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| <p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p> |                   |                                |                                                       |                                                          |                                                   |
| 1. REPORT DATE (DD-MM-YYYY)<br>11-05-2023                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                   | 2. REPORT TYPE<br>Final Report |                                                       | 3. DATES COVERED (From - To)<br>1-May-2015 - 31-Mar-2023 |                                                   |
| 4. TITLE AND SUBTITLE<br>Final Report: Experimental and Quantum Mechanics Investigations for the Development of a Liquid-phase Chemical Reaction Mechanism of RDX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                   |                                | 5a. CONTRACT NUMBER<br>W911NF-15-1-0202               |                                                          |                                                   |
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| 6. AUTHORS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                   |                                | 5d. PROJECT NUMBER                                    |                                                          |                                                   |
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| 13. SUPPLEMENTARY NOTES<br>The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                   |                                |                                                       |                                                          |                                                   |
| 14. ABSTRACT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                   |                                |                                                       |                                                          |                                                   |
| 15. SUBJECT TERMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                   |                                |                                                       |                                                          |                                                   |
| 16. SECURITY CLASSIFICATION OF:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                   |                                | 17. LIMITATION OF ABSTRACT<br>UU                      | 15. NUMBER OF PAGES                                      | 19a. NAME OF RESPONSIBLE PERSON<br>Stefan Thynell |
| a. REPORT<br>UU                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | b. ABSTRACT<br>UU | c. THIS PAGE<br>UU             |                                                       |                                                          | 19b. TELEPHONE NUMBER<br>814-863-0977             |

# RPPR Final Report

as of 12-May-2023

Agency Code: 21XD

Proposal Number: 66503WS

Agreement Number: W911NF-15-1-0202

## INVESTIGATOR(S):

**Name:** Stefan T. Thynell Thynell@ps

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**Principal:** Y

Organization: **Pennsylvania State University**

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Country: USA

DUNS Number: 003403953

EIN: 246000376

**Report Date:** 30-Jun-2023

Date Received: 11-May-2023

**Final Report** for Period Beginning 01-May-2015 and Ending 31-Mar-2023

**Title:** Experimental and Quantum Mechanics Investigations for the Development of a Liquid-phase Chemical Reaction Mechanism of RDX

**Begin Performance Period:** 01-May-2015

**End Performance Period:** 31-Mar-2023

**Report Term:** 0-Other

Submitted By: Stefan Thynell

Email: Thynell@psu.edu

Phone: (814) 863-0977

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

## STEM Degrees:

## STEM Participants:

**Major Goals:** The primary objective of this investigation is to develop a detailed liquid-phase decomposition mechanism of RDX, which includes only elementary reactions. As part of this effort, the liquid-phase RDX mechanism will be used in an ignition and combustion code to predict the flame structure, burn rate and temperature sensitivity of the monopropellant. The liquid-phase RDX mechanism will also be integrated with a chemical kinetics mechanism of a burn-rate modifier, in order to examine the burning behavior of a pseudo-propellant. A liquid-phase decomposition mechanism of the burn-rate modifier, based on elementary chemical reactions, will also be formulated. The integration of these two ingredients will also require the identification of transition states for additional gas-phase, elementary reactions in the ignition and combustion model. The project was extended to include development of reaction mechanisms for HMX and TAGzT, including their interactions during the condensed-phase decomposition. The reaction mechanisms for RDX, HMX, and TAGzT were validated.

**Accomplishments:** Please see attached document for a lengthy summary of the various accomplishments.

**Training Opportunities:** Three students received their Ph.D. degrees as part of this project. Thus they received educational training via extensive course work, as well as training in the use of a wide variety of experimental tools and data analysis techniques. The students also presented their findings at various conferences. They are now employed in the U.S. (one Lawrence Livermore National Lab, and two at a software development company, Gamma Technologies, Chicago, IL).

**Results Dissemination:** Papers were presented and many different conferences in the U.S. and published in various journals. List of manuscripts are included in the attached report.

**Honors and Awards:** Thynell was inducted into the hall of fame in the Department of Mechanical Engineering at West Virginia University.

## Protocol Activity Status:

**Technology Transfer:** Staff members at Army Laboratory were given information about project, including one presentation made at the Aberdeen Proving Ground facility.

Dr. Igor Schweigert, NRL, received our nitramine mechanisms. Some data were incorporated in detonation modeling.

**RPPR Final Report**  
as of 12-May-2023

**PARTICIPANTS:**

**Participant Type:** PD/PI

**Participant:** Stefan Thynell

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

National Academy Member: N

**Participant Type:** Graduate Student (research assistant)

**Participant:** Lalit Patidar

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

National Academy Member: N

**Participant Type:** Graduate Student (research assistant)

**Participant:** Mayank Khichar

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

National Academy Member: N

**Participant Type:** Graduate Student (research assistant)

**Participant:** Tanusree Chatterjee

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

National Academy Member: N

**ARTICLES:**

## RPPR Final Report as of 12-May-2023

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**Journal:** Proceedings of the Eastern States Section of the Combustion Institute

Publication Identifier Type: Other

Publication Identifier:

Volume:

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First Page #:

Date Submitted: 8/30/17 12:00AM

Date Published: 8/27/16 11:11PM

Publication Location: Princeton, NJ

**Article Title:** A quantum mechanics investigation for RDX ring-opening reactions

**Authors:** Lalit Patidar, Stefan T. Thynell

**Keywords:** RDX, cyclic nitramines, ab initio, liquid-phase decomposition

**Abstract:** Cyclotrimethylene trinitramine (RDX) is a commonly used ingredient in solid propellants and explosives. As a result, RDX has been the subject of many experimental and theoretical investigations to elucidate its liquid-phase and gas-phase decomposition. In our experimental effort involving FTIR spectroscopy and time of flight mass spectrometry of fast thermolysis of RDX, the results indicate that ring-opening occurs very early due to the presence of carbon-containing species, such as HCN, H<sub>2</sub>CO, CO and CO<sub>2</sub>. After a lengthy search using quantum mechanics, ring-opening and subsequent reactions have been identified. These ring-opening and subsequent reactions may occur in both liquid and gas phases. The quantum mechanics investigation is based on using density functional theory, as well as various basis sets. The liquid-phase studies use the CPCM solvation model with water as solvent within the Gaussian 09 program package. Intrinsic reaction coordinate calculations have also been performed

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

Acknowledged Federal Support: Y

**Publication Type:** Journal Article

Peer Reviewed: Y

**Publication Status:** 1-Published

**Journal:** Combustion and Flame

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.combustflame.2016.12.024

Volume: 178

Issue:

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Date Submitted: 8/30/17 12:00AM

Date Published: 4/1/17 4:00AM

Publication Location: United States

**Article Title:** Quantum mechanics investigation of initial reaction pathways and early ring-opening reactions in thermal decomposition of liquid-phase RDX

**Authors:** Lalit Patidar, Stefan T. Thynell

**Keywords:** Liquid-phase decomposition, Energetic materials, Quantum mechanics, Cyclic nitramines, RDX

**Abstract:** Cyclotrimethylene trinitramine (RDX) is a commonly used ingredient in solid propellants and explosives. As a result, RDX has been the subject of many experimental and theoretical investigations to elucidate its liquid-phase and gas-phase decomposition. In our experimental effort involving Fourier transform Infrared (FTIR) spectroscopy and time-of-flight mass spectrometry (ToFMS) of fast thermolysis of RDX, the results indicate that ring-opening occurs very early due to the presence of carbon-containing species among the detected gas-phase species, such as HCN, H<sub>2</sub>CO, CO and CO<sub>2</sub>. Two existing pathways: 1) HONO elimination and 2) N–NO<sub>2</sub> homolysis – are re-examined for liquid-phase decomposition and early ring-opening reactions have been identified after a lengthy search using quantum mechanics. Three additional pathways – 1) reaction with NO and formation of ONDNTA, 2) prompt oxidation via HONO and ONNO<sub>2</sub> addition, and 3) hydrogen abstraction via NO<sub>2</sub> – are also identified.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

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## RPPR Final Report as of 12-May-2023

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Combustion and Flame

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.combustflame.2017.09.042

Volume: 188

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Date Submitted: 11/22/17 12:00AM

Date Published: 9/27/17 8:00AM

Publication Location: United States of America

**Article Title:** Identification of Initial Decomposition Reactions in Liquid-Phase HMX using Quantum Mechanics Calculations

**Authors:** Lalit Patidar, Mayank Khichar, Stefan T. Thynell

**Keywords:** Liquid-phase decomposition, Energetic materials, Quantum mechanics, Cyclic nitramines

**Abstract:** Using quantum mechanics, reactions were identified which may occur in both liquid and gas phases of HMX. Two known pathways 1) HONO elimination and 2) N-NO<sub>2</sub> homolysis were re-examined for liquid-phase decomposition, and early ring-opening reactions were identified. Three additional pathways 1) reaction with NO and formation of ONTNTA, 2) prompt oxidation via HONO and ONNO<sub>2</sub> addition, and 3) H abstraction via NO<sub>2</sub> were also identified. The calculations were performed using DFT [B3LYP/6-311++G(d,p)] and CPCM/H<sub>2</sub>O model to account for solvation effects. Similar to RDX, HONO elimination appears to be the initiation followed by early ring-opening reactions. Results also indicate simultaneous formation of CH<sub>2</sub>O and N<sub>2</sub>O from early ring-opening reactions. Competing bimolecular reactions with NO<sub>2</sub>, HONO and ONNO<sub>2</sub> are also investigated, and these explain the experimentally observed autocatalytic behavior. These reactions can assist in simulating combustion of solid propellants containing RDX/HMX.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Combustion and Flame

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Publication Identifier: 10.1016/j.combustflame.2018.10.005

Volume: 198

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Date Submitted: 10/24/18 12:00AM

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Publication Location:

**Article Title:** Improvement and validation of a detailed reaction mechanism for thermal decomposition of RDX in liquid phase

**Authors:** Mayank Khichar, Lalit Patidar, Stefan T. Thynell

**Keywords:** Liquid-phase decomposition, Reaction mechanism, Quantum mechanics, RDX, Dominant decomposition pathway

**Abstract:** The objective of this work is to validate a liquid-phase decomposition mechanism of RDX. The validation involves a comparison of experimental results obtained from confined rapid thermolysis. The spectral transmittances of the gas-phase species are measured using FTIR spectroscopy, which are processed to obtain a temporal behavior of the evolved species. A model was developed to simulate the confined rapid thermolysis experiments. The kinetic rate parameters were optimized by comparing experimental and computational results to yield the experimentally observed trends with reasonable accuracy. The deviations can be explained by experimental uncertainty. Based on this model, initiation of decomposition occurs by HONO elimination. The subsequent decomposition occurs via the pathway starting with HONO addition and followed by ring opening. The detailed mechanism containing 321 species and 500 elementary reactions was reduced to 53 species and 56 reactions using a sensitivity analysis.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

