayden et al. observed that TAGzT starts decomposing earlier (~15 K) when mixed with RDX. Also, mass loss due to RDX decomposition starts at a lower temperature when in mixture with TAGzT. Based on mass spectroscopy (MS) data, they concluded that N$_2$H$_4$ formed during TAGzT decomposition interacts with solid-state RDX to form H$_2$O, N$_2$O and NO leading to early decomposition of RDX in the presence of TAGzT. Furthermore, since the melting point of TAGzT (~468 K) and RDX (~478 K) are within 10 K, the condensed-phase decomposition of RDX is also impacted significantly in the presence of TAGzT. HMX-TAGzT mixtures were also studied by Flanagan et al. [35] using mass spectroscopy and gas chromatography techniques at moderate and high temperatures using high heating rate (2000 K/s). High temperature pyrolysis experiments suggested that the combustion of HMX is modified primarily by NH$_3$, the decomposition product of TAGzT. Hence, it is evident that the presence of TAGzT in the mixture significantly impacts the decomposition characteristics of RDX/HMX in the mixture. Although it is well known that the decomposition products of HMX and RDX are very similar, the melting point of RDX and HMX is significantly different (melting point of HMX is ~70 K higher than RDX). Therefore, it can be concluded that TAGzT will not alter the thermal decomposition characteristics of RDX and HMX in a similar way. Hence, although it is known from Hayden et al.’s [33] study how TAGzT interacts with RDX at low and moderate temperatures, similar study needs to be done for HMX-TAGzT mixtures as well. In this work, using TGA/DSC coupled with FTIR spectroscopy, we studied thermal decomposition characteristics of HMX-TAGzT mixtures at low and moderate temperatures (373-673 K) using low heating rates which has not been studied previously. Understanding the thermal decomposition behavior of solid propellants at low and moderate temperatures is important since processes occurring in condensed phases at these temperatures determine both the amount of heat released on the burning surface of
the propellant and the rate of production and the identity of the reactants in the gas-phase of the flame. Previous studies involving RDX/HMX and TAGzT mixtures were primarily studied by performing experiments. Here-in along with experiments, we have also performed quantum mechanics (QM) calculations to identify important reactions responsible for increased rate of HMX decomposition in presence of TAGzT.

5.2 Details of experimental studies

Using TGA and differential scanning calorimetry (DSC) combined with FTIR spectroscopy, we performed thermal decomposition studies of HMX and TAGzT mixtures. Three different mixtures (10%, 20% and 30% of TAGzT by weight) are used in this work to study interaction between two energetic materials at three different heating rates (15, 20 and 25 K/min). For each experiment, approximately 1 mg of sample was placed in open lid aluminum crucibles. The details of the experimental procedure and the specification of apparatus used for experiments are described in Ref. 36. The spectral transmittance data obtained from FTIR are analyzed following previously used procedures [36] to calculate the mole fraction of gaseous species released during decomposition.

5.3 Details of quantum mechanical (QM) calculations

The Gaussian09 [37] program package was used to study reactions involving TAGzT decomposition products with that of HMX. Searches for transition states were performed using density functional theory (DFT) and low-level basis sets, including B3LYP/6-31G(d). Intrinsic reaction coordinate calculations were performed thereafter to ensure that the obtained transition
state connects the reactants with the expected products [38,39]. To calculate the changes in the thermodynamic properties, such as enthalpy and free energy, higher level basis set, 6-311++G(d,p) was used along with B3LYP [40]. To take into account of reactions taking place in the liquid phase of TAGzT, the CPCM solvation model [41] is used along with acetonitrile as the solvent.

5.4 Results and discussion

The thermal decomposition behavior of HMX and TAGzT mixtures were studied using three different mixture ratios: 1) 90 wt% of HMX mixed with 10 wt% of TAGzT (90-10), 2) 80 wt% of HMX mixed with 20 wt% of TAGzT (80-20) and 3) 70 wt% of HMX mixed with 30 wt% of TAGzT (70-30). For each mixture ratio, we performed experiments at three different heating rates (15, 20 and 25 K/min). The experimental results for each mixture ratio are provided in the following sub-sections, Sects. 5.4.1.1-5.4.1.3.