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**Journal:** Combustion and Flame

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Volume: 200

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Date Submitted: 12/11/18 12:00AM

Date Published: 2/1/19 12:00AM

Publication Location: United States

**Article Title:** Intermolecular potential parameters for transport property modeling of energetic organic molecules

**Authors:** Lalit Patidar, Mayank Khichar, Stefan T. Thynell

**Keywords:** Intermolecular potential, ab initio, quantum chemistry, transport data, Lennard-Jones parameters, energetic organic molecules

**Abstract:** Transport properties such as coefficients of diffusion, viscosities and thermal conductivities of chemical species are required for combustion modeling of energetic materials. Here, we present a theoretical study of intermolecular potential energy surfaces for interactions of various energetic organic molecules with four bath gases. ab initio calculations are used to evaluate the accuracy of various low-level quantum chemistry methods. Intermolecular potential energy surfaces are then calculated for a training set of six molecules. The ab initio data are used to parametrize an analytical pairwise potential, which is employed to calculate Lennard-Jones parameters for the training set, as well as a separate test set containing nine energetic organic molecules. Collision rates for molecules in test set are within ~20% of those obtained via ab initio calculations. Calculated transport properties of nitromethane are in good agreement with experimental results.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

Acknowledged Federal Support: Y

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** AIAA Journal of Propulsion and Power

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Volume: 35

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Publication Location: United States

**Article Title:** Comparative analysis of vaporization and thermal decomposition of cyclotrimethylenetrinitramine (RDX)

**Authors:** Mayank Khichar, Lalit Patidar, Stefan Thynell

**Keywords:** TGA, vaporization, sublimation, decomposition

**Abstract:** Accurate sublimation and vaporization rates of RDX were estimated over a wide range of temperatures. A TGA/DSC-FTIR system was used at slow heating rates. In the solid phase, the mass loss occurs mainly due to sublimation of RDX, whereas, in the liquid phase, both vaporization and thermal decomposition play a significant role. The extent of thermal decomposition was estimated using a computational model based on a recently developed liquid-phase decomposition mechanism for RDX. For each heating rate, a good match between computational and experimental mass loss and species evolution profiles was achieved. As evident from the FTIR data, a major part of the mass loss is attributed to the decomposition products. Results show that vaporization accounts for 29.6, 34, and 35.9 % of the total mass loss for the 5, 10, and 15 °C/min heating rates, respectively. Relatively more RDX vaporizes at higher heating rates because of the initiation of the boiling phenomenon at higher temperatures.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

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## RPPR Final Report as of 12-May-2023

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Peer Reviewed: Y

**Publication Status:** 1-Published

**Journal:** Thermochimica Acta

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.tca.2019.178427

Volume: 682

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Date Submitted: 11/3/19 12:00AM

Date Published: 12/1/19 5:00AM

Publication Location: United States

**Article Title:** Development of a reaction mechanism for liquid-phase decomposition of ammonia borane

**Authors:** Tanusree Chatterjee, Stefan T. Thynell

**Keywords:** Ammonia borane, Quantum mechanics, Hydrogen release, Reaction pathway, Numerical simulation

**Abstract:** The primary objective of this study is to provide comprehensive understanding regarding the chemical kinetics involved in H<sub>2</sub> release during ammonia borane (AB) dehydrogenation, to explore the pathways of oligomerization leading to ring formation during the second phase of AB decomposition and to explain the experimental observations using the proposed mechanism. We also performed TGA/DSC studies coupled with FTIR spectroscopy. Experiments performed confirm the presence of NH<sub>3</sub> in gas phase during both steps of AB decomposition. Using G4(MP2) compound method, thermodynamic properties are calculated for both equilibrium species and transition states using the Gaussian 09 program package. Sensitivity analysis identified important reaction pathways for the formation of gaseous species (H<sub>2</sub>, NH<sub>3</sub>, BH<sub>2</sub>NH<sub>2</sub> and borazine) observed during experiments. A comparison of simulated results with experimental data shows that the proposed mechanism captures the key features of AB decomposition.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

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**Publication Type:** Journal Article

Peer Reviewed: Y

**Publication Status:** 1-Published

**Journal:** Combustion and Flame

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Publication Location: United States

**Article Title:** A comprehensive mechanism for liquid-phase decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX): Thermolysis experiments and detailed kinetic modeling

**Authors:** Lalit Patidar, Mayank Khichar, Stefan T. Thynell

**Keywords:** HMX, Reaction mechanism, TGA, FTIR spectroscopy, Thermal decomposition

**Abstract:** Thermal decomposition of HMX was investigated using experimental and computational methods. Mole fraction profiles of gaseous products evolving from the liquid-phase HMX were obtained using Fourier transform infrared (FTIR) spectroscopy for thermogravimetric analysis (TGA) and confined rapid thermolysis (CRT). In the TGA results, mass loss and rapid decomposition were observed after melting of HMX at 280°C. CH<sub>2</sub>O and N<sub>2</sub>O were the major decomposition products. Smaller quantities of H<sub>2</sub>O, HCN, NO and NO<sub>2</sub>, CO and CO<sub>2</sub> were also formed. In the computational study, liquid-phase elementary reactions were investigated using quantum mechanics calculations. A zero-dimensional model was developed to simulate the TGA and CRT experiments. The predicted mass loss and gas-phase mole fraction profiles of evolved species are in good agreements with corresponding experimental results, indicating that the proposed mechanism captures important reactions occurring during liquid-phase decomposition of HMX.

**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors

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## RPPR Final Report as of 12-May-2023

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**Journal:** Physical Chemistry Chemical Physics

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Volume: 22

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Publication Location: England

**Article Title:** Liquid-phase decomposition mechanism for bis(triaminoguanidinium) azotetrazolate (TAGzT);

**Authors:** Neeraj R. Kumbhakarna, Mayank Khichar, Kaushal J. Shah, Arindrajit Chowdhury, Lalit Patidar, Stefan

**Keywords:** decomposition, reaction mechanism, quantum chemistry calculations

**Abstract:** This work provides new insights for liquid-phase decomposition of bis(triaminoguanidinium) azotetrazolate (TAGzT) using a combined experimental and computational approach. Samples of TAGzT were heated at rates of about 2000 K s<sup>-1</sup> to a set temperature (230 to 260°C) where decomposition occurred under isothermal conditions. FTIR spectroscopy and ToFMS were used to acquire transmittance and mass spectra of evolved gas-phase species, respectively. FTIR spectroscopy was also used to acquire transmittance spectra of condensate and residue formed. N<sub>2</sub>, NH<sub>3</sub>, HCN, N<sub>2</sub>H<sub>4</sub>, triaminoguanidine and 3-azido-1,2,4-triazol-4-ide anion were identified as products of decomposition. QM calculations were used for confirming the identity of species observed in experiments and for identifying chemical reactions that formed these species. Based on the calculated free energy barriers of these elementary reactions, important reaction pathways were identified for the formation of each of the product species.

**Distribution Statement:** 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info  
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Peer Reviewed: Y

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**Journal:** Thermochemica Acta

Publication Identifier Type: DOI

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Volume: 699

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Publication Location: Not specified.

**Article Title:** A reduced mechanism with optimal rate-kinetics parameters for liquid-phase decomposition of bis(triaminoguanidinium) 5,5'-azotetrazolate (TAGzT): Quantum chemical calculations, thermolysis experiments and kinetic modeling

**Authors:** Mayank Khichar, Stefan T. Thynell

**Keywords:** TAGzT Liquid-phase decomposition mechanism Quantum chemical calculations Thermolysis Modeling

**Abstract:** Quantum chemical calculations were performed to develop a detailed reaction mechanism for liquid-phase decomposition of bis(triaminoguanidinium) 5,5'-azotetrazolate (TAGzT). Simultaneous thermal analysis experiments were also performed using a TGA/DSC-FTIR system. The experimentally obtained mass loss and species evolution profiles were used to validate and optimize the developed mechanism. Due to a large number of elementary reactions and species in the detailed mechanism, it was reduced by identifying and removing elementary reactions whose rate-of-progress remained low throughout the decomposition process. The reduced mechanism has 90 elementary reactions and 70 species. The analysis leads to the conclusion that TAGzT decomposition occurs in two steps – 1) anion decomposition and 2) cation decomposition. The anionic part primarily decomposes via a single pathway, whereas the cationic part decomposes via five competing pathways.

**Distribution Statement:** 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info  
Acknowledged Federal Support: Y

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**Journal:** The Journal of Physical Chemistry A

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Publication Location: Not known.

**Article Title:** Quantum Chemical Investigation of Perchloric Acid Decomposition Releasing Oxygen

**Authors:** Tanusree Chatterjee, Stefan T. Thynell

**Keywords:** perchloric acid, quantum chemical, oxygen release, reaction pathway, numerical simulation

**Abstract:** The primary objectives are to identify the initiation steps of HClO<sub>4</sub> decomposition and to validate and provide insight regarding the reaction pathways of O<sub>2</sub> formation. To this end, we have performed quantum chemical (QC) calculations using a double-hybrid DFT method, B2PLYP with Jensen's basis set, aug-pc2, and CPCM solvation model. Numerical simulations are also performed with rates of reactions calculated using transition state theory incorporating diffusion. To consider the non-ideal behavior of a concentrated HClO<sub>4</sub> solution, activity coefficients are used. Activity coefficient of HClO<sub>4</sub> plays a critical role in the calculation of induction period. A comparison of numerically predicted O<sub>2</sub> evolution and duration of the induction period with that of experimental data shows that the simulation using the proposed mechanism predicts both the three-stage decomposition characteristics and the induction period observed during HClO<sub>4</sub> decomposition, thus validating the proposed mechanism.

**Distribution Statement:** 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info  
**Acknowledged Federal Support:** Y

### CONFERENCE PAPERS:

**Publication Type:** Conference Paper or Presentation      **Publication Status:** 1-Published

**Conference Name:** Eastern States Section of the Combustion Institute

Date Received: 30-Aug-2017

Conference Date: 15-Mar-2016

Date Published:

Conference Location: Princeton, NJ

**Paper Title:** A quantum mechanics investigation for RDX ring-opening reactions

**Authors:** Lalit Patidar, Stefan T. Thynell

**Acknowledged Federal Support:** Y

**Publication Type:** Conference Paper or Presentation      **Publication Status:** 1-Published

**Conference Name:** 10th National Combustion Meeting

Date Received: 30-Aug-2017

Conference Date: 23-Apr-2017

Date Published: 23-Apr-2017

Conference Location: College Park, MD

**Paper Title:** A Quantum Mechanics Study on Early Decomposition Reactions for Liquid-phase HMX

**Authors:** Lalit Patidar, Mayank Khichar, Stefan T. Thynell

**Acknowledged Federal Support:** Y

**Publication Type:** Conference Paper or Presentation      **Publication Status:** 1-Published

**Conference Name:** 10th National Combustion Meeting

Date Received: 30-Aug-2017

Conference Date: 23-Apr-2017

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Conference Location: College Park, MD

**Paper Title:** Computational Analysis of RDX Thermolysis in Liquid State

**Authors:** Mayank Khichar, Lalit Patidar, Stefan T. Thynell

**Acknowledged Federal Support:** Y

**RPPR Final Report**  
as of 12-May-2023

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## Abstract

The primary objectives of this investigation were to develop a detailed liquid-phase decomposition mechanism of RDX (hexahydro-1,3,5-trinitro-*s*-triazine), extend the model to the gas phase, and to use the mechanism in a combustion model with the burn rate modifier TAGzT [bis(triaminoguanidinium) 5,5'-azotetrazolate]. The mechanism should be based on elementary reactions with input data from quantum chemistry (QC) calculations. The work was subsequently extended to include HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine), to develop a chemical reaction mechanism for the burn rate modifier, and to identify reactions between RDX and HMX with TAGzT. Such interactions had been observed in experiments and lowered the onset temperature of decomposition of propellants containing RDX and TAGzT. The experimental part included confined rapid thermolysis and TGA/DSC studies with FTIR spectroscopy of the evolved gases. Using spectral line information from the HITRAN data base, many of the evolved IR-active species were quantified. The chemical reaction mechanisms of RDX, HMX, and TAGzT were validated by simulating either the confined rapid thermolysis and/or the TGA/DSC experiments. The QC calculations utilized the Gaussian 16 program package, including density functional theory and compound methods [CBS-QB3 and G4(MP2)]. The condensed-phase calculations used the different solution-phase models available in the Gaussian program package; the results are typically quite insensitive to the selection of both the solution-phase model and to the choice of solvent. The condensed-phase chemical reactions in the validation models account for cage effects.

The results show that the exothermic HONO-elimination reaction is the most important initial step in the condensed-phase decomposition of both RDX and HMX. Cage effects cause the N-N bond homolysis releasing NO<sub>2</sub> to be unimportant. In the gas phase, however, N-N bond homolysis releasing NO<sub>2</sub> is important. The subsequent important reactions include HONO attack, and ring-opening reactions. Typically, these reactions become very important once melting has occurred; the experiments show very little decomposition of the solid phase for the considered heating rates which usually were 15 K/min or greater. For TAGzT, the initiation step is ring-opening releasing N<sub>2</sub>. Subsequently, the remaining portion of AzT<sup>2-</sup> dianion decomposes quickly and highly exothermically to release additional N<sub>2</sub>, HCN, TAG, and CN<sup>-</sup>. Using the QC calculations, the interactions between RDX and TAGzT, and HMX with TAGzT were identified to a significant extent. These calculations show that both the CN<sup>-</sup> anion, the AzT<sup>2-</sup> dianion, and TAG can attack the nitramines by forming HCN, AzT<sup>-</sup> anion, and TAG<sup>+</sup> in H-abstraction reactions with Gibbs free energy barriers of 27.4, 32.2, and 22.1 kcal/mol, respectively, for RDX, and 27.4, 36.7, and 26.1 kcal/mol, respectively, for HMX. In these H-abstraction reactions, the NO<sub>2</sub><sup>-</sup> anion is released, and the nitramine is reduced to the same species as that in the HONO-elimination reaction. The NO<sub>2</sub><sup>-</sup> anion can further abstract an H-atom from the nitramines releasing *cis*-HONO, NO<sub>2</sub><sup>-</sup> and the same nitramine fragment as that in the HONO-elimination step. Thus, the reactions are autocatalytic and become very fast. This type of anionic interaction can be extended. As an example, if a nitrate-containing species is mixed with RDX, the NO<sub>3</sub><sup>-</sup> anion can abstract an H atom, forming HNO<sub>3</sub>, and the same species as mentioned previously; similar behavior is expected if a strong base is mixed the nitramine. The barrier for this reaction with NO<sub>3</sub><sup>-</sup> is 36.6 kcal/mol, which is about 2 kcal/mol lower than the HONO-elimination reaction and has a high symmetry factor. In summary, the results from this project show that the details of the chemical kinetic behavior of RDX, HMX and TAGzT in the condensed phase can be identified, simulated and validated using readily available computational and experimental tools.

## TABLE OF CONTENTS

|                                                                                                                                 |    |
|---------------------------------------------------------------------------------------------------------------------------------|----|
| LIST OF FIGURES .....                                                                                                           | IV |
| LIST OF TABLES.....                                                                                                             | V  |
| CHAPTER 1 LIQUID-PHASE DECOMPOSITION MECHANISM OF RDX AND HMX .....                                                             | 1  |
| 1.1 Introduction .....                                                                                                          | 1  |
| 1.2 Computational Details .....                                                                                                 | 1  |
| 1.3 Results and Discussions.....                                                                                                | 2  |
| 1.3.1 Pathway 1: N-NO <sub>2</sub> bond dissociation.....                                                                       | 2  |
| 1.3.2 Pathway 2: HONO elimination .....                                                                                         | 5  |
| 1.3.3 Pathway 3: Mono-nitroso analogs of RDX and HMX .....                                                                      | 8  |
| 1.3.4 Pathway 4: Autocatalytic prompt oxidation via HONO and ONNO <sub>2</sub> addition .....                                   | 9  |
| 1.3.5 Pathway 5: Autocatalytic hydrogen abstraction via NO <sub>2</sub> .....                                                   | 13 |
| 1.4 Conclusions .....                                                                                                           | 13 |
| CHAPTER 2 IMPROVEMENT AND VALIDATION OF A DETAILED REACTION MECHANISM FOR<br>THERMAL DECOMPOSITION OF RDX IN LIQUID PHASE ..... | 14 |
| 2.1 Introduction .....                                                                                                          | 14 |
| 2.2 Experimental details .....                                                                                                  | 14 |
| 2.3 Data reduction procedure.....                                                                                               | 14 |
| 2.4 Experimental results .....                                                                                                  | 15 |
| 2.4.1 IR spectrum of the gas-phase species.....                                                                                 | 15 |
| 2.4.2 Concentration of gas-phase species .....                                                                                  | 15 |
| 2.5 Model for decomposition of RDX.....                                                                                         | 17 |
| 2.5.1 Liquid-phase reaction mechanism.....                                                                                      | 17 |
| 2.5.2 Analysis of liquid-phase region .....                                                                                     | 17 |
| 2.5.3 Analysis of gas-phase region .....                                                                                        | 19 |
| 2.6 Computational results and comparison with experiments .....                                                                 | 19 |
| 2.6.1 Parameter optimization .....                                                                                              | 19 |
| 2.6.2 Validation of the detailed reaction mechanism .....                                                                       | 20 |
| 2.6.3 Reaction mechanism reduction .....                                                                                        | 24 |
| 2.6.4 Discussion of the reaction mechanism.....                                                                                 | 26 |
| 2.7 Summary and conclusions .....                                                                                               | 28 |
| CHAPTER 3 THERMOLYSIS EXPERIMENTS AND KINETIC MODELING OF HMX .....                                                             | 29 |
| 3.1 Introduction .....                                                                                                          | 29 |
| 3.2 Experimental details and data reduction.....                                                                                | 29 |
| 3.3 Computational details .....                                                                                                 | 29 |
| 3.3.1 Quantum mechanics calculations.....                                                                                       | 29 |
| 3.4 Detailed kinetic modeling for validation of the mechanism .....                                                             | 29 |
| 3.5 Experimental results .....                                                                                                  | 29 |
| 3.5.1 TGA and DSC data .....                                                                                                    | 29 |
| 3.5.2 Species evolution .....                                                                                                   | 30 |
| 3.5.3 Effect of heating rate in TGA experiments .....                                                                           | 31 |
| 3.5.4 Effect of set temperature in CRT experiments.....                                                                         | 31 |
| 3.6 Computational results .....                                                                                                 | 33 |
| 3.6.1 Liquid-to-gas conversion rates.....                                                                                       | 33 |
| 3.6.2 Mechanism development and validation methodology .....                                                                    | 34 |
| 3.6.3 Prediction of mass loss and species evolution profiles .....                                                              | 34 |
| 3.7 Sensitivity analysis .....                                                                                                  | 36 |
| 3.8 Conclusions .....                                                                                                           | 38 |
| CHAPTER 4 TRANSPORT PARAMETERS FOR COMBUSTION MODELING.....                                                                     | 39 |