5.4.1 Details of experimental studies

5.4.1.1 HMX-TAGZT mixture containing 90 wt% of HMX and 10 wt% of TAGzT (90-10)

The thermolysis experiments showed that rates mass loss for the mixture took place in two major exothermic steps for all three heating rates. The first mass loss amounts to ~10%, which is believed to be the wt% of TAGzT added in the mixture. Figure 5.1 (a) and (b) show the comparison of TGA mass loss curves and DSC curves at three different heating ratios (15, 20 and 25 K/min) for the 90-10 mixture ratio. Figure 5.1 (a) shows that depending on the heating rate used, the first phase of decomposition starts at ~483 K. It is to be noted that as the heating rate is reduced, decomposition starts at a lower temperature and vice-versa. As heating rate is reduced, sample of
the mixture is exposed at lower temperatures for longer period of time which increases rate of sample sublimation or solid phase reactions leading to start of decomposition earlier than that at higher heating rates. After completion of first mass loss near ~500 K, the second phase of major mass loss starts from ~553 K, immediately after an endothermic peak is observed in the DSC curve. A similar endothermic peak at 553 K is also observed during pure HMX experiments in this study as well as by Patidar et al. [1]. The comparison of TGA/DSC curves for 90-10 mixture ratio with that of pure HMX and TAGzT is shown in Fig. 5.2 for all three heating rates used in this study. From the figure, it is evident that the endothermic peak at 553 K observed in 90-10 mixture ratio corresponds to the melting of HMX. It is noteworthy that the presence of TAGzT in the mixture did not alter the melting point of HMX in the mixture. Furthermore, from Fig. 5.2 (a) [15 K/min] it is to be noted that the first step of mass loss due to TAGzT decomposition in 90-10 mixture ratio starts at the same temperature as that of pure TAGzT. Hence, it is evident that mixing two ingredients (HMX and TAGzT) in a mixture does not alter the melting point or decomposition temperature of individual ingredient in the 90-10 mixture ratio.
Figure 5.1 TGA and DSC results for HMX-TAGzT (90-10) mixture for three heating rates.
Figure 5.2 Comparison of TGA and DSC results for HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT at three different heating rates (15, 20 and 25 K/min).
In addition to the above-mentioned two major mass loss steps, we noticed that there is a gradual mass loss occurring even after the first phase of decomposition ends by 493-498 K, and it continues until the second major mass loss begins at 553 K. It is to be noticed from Fig. 5.1 (a) that even before HMX melts at $T = 553$ K, ~7-8% of mass loss due to decomposition of HMX in the mixture has already taken place. It is well known that pure HMX undergoes decomposition to some extent even before it melts, either because of sublimation or solid-phase reactions and the amount of decomposition depends on the heating rate used (lower the heating rate, higher is the amount of decomposition before HMX melts) [1]. This has been observed in our experiments on pure HMX as well. However, the amount of mass loss due to solid-phase reactions or sublimation of HMX is not significant (~2% at 25 K/min to ~3.7% at 15 K/min). Hence, it is evident that, owing to interaction of TAGzT or its decomposition products with that of HMX in the mixture, an additional ~4-5% of HMX mass loss occurred even before melting at 553 K. This signifies that even a small amount of TAGzT (10 wt%) in the mixture significantly impacts the decomposition rate of HMX present in the sample.

Along with TGA/DSC curves, we also obtained FTIR spectra which provides information on gaseous species evolved during experiments for wavenumbers ranging from 600-2500 cm$^{-1}$. Figure 5.3 shows the FTIR spectrum at different temperatures. From the figure, it can be observed that during the first major mass loss step, NH$_3$, HCN and N$_2$O are released along with few other species (possibly an azide and hydrazine) observed during TAGzT decomposition. It is to be noted that N$_2$O is not the decomposition product of TAGzT. Hence, from the spectrum it is evident that in addition to TAGzT, HMX also undergoes decomposition to some extent during the first phase of mass loss. Therefore, it can be concluded that TAGzT decomposition products undergo surface reactions with solid-state HMX to accelerate the decomposition process of HMX in the mixture. Once the first mass loss step ends by ~500 K, the strength of N$_2$O peak starts diminishing.
significantly and no peaks corresponding to NH$_3$ and HCN exist, which indicates that TAGzT in the mixture has already undergone almost complete decomposition during the first mass loss step. It is to be noted that peak corresponding to N$_2$O although reduced significantly but still a small peak exists in the spectrum. This indicates that HMX in the mixture undergoes continuous decomposition very slowly even after TAGzT in the mixture is consumed. Other than N$_2$O, no new peaks are observed in the spectrum till ~548 K when peaks corresponding to decomposition products of HMX such as CO$_2$, N$_2$O, CH$_2$O, NO$_2$ and HCN are noted in the spectrum. The intensity of these peaks further increases and few more new peaks (H$_2$O, CO, NO) are observed once HMX melts at 553 K. The FTIR spectrum obtained during liquid-phase decomposition of HMX in the mixture is similar to that of pure HMX.

By performing data reduction using HITRAN spectroscopy database [42], the partial pressure or mole fraction of gaseous species are calculated and shown in Fig. 5.4. The mole fraction of gaseous species released during decomposition of pure TAGzT and HMX are also provided in Fig. 5.4. Mole fraction of each gaseous species released during decomposition of 90-10 mixture is also compared against pure HMX, which is shown in Fig. 5.5. It can be observed from the above figures that the trend of NH$_3$ and HCN evolution during TAGzT decomposition has changed significantly compared to pure TAGzT. In pure TAGzT, HCN evolves first followed by NH$_3$ approximately after 20 K when HCN release during decomposition is almost stopped. Furthermore, the mole fraction of HCN released during pure TAGzT decomposition is much higher than NH$_3$ and occurs over a shorter temperature interval (473-493 K) compared to NH$_3$ which keeps releasing slowly throughout TAGzT decomposition. Unlike pure TAGzT, the release of NH$_3$ and HCN occurs simultaneously for the 90-10 mixture, but the mole fraction of NH$_3$ released is much higher than HCN. Thus, it is evident that in the presence of HMX in the mixture, the reaction pathways involved during TAGzT decomposition has changed relative to that of pure TAGzT.
Although decomposition of TAGzT in the mixture has been impacted significantly in the presence of HMX, the condensed-phase decomposition of HMX is not impacted significantly by the presence of TAGzT in the mixture. It can be observed from Fig. 5.4 that among the gaseous species released during condensed-phase decomposition of pure HMX, N$_2$O and CH$_2$O are the primary ones (mole fraction ~ 0.6%). In addition to N$_2$O and CH$_2$O, mole fraction of other gaseous species released (HCN, NO, NO$_2$, CO$_2$, H$_2$O, CO) are in the range of ~0.1-0.2% with H$_2$O having the highest mole fraction (~0.2%) and CO being the lowest (<~0.1%). Similar trend of gaseous species evolution after HMX melts in the mixture is observed in 90-10 as well. The only difference is that the gaseous species evolution starts a little early at ~549 K for 90-10 mixture compared to pure HMX for which it starts at ~553 K. Thus, it can be concluded that although TAGzT decomposition products react with solid-state HMX during first phase of mass loss to accelerate the rate of HMX decomposition in the mixture, there is no significant effect of TAGzT on condensed-phase HMX decomposition. This is owing to the huge difference (~70 K) in melting point of TAGzT and HMX. TAGzT melts at ~485 K and undergoes almost complete decomposition by ~500 K. Hence, by the time HMX melts at 553 K and starts decomposing in condensed-phase, TAGzT or its decomposition products do not exist in the mixture. Therefore, we do not observe any significant influence of TAGzT on liquid phase HMX decomposition products beyond 553 K. This is unlike to that of RDX whose melting point is very similar to that of TAGzT and hence, liquid-phase decomposition of RDX was observed to be significantly impacted by TAGzT decomposition products [33].
Figure 5.3 FTIR transmission spectra of evolved gases for HMX-TAGzT (90-10) mixture at different temperatures for 25K/min heating rate.
Figure 5.4 Comparison of mole fractions of evolved IR-active species deduced from FTIR transmission spectra during decomposition of HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT.
Figure 5.5 Mole fraction of evolved IR-active species released from HMX-TAGzT (90-10) mixture compared against pure HMX and pure TAGzT for a heating rate of 25K/min.
5.4.1.2 HMX-TAGzT mixture containing 80 wt% of HMX and 20 wt% of TAGzT (80-20)