|           |                                                                                                                                                        |    |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 4.1       | Introduction .....                                                                                                                                     | 39 |
| 4.2       | Theory and Computational methods.....                                                                                                                  | 39 |
| 4.3       | Results and discussions .....                                                                                                                          | 40 |
| 4.3.1     | Validation of low-level quantum chemistry methods .....                                                                                                | 40 |
| 4.3.2     | Separable approximation to potential energy surface .....                                                                                              | 42 |
| 4.3.3     | Validation of the exp/6 potential energy surface.....                                                                                                  | 45 |
| 4.3.4     | Gas-phase transport properties of CH <sub>3</sub> NO <sub>2</sub> .....                                                                                | 46 |
| 4.4       | Application .....                                                                                                                                      | 50 |
| 4.4.1     | Transport properties database for combustion modeling of nitramines .....                                                                              | 50 |
| 4.4.2     | Comparative sensitivity analysis of transport vs. reaction rate parameters.....                                                                        | 50 |
| 4.5       | Summary and Conclusions .....                                                                                                                          | 53 |
| CHAPTER 5 | MULTI-PHASE COMBUSTION MODELING OF HMX .....                                                                                                           | 54 |
| 5.1       | Introduction .....                                                                                                                                     | 54 |
| 5.2       | Model description and input parameters.....                                                                                                            | 55 |
| 5.3       | Results and Discussions.....                                                                                                                           | 55 |
| 5.4       | Conclusions .....                                                                                                                                      | 61 |
| CHAPTER 6 | A MULTI-PHASE COMBUSTION MODEL FOR RDX WITH BUBBLE FORMATION<br>AND DETAILED CHEMICAL KINETICS .....                                                   | 63 |
| 6.1       | Introduction .....                                                                                                                                     | 63 |
| 6.2       | Model description.....                                                                                                                                 | 63 |
| 6.2.1     | Solid-phase region.....                                                                                                                                | 63 |
| 6.2.2     | Liquid-phase region .....                                                                                                                              | 63 |
| 6.2.3     | Gas-phase region.....                                                                                                                                  | 64 |
| 6.2.4     | Numerical solution of the governing equations .....                                                                                                    | 65 |
| 6.3       | Results and discussion .....                                                                                                                           | 65 |
| 6.4       | Conclusions .....                                                                                                                                      | 75 |
| CHAPTER 7 | A REDUCED REACTION MECHANISM FOR LIQUID-PHASE DECOMPOSITION OF<br>TAGZT WITH OPTIMIZED PARAMETERS .....                                                | 76 |
| 7.1       | Introduction .....                                                                                                                                     | 76 |
| 7.2       | Quantum chemical calculations .....                                                                                                                    | 76 |
| 7.3       | Thermolysis experiments.....                                                                                                                           | 76 |
| 7.3.1     | Conversion of FTIR data to species evolution profiles .....                                                                                            | 77 |
| 7.4       | Kinetic modeling .....                                                                                                                                 | 77 |
| 7.5       | Results and discussion .....                                                                                                                           | 77 |
| 7.5.1     | Experimental mass loss and heat release.....                                                                                                           | 77 |
| 7.5.2     | The liquid-phase reaction mechanism.....                                                                                                               | 79 |
| 7.5.3     | Sensitivity analysis of the decomposition pathways .....                                                                                               | 82 |
| 7.5.4     | Validation of the reaction mechanism.....                                                                                                              | 83 |
| 7.6       | Summary and conclusions.....                                                                                                                           | 87 |
| CHAPTER 8 | A MULTI-PHASE COMBUSTION MODEL FOR RDX-TAGZT PSEUDO-PROPELLANT<br>WITH BUBBLE FORMATION AND DETAILED CHEMICAL KINETICS .....                           | 89 |
| 8.1       | Introduction .....                                                                                                                                     | 89 |
| 8.2       | Model description.....                                                                                                                                 | 89 |
| 8.2.1     | Liquid-phase decomposition .....                                                                                                                       | 89 |
| 8.2.2     | Gas-phase decomposition .....                                                                                                                          | 91 |
| 8.3       | Results and discussion .....                                                                                                                           | 92 |
| 8.4       | Conclusions .....                                                                                                                                      | 97 |
| CHAPTER 9 | INVESTIGATION OF THERMAL DECOMPOSITION PROCESSES OF HMX AND<br>TAGZT MIXTURES USING THERMOLYSIS EXPERIMENTS AND QUANTUM CHEMICAL<br>CALCULATIONS ..... | 98 |
| 9.1       | Introduction .....                                                                                                                                     | 98 |

|                          |                                                    |     |
|--------------------------|----------------------------------------------------|-----|
| 9.2.                     | Details of experimental studies.....               | 98  |
| 9.3                      | Details of quantum chemical (QC) calculations..... | 98  |
| 9.4.                     | Results and discussion.....                        | 98  |
| 9.4.1                    | Results from TGA and DSC studies.....              | 99  |
| 9.4.2                    | Results for species profiles of evolved gases..... | 101 |
| 9.4.3                    | Results from quantum chemical calculations.....    | 103 |
| 9.5                      | Conclusions.....                                   | 104 |
| LIST OF MANUSCRIPTS..... |                                                    | 106 |
| REFERENCES.....          |                                                    | 106 |

## LIST OF FIGURES

|                                                                                                                                                                                                                                                                            |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2-1. Schematics of the thermolysis chamber and the accessories required for species detection in gas phase.                                                                                                                                                         | 14 |
| Figure 2-2. IR spectrum of species in gas-phase region evolved during RDX decomposition for a set temperature of 558 K and 1 atm pressure.                                                                                                                                 | 16 |
| Figure 2-3. Temporal species evolution for two experiments with slightly different sample masses at a set temperature of 568 K and 1 atm pressure.                                                                                                                         | 16 |
| Figure 2-4. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 538 K.                                                                                                                                    | 21 |
| Figure 2-5. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 548 K.                                                                                                                                    | 23 |
| Figure 2-6. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 558 K.                                                                                                                                    | 23 |
| Figure 2-7. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 568 K.                                                                                                                                    | 24 |
| Figure 2-8. Important pathways for decomposition of INT175a, an intermediate produced by HONO elimination from RDX.                                                                                                                                                        | 27 |
| Figure 2-9. Molecular structures of important intermediates formed during RDX decomposition in liquid phase.                                                                                                                                                               | 28 |
| Figure 3-1. (a) TGA data and (b) DSC data.                                                                                                                                                                                                                                 | 30 |
| Figure 3-2. DSC data for two experimental runs at 15 K/min. Inset shows the endothermic peaks around 190 °C corresponding to $\beta$ -HMX to $\delta$ -HMX phase transformation.                                                                                           | 30 |
| Figure 3-3. FTIR spectrum of the evolved gases (a) TGA setup (heating rate = 20 K/min and temperature = 285°C) and (b) CRT setup ( $T_{\text{set}} = 300^\circ\text{C}$ and $t = 10.08$ s).                                                                                | 31 |
| Figure 3-4. Variation of species mole fractions in the gas phase with temperature during HMX decomposition in TGA-FTIR setup (a) 5 K/min, (b) 10 K/min, (c) 15 K/min and (d) 20 K/min.                                                                                     | 32 |
| Figure 3-5. Species mole fractions profiles in the gas phase during HMX decomposition in CRT-FTIR setup at a set temperature of (a) 290°C, (b) 300°C, (c) 310°C and (d) 320°C.                                                                                             | 33 |
| Figure 3-6. Mass loss curve for HMX decomposition at four heating rates.                                                                                                                                                                                                   | 35 |
| Figure 3-7. HMX decomposition for a heating rate of 15 K/min. Species mole fractions profiles in the gas phase (a) computational and (b) experimental.                                                                                                                     | 35 |
| Figure 3-8. HMX decomposition in the liquid phase at 300°C. Temporal evolution of species relative mole fractions in the gas phase (a) computational and (b) experimental.                                                                                                 | 36 |
| Figure 3-9. Sensitivity coefficients of forward rate constants on HMX mass fraction in the liquid phase at 15 K/min heating rate and 283°C during TGA simulations.                                                                                                         | 37 |
| Figure 3-10. Summary of liquid-phase decomposition mechanism of HMX.                                                                                                                                                                                                       | 38 |
| Figure 4-1. $\text{CH}_2\text{NNO}_2 + \text{He}$ interaction potential for three approaches. Solid lines are QCISD(T)/CBS energies while the dashed lines are (a) MP2/CBS and (b) $\omega\text{B97X-D/CBS}$ energies.                                                     | 41 |
| Figure 4-2. $\text{CH}_3\text{NO}_2 + \text{He}$ interaction potential for three approaches. Solid lines are QCISD(T)/CBS energies while the dashed lines are (a) MP2/CBS and (b) $\omega\text{B97X-D/CBS}$ energies.                                                      | 42 |
| Figure 4-3. $\text{CH}_2\text{NNO}_2 + \text{He}$ interaction potential for five different approaches. Solid lines are MP2/CBS energies while the dashed lines are exp/6 energies. Van der Waals wells are highlighted in the inset.                                       | 44 |
| Figure 5-1. Variation of the burn-rate with pressure for self-deflagrating HMX. The initial temperature of the unburnt propellant is 298 K. <sup>a</sup> :Ref. [68], <sup>b</sup> :Ref. [73], <sup>c</sup> :Ref. [73], <sup>d</sup> :Ref. [114], <sup>e</sup> :Ref. [103]. | 57 |
| Figure 5-2. Variation of the burn-rate with pressure for self-deflagrating HMX. The initial temperature of the unburnt propellant is 223 K. <sup>a</sup> :Ref. [103].                                                                                                      | 57 |
| Figure 5-3. Variation of the burn-rate with pressure for self-deflagrating HMX. The initial temperature of the unburnt propellant is 373 K. <sup>a</sup> :Ref. [103].                                                                                                      | 58 |
| Figure 5-4. Temperature profiles in the gas phase during self-deflagration of HMX monopropellant at various pressures.                                                                                                                                                     | 58 |
| Figure 5-5. Temperature profiles in the liquid melt layer during self-deflagration of HMX monopropellant at various pressures.                                                                                                                                             | 59 |
| Figure 5-6. Thickness of the melt layer with pressure during self-deflagration of HMX. <sup>a</sup> :Ref. [73], <sup>b</sup> :Ref. [114].                                                                                                                                  | 59 |
| Figure 5-7. HMX decomposition in the gas phase near the surface at a pressure of 1 atm.                                                                                                                                                                                    | 60 |
| Figure 5-8. HMX flame structure in the gas phase at a pressure of 1 atm.                                                                                                                                                                                                   | 61 |
| Figure 5-9. Species mass fraction profiles in the melt layer for self-deflagration of HMX monopropellant at 1 atm. $x = 0$ represents the solid-liquid interface.                                                                                                          | 61 |

|                                                                                                                                                                                                                           |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 6-1. Variation of burn-rate with pressure for self-deflagration of RDX mono-propellant. The initial temperature of the unburnt propellant was 293 K. References are provided in text. ....                         | 66  |
| Figure 6-2. Temperature profiles for self-deflagration of RDX mono-propellant. The initial temperature of the unburnt propellant was 293 K. ....                                                                          | 67  |
| Figure 6-3. Melt layer temperature profiles during self-deflagration of RDX. The initial temperature of the unburnt propellant was 293 K. ....                                                                            | 67  |
| Figure 6-4. Extent of RDX decomposition in the melt layer during its self-deflagration. The initial temperature of the unburnt propellant was 293 K. ....                                                                 | 68  |
| Figure 6-5. Variation of propellant surface temperature with pressure for self-deflagration of RDX monopropellant. The initial temperature of the unburnt propellant was 293 K. References are provided in the text. .... | 69  |
| Figure 6-6. Melt layer thickness variation pressure during self-deflagration of RDX. The initial temperature of the unburnt propellant was 293 K. References are provided in the text. ....                               | 69  |
| Figure 6-8. Variation of void fraction in the melt layer during self-deflagration of RDX. The initial temperature of the unburnt propellant was 293 K. ....                                                               | 70  |
| Figure 6-7. RDX flame structure in the gas phase at 1 atm. ....                                                                                                                                                           | 70  |
| Figure 6-9. RDX flame structure in the gas phase at high pressures. ....                                                                                                                                                  | 72  |
| Figure 6-10. Species profiles in the liquid-phase volume fraction of the melt layer during RDX deflagration. ....                                                                                                         | 73  |
| Figure 6-11. Effect of adding liquid-phase decomposition reactions and bubble formation in the melt layer on the propellant burn-rate. ....                                                                               | 74  |
| Figure 7-1. Mass loss profiles for TAGzT samples heated at three different heating rates under atmospheric pressure. ....                                                                                                 | 78  |
| Figure 7-2. DSC profiles for TAGzT samples heated at three different heating rates under atmospheric pressure. ....                                                                                                       | 79  |
| Figure 7-3. Reaction pathways for the liquid-phase decomposition of azotetrazolate dianion ( $AzT^{2-}$ ). ....                                                                                                           | 80  |
| Figure 7-4. Reaction pathways for the liquid-phase decomposition of triaminoguanidinium cation ( $TAG^+$ ). ....                                                                                                          | 81  |
| Figure 7-5. Relative significance of the liquid-phase decomposition pathways of TAGzT. ....                                                                                                                               | 83  |
| Figure 7-6. Comparison between the experimental and model results for product species evolution from 1 mg of TAGzT sample. ....                                                                                           | 84  |
| Figure 7-7. Comparison between the experimental and model results for mass loss from TAGzT sample. ....                                                                                                                   | 85  |
| Figure 7-8. Product distribution for TAGzT decomposition at 5 °C/min heating rate. ....                                                                                                                                   | 87  |
| Figure 8-1. The effect of the presence of TAGzT on RDX decomposition. A 15 °C/min heating rate was used for all the samples. ....                                                                                         | 90  |
| Figure 8-2. Species evolution during thermal decomposition of RDX, TAGzT, and RDX-TAGzT mixtures at 15 °C/min heating rate. ....                                                                                          | 92  |
| Figure 8-3. Variation of burn-rate with pressure for self-deflagration of RDX-TAGzT pseudo-propellant and RDX monopropellant. References are provided in text. ....                                                       | 94  |
| Figure 8-4. Temperature profiles for self-deflagration of RDX-TAGzT (75:25) pseudo-propellant and RDX monopropellant. ....                                                                                                | 94  |
| Figure 8-5. RDX-TAGzT (75:25 by mass) flame structure in the gas phase. ....                                                                                                                                              | 96  |
| Figure 8-6. Species profiles in the liquid-phase volume fraction of the melt layer during self- deflagration of 75:25 RDX-TAGzT mixture at 90 atm. ....                                                                   | 97  |
| Figure 9-1. TGA and DSC results for HMX-TAGzT (90-10) mixture for three heating rates. ....                                                                                                                               | 99  |
| Figure 9-2. Comparison of TGA and DSC results for HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT (15 K/min). ....                                                                                                 | 100 |
| Figure 9-3. TGA and DSC results for HMX and HMX-TAGzT mixtures at different mass ratios (25 K/min). ....                                                                                                                  | 100 |
| Figure 9-4. 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 (25 K/min). ....              | 101 |
| Figure 9-5. Mole fraction of gaseous species released during decomposition of HMX-TAGzT (80-20) mixture (25 K/min). ....                                                                                                  | 102 |
| Figure 9-6. Mole fraction of gaseous species released during decomposition of HMX-TAGzT (70-30) mixture (25 K/min). ....                                                                                                  | 102 |
| Figure 9-7. Molecular structure of INT249a. ....                                                                                                                                                                          | 103 |

## LIST OF TABLES

|                                                                                                                 |    |
|-----------------------------------------------------------------------------------------------------------------|----|
| Table 2-1. Wavenumber range used for different molecules in data reduction model. ....                          | 15 |
| Table 2-2. Optimized parameters of modified Arrhenius form for calculating liquid-to-gas conversion rates. .... | 20 |

|                                                                                                                                                                                                                                                                    |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 2-3. Reduced reaction mechanism for RDX decomposition in liquid phase. All quantities are in kcal/mol.....                                                                                                                                                   | 24  |
| Table 4-1. Errors for low-level quantum chemistry methods relative to counterpoise corrected QCISD(T)/CBS calculations for CH <sub>2</sub> NNO <sub>2</sub> —He and CH <sub>3</sub> NO <sub>2</sub> —He interactions along three approaches for each molecule..... | 41  |
| Table 4-2. Exp/6 parameters for Eq. (4-10).....                                                                                                                                                                                                                    | 43  |
| Table 4-3. Errors for exp/6 potential relative to counterpoise corrected MP2/CBS calculations for six molecules in the training set.....                                                                                                                           | 43  |
| Table 4-4. Lennard-Jones parameters and collision rates for molecules in training set.....                                                                                                                                                                         | 45  |
| Table 4-5. Lennard-Jones parameters and collision rates for molecules in test set .....                                                                                                                                                                            | 46  |
| Table 4-6. Comparison of experimental and calculated viscosity of CH <sub>3</sub> NO <sub>2</sub> using Lorentz-Berthelot combining rules and individual bath gases .....                                                                                          | 47  |
| Table 4-7. Comparison of experimental and calculated viscosity of CH <sub>3</sub> NO <sub>2</sub> using all four bath gases with different combining rules .....                                                                                                   | 48  |
| Table 4-8. Comparison of experimental and calculated thermal conductivity of CH <sub>3</sub> NO <sub>2</sub> using all four bath gases with different combining rules.....                                                                                         | 49  |
| Table 4-9. Comparison of calculated binary diffusion coefficient of CH <sub>3</sub> NO <sub>2</sub> in air with experimental values for CH <sub>3</sub> NO <sub>2</sub> in air.....                                                                                | 49  |
| Table 4-10. List of the top 15 normalized reaction temperature sensitivities for RDX at 1 atm for the second grid point.....                                                                                                                                       | 51  |
| Table 4-11. List of the top 15 normalized temperature sensitivities for RDX at 1 atm for the second grid point with respect to Lennard-Jones collision diameters .....                                                                                             | 52  |
| Table 4-12. List of the top 12 normalized temperature sensitivities for RDX at 1 atm for the second grid point with respect to Lennard-Jones well depth.....                                                                                                       | 52  |
| Table 5-1. Different types of monopropellant combustion models .....                                                                                                                                                                                               | 54  |
| Table 5-2. Combustion wave parameters for self-deflagrating HMX monopropellant at 1 atm with and without liquid-phase decomposition effects.....                                                                                                                   | 56  |
| Table 6-1. Heat feedback from gas-to-liquid phase and overall heat release in the melt layer during self-deflagration of RDX. ....                                                                                                                                 | 74  |
| Table 7-1. Optimized parameters of the Arrhenius form for calculating liquid-to-gas conversion rates, $klg = A \exp(-Ev/RuT)$ . ....                                                                                                                               | 86  |
| Table 9-1. Gibbs free energy barrier $\Delta G$ in forward ( <i>f</i> ) and backward ( <i>b</i> ) direction and enthalpy of reaction (kJ/mol). ....                                                                                                                | 104 |

## CHAPTER 1

### LIQUID-PHASE DECOMPOSITION MECHANISM OF RDX AND HMX

#### 1.1 Introduction

During thermal decomposition of RDX and HMX, various gaseous species, including  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , evolve from the condensed phase depending on the experimental conditions such as heating rate, sample size and environment [1–4]. These products have been identified by rapid-scan/FTIR spectroscopy [1] and triple quadrupole mass spectrometry [4]. Temporal evolution profiles of gaseous decomposition products of various energetic materials have been probed using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) [5,6] and confined rapid thermolysis (CRT)/FTIR spectroscopy [7]. However, due to fast reactions and short-lived intermediates, experimental identification of the reaction products and the elementary reactions is quite challenging. Recently, quantum mechanics calculations have been performed in many theoretical studies to probe solid-phase and gas-phase decomposition of HMX. A brief review of these pathways in the solid phase and the gas phase is given in [8–12].

Due to the difficulties in experimental identification of intermediates and elementary reactions in liquid-phase, a complementary study using quantum mechanics is performed to identify early ring-opening and subsequent reactions during thermal decomposition of RDX and HMX.

#### 1.2 Computational Details

Gaussian 09 quantum chemistry software package is used for carrying out all electronic structure calculations [13]. Density functional theory (DFT) with the Becke three-parameter hybrid density functional approximation with the Lee–Yang–Parr correlation functional approximation (B3LYP) [14] has been used. The basis set 6-311++G(d,p) is used to optimize the geometries of reactants, products, intermediates and transition states. Three implicit solvation models, IEFPCM [15], SMD [16] and CPCM [17] along with three solvents – water ( $\epsilon = 78.36$ ), acetonitrile ( $\epsilon = 35.69$ ) and diethyl ether ( $\epsilon = 4.24$ ) – are compared for liquid-phase calculations. Gaussian 09 quantum chemistry software package is used for carrying out all electronic structure calculations [13]. Density functional theory (DFT) with the Becke three-parameter hybrid density functional approximation with the Lee–Yang–Parr correlation functional approximation (B3LYP) [14] has been used. The basis set 6-311++G(d,p) is used to optimize the geometries of reactants, products, intermediates and transition states. Three implicit solvation models, IEFPCM [15], SMD [16] and CPCM [17] along with three solvents – water ( $\epsilon = 78.36$ ), acetonitrile ( $\epsilon = 35.69$ ) and diethyl ether ( $\epsilon = 4.24$ ) – are compared for liquid-phase calculations. The details are given in [10] and [18].

All thermochemistry calculations are performed at the default value of temperature in Gaussian 09 which is 298.15 K. Temperature dependence of thermodynamic properties such as Gibbs free energy can be computed using solvation models such as SM8T [19] which account for the temperature dependence of free energy of solvation. The primary goal of this study is to identify potential pathways and to calculate activation barriers for liquid phase decomposition of RDX and HMX. Hence only activation barriers (both  $\Delta H_f^\ddagger$  and  $\Delta G_f^\ddagger$ ), enthalpy of reaction  $\Delta H_r$  and Gibbs free energy of reaction  $\Delta G_r$  are calculated and discussed. Activation barriers  $\Delta G_f^\ddagger$  obtained from thermochemistry calculations are used to compute the rate constants  $k(T)$  using the thermodynamic formulation of conventional transition state theory [20–23] given by Eq. (1-1),

$$k = \sigma_s \tau_{tun} \frac{k_B T}{h c_{ref}^{n-1}} \exp\left(\frac{-\Delta G_f^\ddagger}{RT}\right) \quad (1-1)$$

where  $\sigma_s$  is a symmetry factor [24],  $\tau_{tun}$  is a tunneling factor [25,26],  $k_B$  is Boltzmann's constant,  $h$  is Planck's constant,  $c_{ref}$  is the standard state concentration,  $n$  is the order of the reaction, and  $\Delta G_f^\ddagger$  is the free energy barrier and  $R$  is the universal gas constant.