Figure 5.6 shows the TGA results for HMX-TAGzT (80-20) mixture at three different heating rates. Similar to the HMX-TAGzT (90-10) mixture results discussed earlier, two major mass loss steps are observed. Furthermore, the first mass loss again corresponds to the mass percentage of TAGzT present in the mixture, i.e., 20% by weight. However, it is to be noticed that unlike results for the HMX-TAGzT (90-10) mixture ratio, the amount of mass loss between two major steps of decomposition is significantly high. The results indicated that for the HMX-TAGzT (90-10) mixture ratio, the amount of mass loss in the temperature range of 500-553 K (that is after the first mass loss step ends and before the melting of HMX in the mixture begins) is ~7-8 wt%. However, for HMX-TAGzT (80-20) mixture ratio, the mass loss during this intermediate phase of decomposition is significantly higher (ranging from ~10% at 25 K/min to ~25% at 15 K/min). From FTIR spectra, it was observed that although similar gaseous species are released during decomposition at both mixture ratios, the amount of N₂O formed during first phase of decomposition is much more for the 80-20 ratio compared to that of the 90-10 mixture ratio. Therefore, it is evident that the interaction of HMX and TAGzT increases with the wt% of TAGzT in the mixture, and the effect is more predominant at lower heating rates leading to increased decomposition of HMX in the presence of TAGzT.
The evolution of IR-active species mole fraction for the HMX-TAGzT (80-20) mixture is shown in Fig. 5.7 for the 25 K/min heating rate. The mole fraction of each gaseous species released during decomposition of HMX-TAGzT (80-20) mixture is also compared against the HMX-TAGzT (90-10) mixture ratio and pure HMX, which is shown in Fig. 5.8. It can be observed from the above figures that TAGzT decomposition in the HMX-TAGzT (80-20) mixture is impacted in a similar way to that of the HMX-TAGzT (90-10) mixture. However, regarding decomposition of HMX in the mixture, there exists significant differences among two mixture ratios. Although the trend of species evolution remains similar with N₂O and CH₂O being the primary gaseous species released and CO having the lowest mole fraction among all species, the mole fraction of gaseous species released during condensed-phase HMX decomposition has reduced significantly compared to 90-10 mixture. Furthermore, from TGA curve in Fig. 5.6 it can be observed that unlike 90-10 and pure HMX mixture, the 80-20 the mixture is not completely consumed till the end of
decomposition at 573 K. This indicates that unlike HMX-TAGzT (90-10) mixture ratio, where no significant impact of TAGzT is observed on the condensed-phase decomposition of HMX in the mixture, in HMX-TAGzT (80-20) mixture the effect is more significant.

Figure 5.7 Mole fraction of gaseous species released during decomposition of HMX-TAGzT (80-20) mixture.
Figure 5.8 Mole fraction of gaseous species released from pure HMX and two different mixture ratios of HMX-TAGzT (90-10 and 80-20) for a heating rate of 25K/min.
5.4.1.3 HMX-TAGzT mixture containing 70 wt% of HMX and 30 wt% of TAGzT (70-30)