### 1.3 Results and Discussions

Energy ordering of various conformers of RDX in the gas phase have been computed at very accurate *ab initio* MP2 and CCSD(T) levels by Molt et al. [27] and six geometries – four chairs (*AAA*, *AAE*, *AAE*, and *EEE*), one *boat*, and one *twist* – were considered. *AAE* was found to be the global minimum, whereas the *AAA* had one imaginary frequency. With the exception of *EEE* form, all the six geometries considered by Molt et al. [27] in the gas phase are relatively close in energy. Since our objective is to choose a starting structure in the liquid-phase for identifying potential decomposition pathways, only five conformations of RDX, i.e., three chairs (*AAA*, *AAE*, and *AAE*), one *boat* and one *twist*, are considered. *EEE* form, the least stable of all, was not considered. The geometries are optimized for liquid-phase at B3LYP/6-311++G(d,p) level of theory with CPCM solvation model and water as a solvent, and the energy is calculated at the same level of theory. We have found *AAA* conformer to be the global minimum. In our liquid phase calculations, *AAA* has zero imaginary frequencies and hence is a minimum, but the enthalpy difference between our *AAA* and *AAE* forms is less than 0.8 kcal/mol. *AAE* and *boat* conformers are less stable than *AAA* conformer by 2.3 kcal/mol and 2.9 kcal/mol, respectively where the values represent relative enthalpies of the conformers. *Twist* conformer is also identified as a minimum and is ~3 kcal/mol higher in enthalpy than the *AAA* form. Similar differences in the relative energies of different conformers are obtained in the gas phase by various studies [28,29]. Hence, all the subsequent calculations are performed in the liquid-phase with *AAA* conformation of RDX.

HMX has four crystalline polymorphs:  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . The  $\beta$  polymorph (chair-like conformation) is stable at room temperature while  $\alpha$ ,  $\gamma$ , and  $\delta$  polymorphs (boat-like conformation) are stable at higher temperature ranges [30].  $\gamma$  and  $\delta$  conformations merge to  $\alpha$  conformation in gas phase which is the most stable structure at higher temperatures relevant to ignition and combustion conditions [31]. Hence, only  $\alpha$  and  $\beta$  conformations of HMX are considered. In our gas-phase calculation at B3LYP/6-311++G(d,p) level, the  $\beta$  form was found to be more stable by 1.8 kcal/mol (relative enthalpy), however, in the liquid-phase calculations,  $\alpha$  form is found to be more stable by 2.1 kcal/mol (relative enthalpy). Hence, all the subsequent calculations are performed in the liquid phase with  $\alpha$  conformation of HMX.

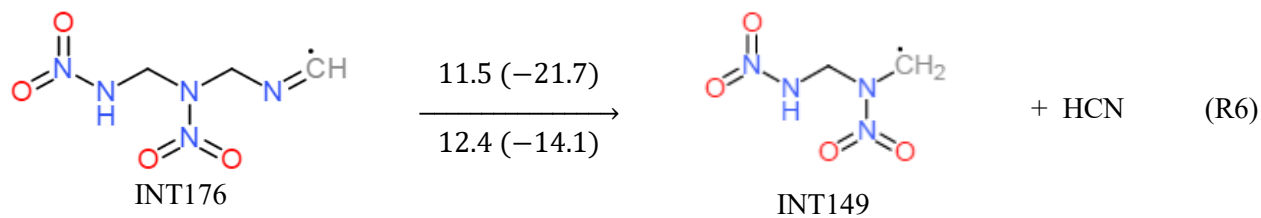
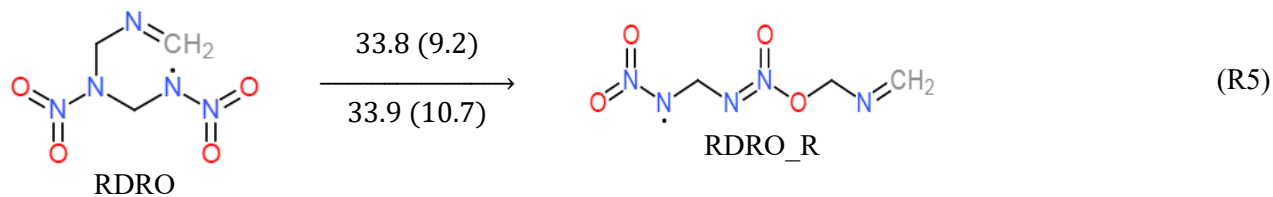
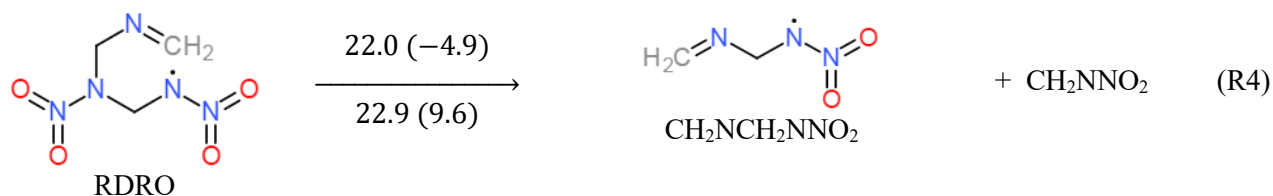
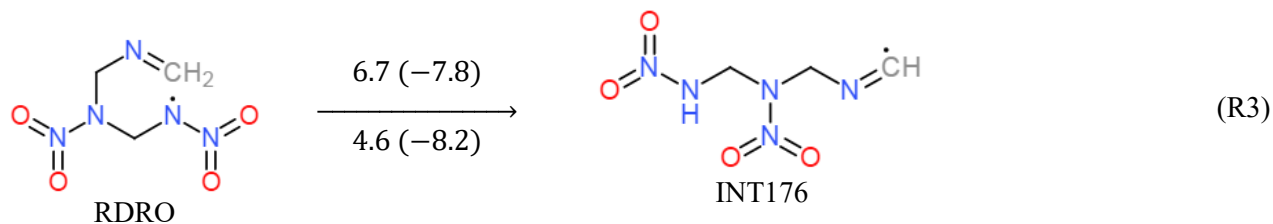
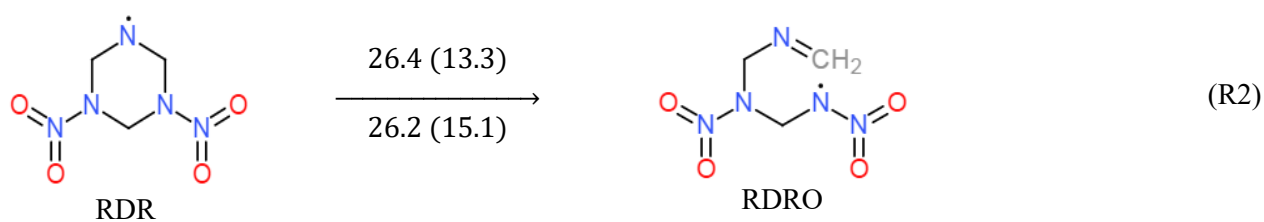
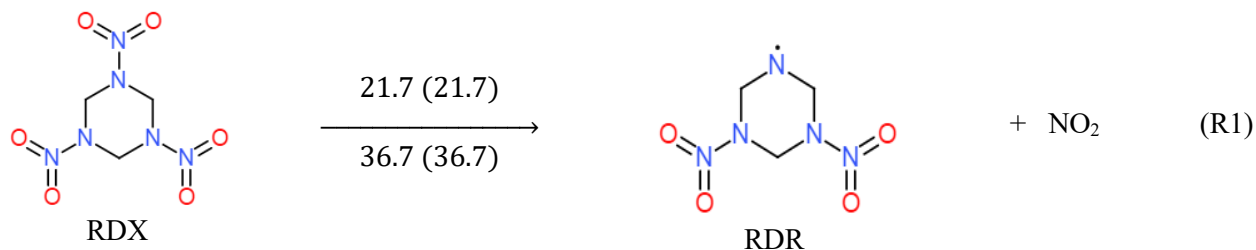
Two existing pathways for gas-phase decomposition of RDX and HMX, i.e., N-NO<sub>2</sub> bond dissociation and HONO elimination are investigated in the liquid phase and labeled as Pathway 1 and Pathway 2, respectively. Decomposition of RDX and HMX via formation of mono-nitroso analogues and autocatalytic behavior, as observed experimentally by Behrens [6], are also examined quantum mechanically in the present study and are labeled as pathways Pathway 3 and Pathway 4, respectively. Pathway 5 represents decomposition of RDX and HMX via hydrogen abstraction by NO<sub>2</sub>. Pathways 1 to 5 for the liquid-phase decomposition of RDX and HMX are discussed next.

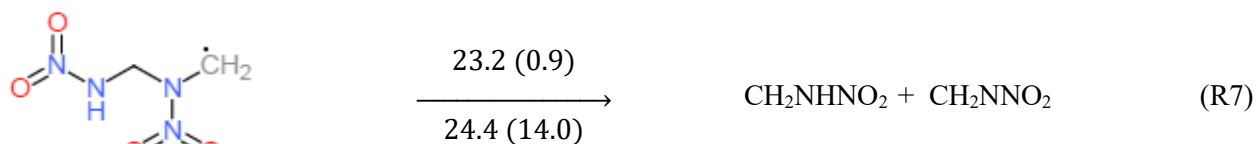
#### 1.3.1 Pathway 1: N-NO<sub>2</sub> bond dissociation

N-NO<sub>2</sub> bond dissociation and subsequent decomposition have been considered a major channel in the gas-phase decomposition of RDX and HMX, where molecular mobility is high. Even though the cage effect reduces molecular mobility in the liquid phase and the barrier for reverse radical recombination to form RDX is low, the possibility of this pathway in the liquid phase cannot be ruled out as observed experimentally by Behrens [32]. Major reactions in this pathway are thoroughly discussed by Chakraborty et al. [33] for the gas phase decomposition. Here we have performed liquid phase calculations for this pathway and obtained some additional reactions. The numbers above the arrow represent the Gibbs free energy of activation for forward reaction  $\Delta G_f^\ddagger$  (in kcal/mol) followed by Gibbs free energy of reaction  $\Delta G_r$  (in kcal/mol) in parenthesis. Similarly, the number below the arrow represent the enthalpy of activation for forward reaction  $\Delta H_f^\ddagger$  (in kcal/mol) followed by enthalpy of reaction  $\Delta H_r$  (in kcal/mol) in parenthesis.

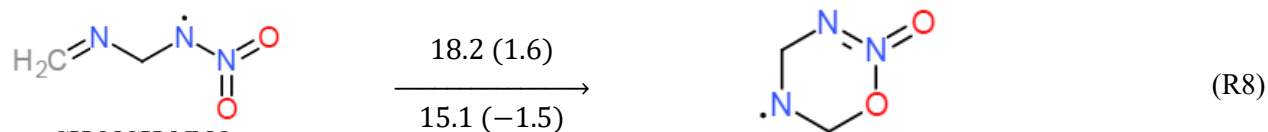
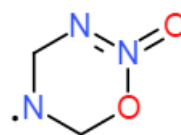
With bond dissociation enthalpy of 36.7 kcal/mol as shown in reaction (R1), RDX produces the radical RDR which readily undergoes ring-opening reaction (R2) to form RDRO. RDRO is 15.1 kcal/mol less stable than RDR and decomposes via three reactions (R3)-(R5). In the first pathway, i.e., reaction (R3), intramolecular hydrogen transfer takes place from carbon to nitrogen forming a carbon radical center in intermediate INT176. Decomposition of INT176 occurs through INT149 via reactions (R6)-(R7). Through

the second pathway, RDRO can also dissociate to  $\text{CH}_2\text{NCH}_2\text{NNO}_2$  and  $\text{CH}_2\text{NNO}_2$  with barrier and enthalpy of reaction shown by reaction (R4). The intermediate  $\text{CH}_2\text{NCH}_2\text{NNO}_2$  decomposes to  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{N}$ , and  $\text{HONO}$  through the formation of a 6-member ring intermediate INT102 via reaction (R8) along with subsequent reactions (R9) and (R10). Intramolecular H-transfer also occurs in  $\text{CH}_2\text{NCH}_2\text{NNO}_2$  as shown by reaction (R11) which leads to the formation of  $\text{HCN}$ ,  $\text{CH}_2\text{N}$ , and  $\text{HONO}$  via reactions (R12) and (R13).



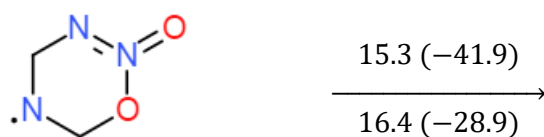


INT149

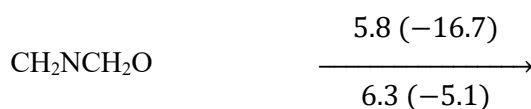
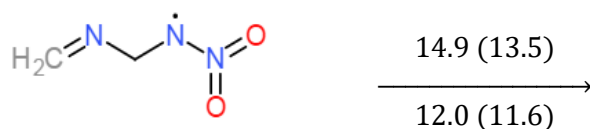
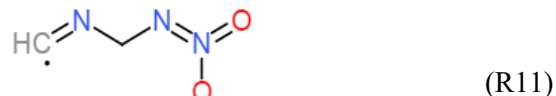
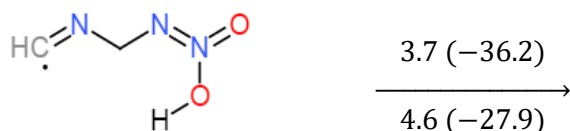
CH<sub>2</sub>NCH<sub>2</sub>NNO<sub>2</sub>

INT102

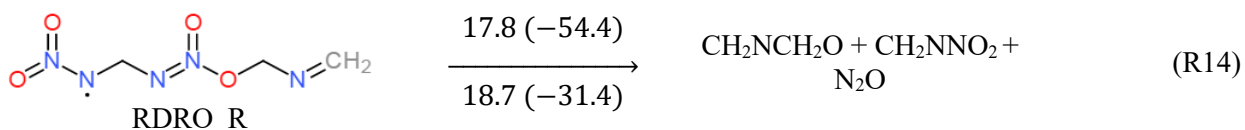
(R8)



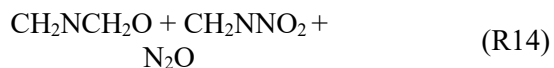
INT102

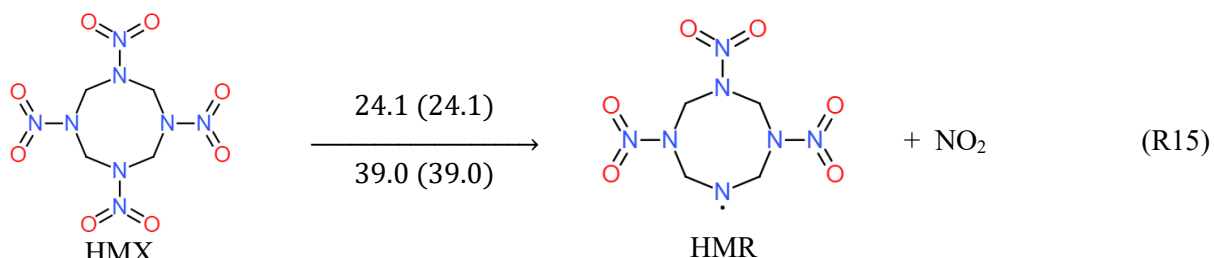
CH<sub>2</sub>NCH<sub>2</sub>OCH<sub>2</sub>NCH<sub>2</sub>OCH<sub>2</sub>NCH<sub>2</sub>NNO<sub>2</sub>HCNCH<sub>2</sub>NN(OH)OHCNCH<sub>2</sub>NN(OH)OCH<sub>2</sub>NN(OH)OCH<sub>2</sub>NN(OH)O

The third possibility for RDRO decomposition, with a slightly higher barrier, is a rearrangement reaction (R5). The rearranged product of this reaction (i.e. RDRO\_R) readily decomposes to CH<sub>2</sub>O, N<sub>2</sub>O, CH<sub>2</sub>N and CH<sub>2</sub>NNO<sub>2</sub> via reactions (R14) and (R10), both of which are thermodynamically highly favorable.



RDRO\_R

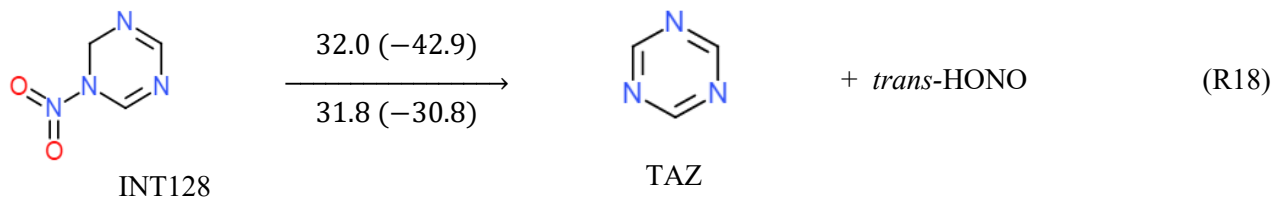
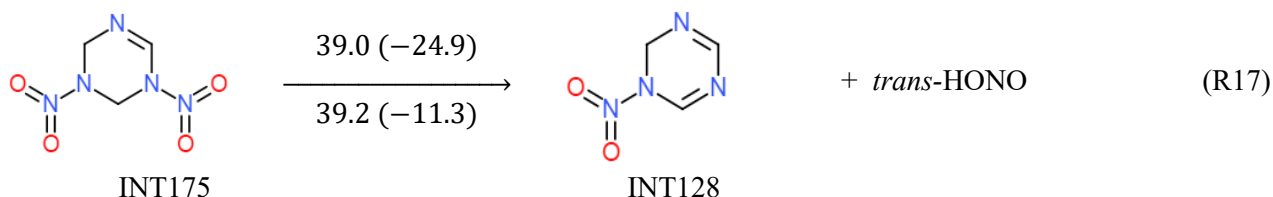
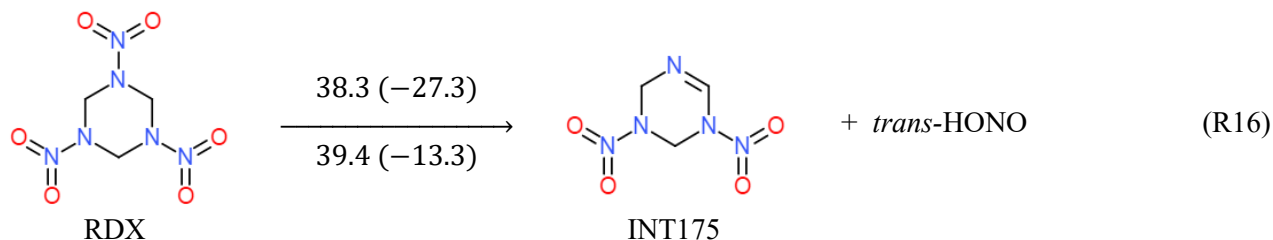




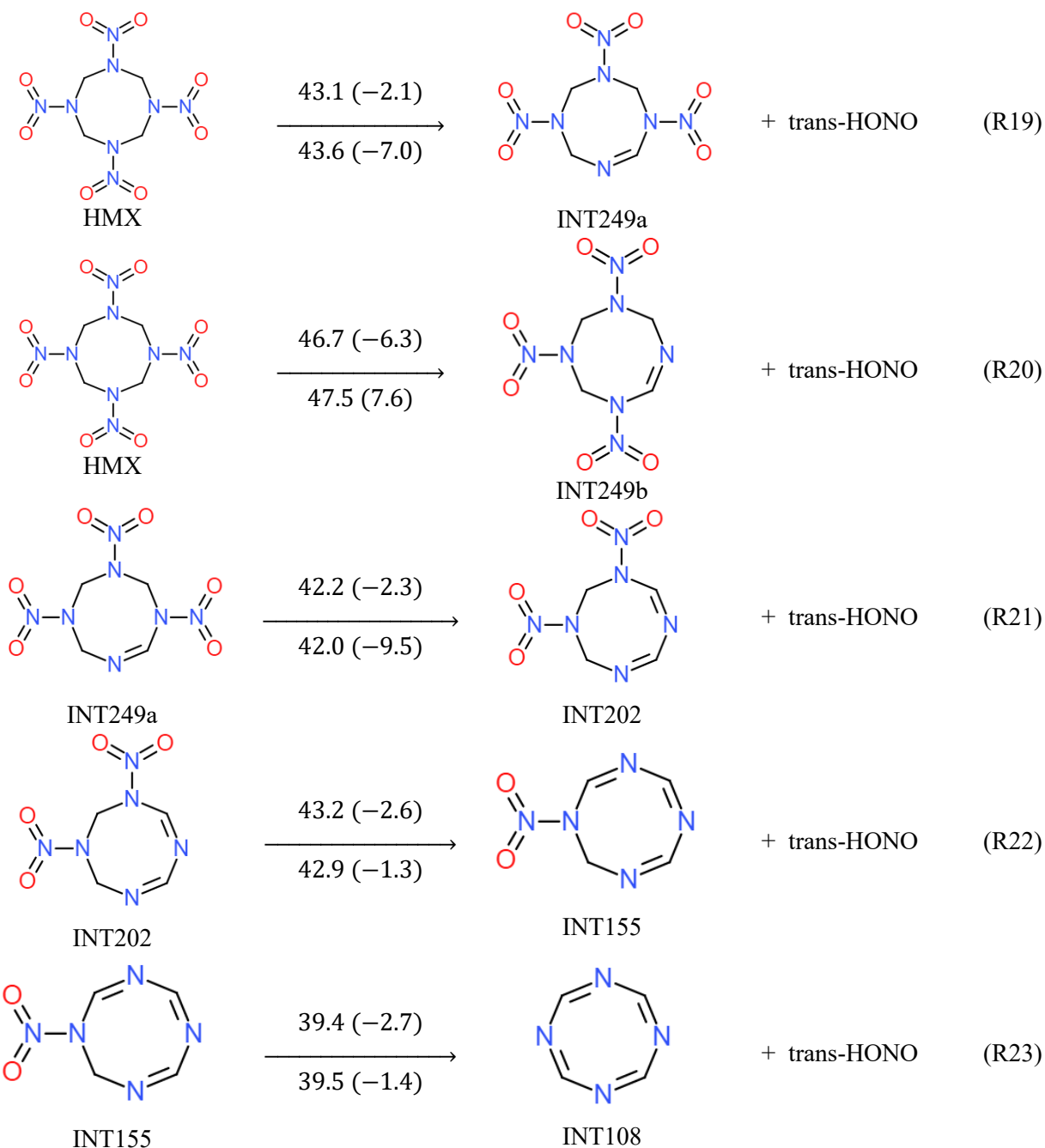
In HMX, *N-N* homolytic bond dissociation form  $\text{NO}_2$  and a radical intermediate HMR, which undergoes subsequent reactions. The bond dissociation energy in the gas phase is estimated to be about 40 kcal/mol [30,33]. In our liquid-phase calculation, the bond dissociation energy is found to be 39.0 kcal/mol as shown by reaction (R15). Based on our study on validation of the liquid-phase mechanism for RDX [34], *N-NO<sub>2</sub>* bond dissociation pathway was found to not play an important role in the liquid phase. Hence, this pathway was not investigated further for HMX decomposition in the liquid phase.