The comparison of all three different mixture ratios used to study thermal decomposition behavior of HMX-TAGzT are shown in Fig. 5.9. As can be observed from the figure, unlike other two mixture ratios discussed previously, mass loss during the first phase of decomposition for 70-30 is significantly higher than that of wt% of TAGzT in the mixture (~60% mass loss). This indicates that along with TAGzT, HMX in the 70-30 mixture is also undergoing significant decomposition during the first phase of mass loss in the temperature range of ~473-493 K. FTIR spectra over different temperatures during decomposition of 70-30 mixture are shown in Fig. 5.10. From these FTIR spectra, it can be observed that during the first phase of decomposition, in addition to N$_2$O, additional species are detected corresponding to HMX decomposition, including HCN, NO, CH$_2$O, CO, CO$_2$ and H$_2$O, along with TAGzT decomposition products NH$_3$ and HCN. The presence of CH$_2$O, CO, CO$_2$ confirms that the ring opening of HMX has taken place during the first mass loss step even before it melts. Similar to HMX-TAGzT (90-10) and (80-20) mixtures, it is noted that N$_2$O vanishes after the first phase of decomposition and also the amount of N$_2$O formed diminishes significantly. In addition to N$_2$O, IR-active species are again detected near ~540 K when CH$_2$O and HCN are observed in the spectra. It is to be noticed that the decomposition of HMX in the mixture started early for the HMX-TAGzT (70-30) mixture relative to that of HMX-TAGzT (80-20) or (90-10) mixtures, for which IR-active species were detected near 548 K. Once HMX in the mixture melts at 553 K, several additional species are detected. However, the amount of these species, which corresponds to the condensed-phase decomposition of HMX in the mixture, is significantly less than that of observed for the HMX-TAGzT (80-20) and (90-10) mixtures. The mole fraction of gaseous species released during decomposition and their comparison against 80-20, 90-10 and pure HMX is shown in Fig. 5.11 and Fig. 5.12, respectively. As can be observed from these figures, significant amount of HMX decomposition has taken place during the first mass
loss step in the temperature range of 473-493 K. Beyond this temperature range, the remaining HMX in the mixture slowly undergoes decomposition releasing gaseous products similar to that of other mixture ratios and pure HMX. From the above discussion, it is evident that using different HMX-TAGzT mixture ratios, the extent of decomposition of HMX can be greatly affected.

![TGA and DSC results for HMX-TAGzT (80-20) mixture at different heating rates.](image)

Figure 5.9 TGA and DSC results for HMX-TAGzT (80-20) mixture at different heating rates.
Figure 5.10 FTIR transmission spectra of evolved gases for HMX-TAGzT (70-30) mixture at different temperatures for 25K/min heating rate.
Figure 5.11 Mole fraction of gaseous species released during decomposition of HMX-TAGzT (80-20) mixture.
Figure 5.12 Mole fraction of gaseous species released at 25 KPM for pure HMX and three different mixture ratios of HMX-TAGzT (90-10, 80-20 and 70-30).
5.4.2 Quantum mechanics (QM) calculations

Using QM calculations, Patidar et al. [1] concluded that HMX starts decomposition via unimolecular reaction to form HONO and a cyclic intermediate (INT249a; 249 is the molecular weight) having forward free energy barrier of 43 kcal/mol. The molecular structure of INT249a is provided in Fig. 15. HONO is a very reactive species and participate in many different bimolecular reactions. It can undergo a self-reaction to form NO and NO$_2$, it can react with INT249a formed during initiation to open the ring structure of HMX forming CH$_2$O, N$_2$O, and it can react other decomposition products via several reactions [1]. Hence, based on experimental studies discussed in previous section, it can be concluded that in presence of TAGzT, other reactions than the HONO-elimination reaction must be responsible for the observed decomposition of HMX. Such reactions are likely to involve TAGzT decomposition products. In this work, using QM calculations we studied assisted HONO elimination reactions involving TAGzT decomposition products/intermediates and HMX. It is to be noted that TAGzT in the mixture melts at ~473 K and undergoes condensed-phase decomposition to form NH$_3$, HCN, N$_2$H$_4$ and many other intermediates [34] during the first mass loss step. However, during this phase of decomposition, HMX in the mixture remains in its solid state as it melts at ~553 K. Therefore, condensed-phase TAGzT decomposition products undergo surface reactions with that of solid-state HMX in the mixture. However, in this work, we considered HMX to be in a “molten” condensed phase as well to simplify the computational effort. Although this is a crude way of studying the interaction of TAGzT decomposition products and HMX in the mixture, this study provides a qualitative idea about important low barrier pathways through which HONO can be formed during decomposition of HMX-TAGzT mixtures. The details of the reactions studied in this work are provided in Table 1. Here-in we studied assisted HONO elimination reactions involving TAGzT decomposition products/intermediates such as NH$_3$ (R1), N$_2$H$_4$ (R2) and HCN (R3). As can be observed from
Table 5.1, reactions **R1**, **R2** and **R3** have very similar forward barrier to that of unimolecular reaction involving HMX (43 kcal/mol). Hence, based on QM calculations, it can be concluded that TAGzT decomposition products such as HCN, N$_3$H$_4$ and NH$_3$ do not play critical role in accelerating the rate of HMX decomposition in the mixture.

![Figure 5.13 Molecular structure of INT249a](image)