### 1.3.2 Pathway 2: HONO elimination

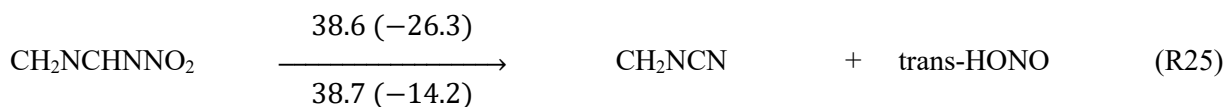
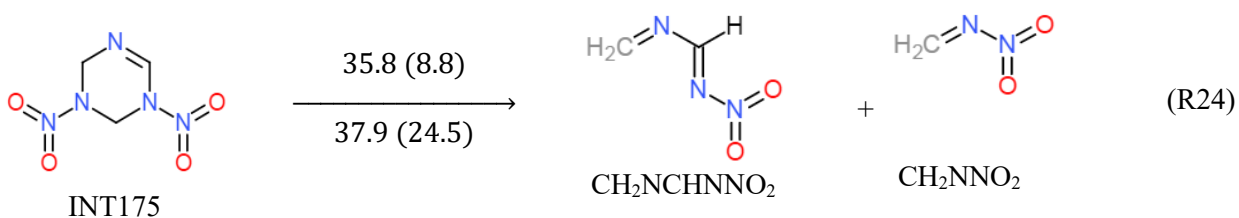
Because of the close non-bonded contact of H and  $\text{NO}_2$  in RDX and HMX, H migration takes place from carbon to oxygen leading to HONO elimination and formation of the intermediate INT175 and INT249 in RDX and HMX respectively. The HONO elimination leads to the formation of C-N double bond in INT175, as shown by reaction (R16), causing the neighboring  $\text{NO}_2$  group to reorient from axial position to equatorial position. INT175 undergoes HONO elimination to form INT128 via reaction (R17). Similarly, INT128 form 1,3,5 triazine (TAZ) via reaction (R18) through another HONO elimination.



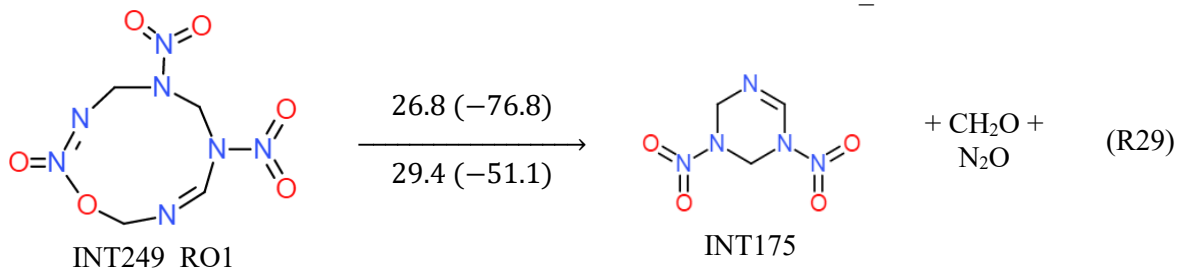
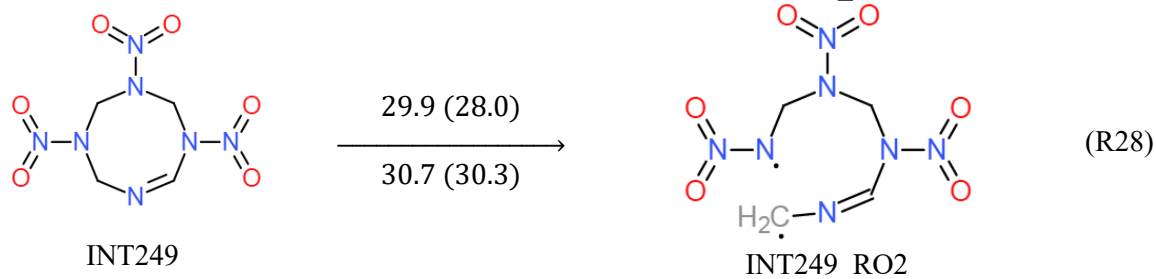
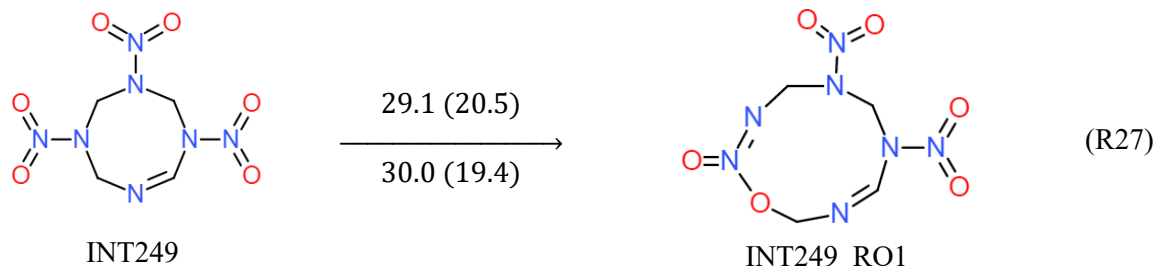
In HMX, the non-bonded distance between H on carbon and O on  $-\text{NO}_2$  is smaller for equatorial  $\text{NO}_2$  (2.16 Å) as compared to axial  $\text{NO}_2$  (2.39 Å). Hence, preferential HONO elimination occurs in HMX via equatorial  $\text{NO}_2$  as shown by reaction (R19) as compared to axial  $\text{NO}_2$  shown by reaction (R20). INT249 undergoes three successive HONO eliminations to form INT202 via reaction (R21), INT155 via reaction (R22) and INT108 via reaction (R23).

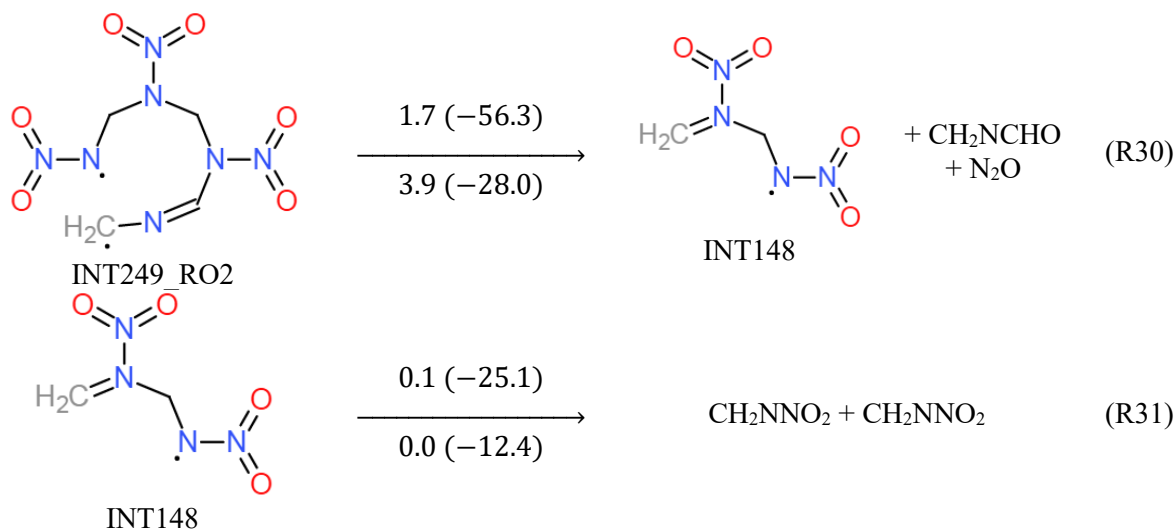


These reactions may play an important role in the liquid phase. However, the experimental results indicate the presence of carbon-containing species very early. Hence extensive search is carried out for early ring-opening reactions. The decomposition of RDX and HMX begins with HONO elimination to form INT175 and INT249 respectively. However, the next step in the decomposition does not involve another HONO elimination reaction. Instead, INT175 undergoes ring-opening reaction (R24) to form  $\text{CH}_2\text{NCHNNO}_2$  and  $\text{CH}_2\text{NNO}_2$ . The barrier for second HONO elimination from INT175 is 39.0 kcal/mol in the liquid phase whereas the barrier for the ring-opening reaction of INT175 is 35.8 kcal/mol. Hence it is more likely to undergo ring opening. The product of the ring-opening reaction (R24), i.e.,  $\text{CH}_2\text{NCHNNO}_2$  further decomposes to HONO and  $\text{CH}_2\text{NCN}$  via HONO elimination reaction (R25). Similarly,  $\text{CH}_2\text{NNO}_2$  undergoes HONO elimination reaction (R26) to form HCN.



In case of HMX, INT249 undergoes ring-opening reactions (R27) and (R28) with a barrier of ~29 kcal/mol. We have investigated various possibilities of ring opening from INT249 and found five transition states. Only two ring-opening reactions and subsequent steps are being shown here. The remaining three ring-opening reactions have forward barriers of 30.1, 31.9 and 39.6 kcal/mol. The barrier for second HONO elimination from INT249 to form INT202 is 42.2 kcal/mol in the liquid phase whereas the barriers for ring-opening reactions are 29.1 kcal/mol (forming INT249\_RO1) and 29.9 kcal/mol (forming INT249\_RO2). Hence, it is more likely to undergo ring-opening reaction.