We studied another pathway through which HONO can be formed from HMX having forward barrier of only ~26 kcal/mol. The QM calculations reveal that the CN$^-$ anion formed during TAGzT decomposition [34] can abstract an H$^+$ from HMX to form HCN and in the process release an NO$_2^-$ anion and the cyclic intermediate INT249a via **R4**. The formed NO$_2^-$ anion can further react with HCN released during TAGzT decomposition to form HONO and CN$^-$ anion via **R5**. It is to be noted that the overall barrier involved in the HONO elimination from HMX in the presence of CN$^-$ anion from TAGzT decomposition is ~17 kcal/mol lower than that in case of pure HMX. The above-mentioned HONO formation pathway based on QM calculations also explains the observation from FTIR spectrum that in the presence of HMX, HCN release in gaseous phase during TAGzT decomposition is reduced. In addition to this, few more reactions are studied involving decomposition products of TAGzT [34] through which HONO and other HMX decomposition products such as N$_2$O, NO, H$_2$O can be formed. The details of these reactions are
provided in Table 5.1 and the structures of TAGzT decomposition products involved in pathways of HONO formation during decomposition of mixture is provided in Fig. 5.14. As can be observed from Table 5.1, NO$_2^-$ anion formed via R4 can also undergo nucleophilic substitution reaction with TAG$^+$ which is a decomposition product of TAGzT to form HONO via R6 and R7. Simultaneously, N$_2$H$_4$ and NH$_3$ formed during TAGzT decomposition can react with HONO to form N$_2$O, NO, NO, H$_2$O via reactions R8-R24. During these reactions, HONO is reformed as well. The intermediate formed during these reactions can also react further with HONO to form N$_2$O, NO, H$_2$O and reform HONO via several reactions (R28-R38). It is to be noted that N$_2$H$_4$ formed during TAGzT decomposition plays a critical role in formation of several HMX decomposition products (N$_2$O, NO$_2$, NO, H$_2$O) which was also previously concluded by Hayden et al. [33] and Flanagan et al. [35] based on reduced ion intensity of N$_2$H$_4$ in mass spectra.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta G_f$ (kcal/mol)</th>
<th>$\Delta G_b$ (kcal/mol)</th>
<th>$\Delta H_f$ (kcal/mol)</th>
<th>$\Delta H_b$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>HMX+NH$_3$ $\leftrightarrow$ INT249a$+$trans-HONO$+$NH$_3$</td>
<td>174.5</td>
<td>263.2</td>
<td>135.1</td>
<td>164.0</td>
</tr>
<tr>
<td>R2</td>
<td>HMX+N$_2$H$_4$ $\leftrightarrow$ INT249a$+$trans-HONO$+$N$_2$H$_4$</td>
<td>174.5</td>
<td>263.2</td>
<td>133.5</td>
<td>162.8</td>
</tr>
<tr>
<td>R3</td>
<td>HMX+HCN+CN$^-$ $\leftrightarrow$ INT249a$+$trans-HONO$+$HCN+CN$^-$</td>
<td>146.4</td>
<td>252.3</td>
<td>79.9</td>
<td>139.7</td>
</tr>
<tr>
<td>R4</td>
<td>HMX+CN$^-$ $\leftrightarrow$ INT249a$+$NO$_2^-$+HCN</td>
<td>108.8</td>
<td>260.2</td>
<td>79.9</td>
<td>190.0</td>
</tr>
<tr>
<td>R5</td>
<td>NO$_2^-$+HCN $\leftrightarrow$ trans-HONO$+$CN$^-$</td>
<td>39.7</td>
<td>0.0</td>
<td>54.8</td>
<td>0.0</td>
</tr>
<tr>
<td>R6</td>
<td>TAG$^+$NO$_2^-$ $\leftrightarrow$ TAG$+$trans-HONO</td>
<td>50.2</td>
<td>0.0</td>
<td>50.2</td>
<td>0.0</td>
</tr>
<tr>
<td>R7</td>
<td>TAG$^+$NO$_2^-$ $\leftrightarrow$ TAG$+$cis-HONO</td>
<td>55.6</td>
<td>0.0</td>
<td>55.6</td>
<td>0.0</td>
</tr>
<tr>
<td>R8</td>
<td>N$_2$H$_4$+trans-HONO $\leftrightarrow$ INTT61A+H$_2$O</td>
<td>120.1</td>
<td>204.6</td>
<td>74.5</td>
<td>160.7</td>
</tr>
<tr>
<td>R9</td>
<td>N$_2$H$_4$+cis-HONO $\leftrightarrow$ INTT61A+H$_2$O</td>
<td>118.4</td>
<td>208.4</td>
<td>73.6</td>
<td>165.7</td>
</tr>
<tr>
<td>R10</td>
<td>INTT61A+cis-HONO $\leftrightarrow$ INTT62A+NO$_2$</td>
<td>103.8</td>
<td>0.0</td>
<td>103.8</td>
<td>0.0</td>
</tr>
<tr>
<td>R11</td>
<td>INTT62A+CN$^-$ $\leftrightarrow$ N$_2$O+NH$_3$+HCN</td>
<td>0.0</td>
<td>322.6</td>
<td>0.0</td>
<td>297.1</td>
</tr>
<tr>
<td>R12</td>
<td>N$_2$H$_4$+cis-HONO $\leftrightarrow$ N$_2$H$_3$+H$_2$O+NO</td>
<td>131.4</td>
<td>155.2</td>
<td>86.2</td>
<td>64.4</td>
</tr>
<tr>
<td>Reaction</td>
<td>Equation</td>
<td>$E_{a}$ (kcal/mol)</td>
<td>$E_{d}$ (kcal/mol)</td>
<td>$ZPE$ (kcal/mol)</td>
<td>$G$ (kcal/mol)</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>---------------</td>
<td>-------------</td>
</tr>
<tr>
<td>R13</td>
<td>$N_2H_3+\text{cis-HONO} \leftrightarrow N_2H_2+H_2O+NO$</td>
<td>87.4</td>
<td>190.4</td>
<td>43.9</td>
<td>105.9</td>
</tr>
<tr>
<td>R14</td>
<td>$N_2H_3+\text{NO} \leftrightarrow \text{INTT61A}$</td>
<td>0.0</td>
<td>66.1</td>
<td>0.0</td>
<td>113.8</td>
</tr>
<tr>
<td>R15</td>
<td>$N_2H_2+\text{cis-HONO} \leftrightarrow N_2H+H_2O+NO$</td>
<td>95.0</td>
<td>200.0</td>
<td>49.0</td>
<td>108.8</td>
</tr>
<tr>
<td>R16</td>
<td>$N_2H+\text{cis-HONO} \leftrightarrow N_2+H_2O+NO$</td>
<td>49.0</td>
<td>376.6</td>
<td>7.9</td>
<td>300.4</td>
</tr>
<tr>
<td>R17</td>
<td>$N_2H_2+\text{NO}_2 \leftrightarrow N_2H_3+\text{cis-HONO}$</td>
<td>3.8</td>
<td>0.0</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>R18</td>
<td>$N_2H_3+\text{NO}_2 \leftrightarrow N_2H_2+\text{cis-HONO}$</td>
<td>0.0</td>
<td>74.9</td>
<td>0.0</td>
<td>78.7</td>
</tr>
<tr>
<td>R19</td>
<td>$N_2H_2+\text{NO}_2 \leftrightarrow \text{cis-HONO}+N_2H$</td>
<td>0.0</td>
<td>77.4</td>
<td>0.0</td>
<td>77.0</td>
</tr>
<tr>
<td>R20</td>
<td>$N_2H+\text{NO}_2 \leftrightarrow N_2+\text{cis-HONO}$</td>
<td>0.0</td>
<td>300.0</td>
<td>0.0</td>
<td>309.2</td>
</tr>
<tr>
<td>R21</td>
<td>$\text{NH}_3+\text{cis-HONO} \leftrightarrow \text{NH}_2\text{NO}+H_2O$</td>
<td>148.5</td>
<td>214.6</td>
<td>105.0</td>
<td>172.0</td>
</tr>
<tr>
<td>R22</td>
<td>$\text{NH}_2\text{NO} \leftrightarrow \text{INTT46A}$</td>
<td>148.5</td>
<td>126.4</td>
<td>147.3</td>
<td>125.9</td>
</tr>
<tr>
<td>R23</td>
<td>$\text{NH}_2\text{NO}+\text{cis-HONO} \leftrightarrow \text{trans-HONO}+\text{INTT46A}$</td>
<td>24.7</td>
<td>7.9</td>
<td>-12.6</td>
<td>-28.5</td>
</tr>
<tr>
<td>R24</td>
<td>$\text{INTT46A}+\text{cis-HONO} \leftrightarrow N_2+H_2O+\text{cis-HONO}$</td>
<td>118.8</td>
<td>461.1</td>
<td>77.0</td>
<td>379.1</td>
</tr>
<tr>
<td>R25</td>
<td>$\text{INTT61A}+\text{trans-HONO} \leftrightarrow \text{INTT90A}+H_2O$</td>
<td>140.2</td>
<td>181.6</td>
<td>94.1</td>
<td>138.1</td>
</tr>
<tr>
<td>R26</td>
<td>$\text{INTT61A}+\text{cis-HONO} \leftrightarrow \text{INTT90A}+H_2O$</td>
<td>140.6</td>
<td>187.0</td>
<td>95.0</td>
<td>144.3</td>
</tr>
<tr>
<td>R27</td>
<td>$\text{INTT61A}+\text{ONNO}_2 \leftrightarrow \text{INTT90A}+\text{cis-HONO}$</td>
<td>71.5</td>
<td>92.0</td>
<td>22.2</td>
<td>45.6</td>
</tr>
<tr>
<td>R28</td>
<td>$\text{INTT90A} \leftrightarrow \text{INTT90B}$</td>
<td>58.6</td>
<td>27.2</td>
<td>57.7</td>
<td>30.5</td>
</tr>
<tr>
<td>R29</td>
<td>$\text{INTT90B} \leftrightarrow \text{INTT46A}+N_2O$</td>
<td>27.2</td>
<td>229.7</td>
<td>31.4</td>
<td>187.9</td>
</tr>
<tr>
<td>R30</td>
<td>$\text{INTT90A}+\text{cis-HONO} \leftrightarrow \text{INTT89A}+H_2O+NO$</td>
<td>82.0</td>
<td>95.0</td>
<td>37.7</td>
<td>5.9</td>
</tr>
<tr>
<td>R31</td>
<td>$\text{INTT89A} \leftrightarrow \text{HNNO}+N_2O$</td>
<td>80.8</td>
<td>238.5</td>
<td>83.3</td>
<td>197.9</td>
</tr>
<tr>
<td>R32</td>
<td>$\text{HNNO}+\text{cis-HONO} \leftrightarrow N_2O+H_2O+NO$</td>
<td>80.8</td>
<td>316.3</td>
<td>36.8</td>
<td>235.6</td>
</tr>
<tr>
<td>R33</td>
<td>$\text{HNNO}+\text{NO}_2 \leftrightarrow \text{cis-HONO}+N_2O$</td>
<td>0.0</td>
<td>207.5</td>
<td>0.0</td>
<td>215.5</td>
</tr>
<tr>
<td>R34</td>
<td>$\text{INTT89A}+\text{cis-HONO} \leftrightarrow \text{INTT88A}+H_2O+NO$</td>
<td>75.7</td>
<td>76.6</td>
<td>30.5</td>
<td>-10.5</td>
</tr>
<tr>
<td>R35</td>
<td>$\text{INTT88A} \leftrightarrow N_2+\text{NO}+\text{NO}$</td>
<td>0.0</td>
<td>409.6</td>
<td>0.0</td>
<td>323.8</td>
</tr>
</tbody>
</table>
Figure 5.14 Molecular structures of intermediates formed during decomposition of HMX-TAGzT mixtures

(Color code: Carbon: Blue; Nitrogen: Dark gray; Hydrogen: Light gray; Oxygen: Red)
5.5 Conclusions

In this work, using thermo-analytical methods TGA/DSC coupled with FTIR spectroscopy, it has been observed that HMX-TAGzT mixtures undergo decomposition via two major mass loss steps. The first mass loss step corresponds primarily to the decomposition of TAGzT after it melts at ~480 K and the second major mass loss step is associated with the liquid-phase decomposition of HMX in the mixture after it melts near 550 K. It has been noted that mixing two energetic ingredients (HMX and TAGzT) does not impact their corresponding melting points in the mixture. Although the first mass loss step is primarily associated with TAGzT decomposition, it has been observed that TAGzT decomposition products react with solid-state HMX in the mixture to release N$_2$O and other decomposition products of HMX even before it melts at 550 K. As the mass fraction of TAGzT in the mixture increases from 10% to 30%, the interaction between TAGzT decomposition products and HMX increases drastically leading to early decomposition of HMX in the presence of TAGzT. For HMX-TAGzT (90-10) and (80-20) mixture ratios, mass loss during the first phase of decomposition is approximately equal to the wt% of TAGzT in the mixture. However, mass loss does not cease to take place even after TAGzT in the mixture is consumed by the end of first major mass loss phase. A gradual mass loss occurs till 550 K (near HMX melting point) due to release of N$_2$O from solid-state HMX in the presence of TAGzT decomposition products. Unlike 90-10 and 80-20, in case of 70-30 mixture ratio, the mass loss during the first phase of decomposition is significantly higher than the wt% of TAGzT in the mixture (~60% mass loss) which signifies that ~50% of HMX in the mixture has undergone decomposition during the first mass loss step itself. FTIR spectra shows that in addition to N$_2$O observed during first phase of decomposition in 90-10 and 80-20, several new HMX decomposition products are observed in case of 70-30 mixture ratio. Thus, it is evident that the rate of HMX decomposition can be altered as needed by using different mixture ratios. Using QM calculations, we identified important
pathways through which HMX can decompose in the presence of TAGzT decomposition products. It has been observed that CN⁻ anion produced during TAGzT decomposition can react with HMX to form the critical intermediate (HONO) required to decompose HMX in a reaction pathway having forward barrier of only 24 kcal/mol. Therefore, compared to the barrier involved during unimolecular decomposition of HMX forming HONO during initiation (43 kcal/mol), the barrier of HONO formation pathway from HMX in presence of TAGzT is reduced by ~20 kcal/mol. In addition, several other HONO formation reactions involving TAGzT decomposition products are studied having barrier lower than 40 kcal/mol. By performing QM calculations along with experiments, this work provides a detailed understanding of the thermal decomposition behavior of HMX-TAGzT mixtures at low heating rates.

5.6 References


[42] I.E. Gordon; L.S. Rothman; C. Hill; R.V. Kochanov; Y. Tan; P.F. Bernath; M. Birk; V. Boudon; A. Campargue; K.V. Chance; B.J. Drouin; J.-M. Flaud; R.R. Gamache; J.T. Hodges; D. Jacquemart; V.I. Perevalov; A. Perrin; K.P. Shine; M.-A.H. Smith; J. Tennyson; G.C. Toon; H. Tran; V.G. Tyuterev; A. Barbe; A.G. Császár, V. M. Devi; T. Furtenbacher; J.J. Harrison; J.-M. Hartmann; A. Jolly; T.J. Johnson; T. Karman; I. Kleiner; A.A. Kyuberis; J. Loos; O.M. Lyulin; S.T. Massie; S.N. Mikhailenko; N. Moazzen-Ahmadi; H.S.P. Müller; O.V. Naumenko; A.V. Nikitin; O.L. Polyansky; M. Rey; M. Rotger; S.W. Sharpe; K. Sung; E. Starikova; S.A. Tashkun;
Chapter 6
SUMMARY AND FUTURE WORK

This work shows that the synergistic application of experimental and computational methods is critical to understand the intricate details of thermal decomposition processes of energetic materials. From discussions in Chapter 2-5, it is evident that experiments provide invaluable information regarding decomposition characteristics and the critical species formed during decomposition at different heating rates and temperatures. However, due to fast reaction rate and extreme reaction conditions involved during decomposition which often impede direct experimental measurement, it is difficult to resolve the complex chemistry involved during decomposition only by performing experiments. To make a knowledge-based improvement and engineering of propellants, it is of paramount importance to understand the chemistry involved during decomposition. Computational methods such as quantum mechanics (QM) calculations, provide a safer and convenient way to study the chemistry/chemical kinetics involved during thermal decomposition of energetic materials.

In Chapter 2 and 3, using quantum mechanics (QM) calculations and thermo-analytical methods (TGA/DSC coupled with FTIR), chemical kinetics involved during condensed-phase AB dehydrogenation is studied in greater detail. One of the key findings of this work is that in contrary to the previous belief, DADB is not the only pathway through which AB dehydrogenation starts. QM calculations suggests that in addition to DADB, another key intermediates required in the formation of H$_2$ is an ionic species, [BH$_4$][NH$_4$]$^+$. This work explains the formation of species observed during experiments and shows that the reaction pathway of all the experimentally observed species (DADB, CDB, BCDB, CTB and borazine) involve BH$_2$NH$_2$ as the critical intermediate. Based on the results shown in this work, further details have been provided on the initiation of decomposition of AB, as well as identification of intermediates and reactions
responsible for the growth to borazine and larger molecular weight ring-containing compounds. Furthermore, it provides additional information on H₂ release pathways which can provide ways to further improve the process of condensed phase AB dehydrogenation. For instance, QM calculations suggest that H₂ release pathway during condensed-phase AB dehydrogenation is diffusion controlled and cyclization during second phase of AB decomposition enhances dehydrogenation. Simulated results match quite well with the experimental findings which confirms the validity of the proposed mechanism.

It is well known that to understand the decomposition behavior of propellant ingredients, one need to study the process at both low (≤ 50 K/min) and high heating rates (2000 K/s). Hence, as a future work, the developed reaction mechanism can be extended further to study AB dehydrogenation at high heating rates (2000 K/s).

In Chapter 4, a detailed reaction mechanism that explains the chemical kinetics involved during the thermal decomposition of perchloric acid solutions below 373 K releasing O₂ is proposed. QM suggests that the decomposition process involves ionic reactions. These ionic reactions make the decomposition process self-sustaining by forming H₂O, which is a critical species required to form ions during decomposition. This is one of the important findings of this study on HClO₄ decomposition. By performing numerical simulations, it has been observed that H₂O and ions are formed in the HClO₄ solution in an exponential manner, which reveals itself as an S-shaped curve in the O₂ evolution. For the first time, a detailed reaction pathway for O₂ formation during decomposition is proposed. QM calculations show that O₂ is possibly formed via three unimolecular steps involving isomer of O₃ClOClO₃ and lower molecular weight ClₓOᵧ compounds formed during decomposition. Furthermore, by performing numerical simulations, this study shows that the newly proposed reaction mechanism is able to predict all the experimentally observed phenomena which confirms the validity of the proposed mechanism. This work can be
viewed as a first step towards development of detailed liquid-phase reaction mechanism for AP combustion modeling. Hence, to develop a comprehensive condensed-phase AP reaction mechanism which is the ultimate goal of this study, as a future work, the logical next step is to study reactions involving HClO$_4$ decomposition products and NH$_3$, another decomposition product of AP.

In Chapter 5, using thermo-analytical methods (TGA/DSC coupled with FTIR), the thermal decomposition characteristics of HMX and TAGzT mixtures are studied at low heating rates (≤ 50 K/min). Three different heating rates (15, 20 and 25 KPM) are used to study the interaction between two energetic materials (HMX and TAGzT) using weight ratios of TAGzT (10%, 20% and 30% of TAGzT by weight). From this study, it is evident that high-nitrogen additives like TAGzT can significantly affect the performance of HMX as a propellant. As the mass fraction of TAGzT in the mixture increases from 10% to 30%, the interaction between TAGzT decomposition products and HMX increases drastically leading to early decomposition of HMX in the presence of TAGzT. Unlike 90-10 and 80-20, in case of 70-30 mixture ratio, the mass loss during the first phase of decomposition is significantly higher than the wt% of TAGzT in the mixture (~60% mass loss) which signifies that ~50% of HMX in the mixture has undergone decomposition during the first mass loss step itself. FTIR spectra shows that in addition to N$_2$O observed during first phase of decomposition in 90-10 and 80-20, several new HMX decomposition products are observed in case of 70-30 mixture ratio. Thus, it is evident that the rate of HMX decomposition can be altered as needed by using different mixture ratios. Using QM calculations, important pathways are identified through which HMX can decompose in the presence of TAGzT decomposition products. It has been observed that CN$^-$ anion produced during TAGzT decomposition can react with HMX to form the critical intermediate (HONO) required to decompose HMX in a reaction pathway having forward barrier of only 24 kcal/mol. Therefore, compared to the barrier involved during
unimolecular decomposition of HMX forming HONO during initiation (43 kcal/mol), the barrier of HONO formation pathway from HMX in presence of TAGzT is reduced by ~20 kcal/mol. As a future work, reaction pathways leading to early formation of N₂O during decomposition of HMX-TAGzT mixtures need to be studied in further detail.
VITA
Tanusree Chatterjee

EDUCATIONAL QUALIFICATION:

- **Ph.D. (2015-2020)** from The Pennsylvania State University, PA, USA (GPA: 4.00/4.00).
  Research Area: Development of detailed chemical reaction mechanisms to investigate the chemical kinetics involved during thermal decomposition and combustion of hydrogen storage and energetic materials using both theoretical (quantum mechanics) and experimental methods (TGA/DSC/FTIR).

- **M.Tech. (2008-2010)** from Indian Institute of Technology (IIT) Kharagpur, India (GPA: 9.28/10.00)

- **B.E. (2004-2008)** from Jadavpur University, Kolkata, India (GPA: 8.84/10.00)

WORK EXPERIENCE:

- **Feb,2011-July,2015**: Prior to coming to Penn State, I had been working for Research and Development wing of General Electric (GE) Aviation for 4.5 years as “Lead engineer” in Combustion Aero Thermal Design team. Worked extensively in combustion CFD doing reacting flow analysis, LES, developing meshing strategy and designing several combustor components.

- **July,2010-Feb,2011**: Worked at Daimler India Commercial Vehicles (DICV) in Thermal analysis of engine team. Performed engine testing at “Automotive Research Association of India” (ARAI), Pune, India.

SUBJECTS OF INTERESTS:

Combustion, CFD, Chemical Kinetics, Quantum Mechanics, Computational Chemistry, Molecular Dynamics, Fluid Mechanics, Turbulence, Thermodynamics, Heat Transfer

PUBLICATIONS:

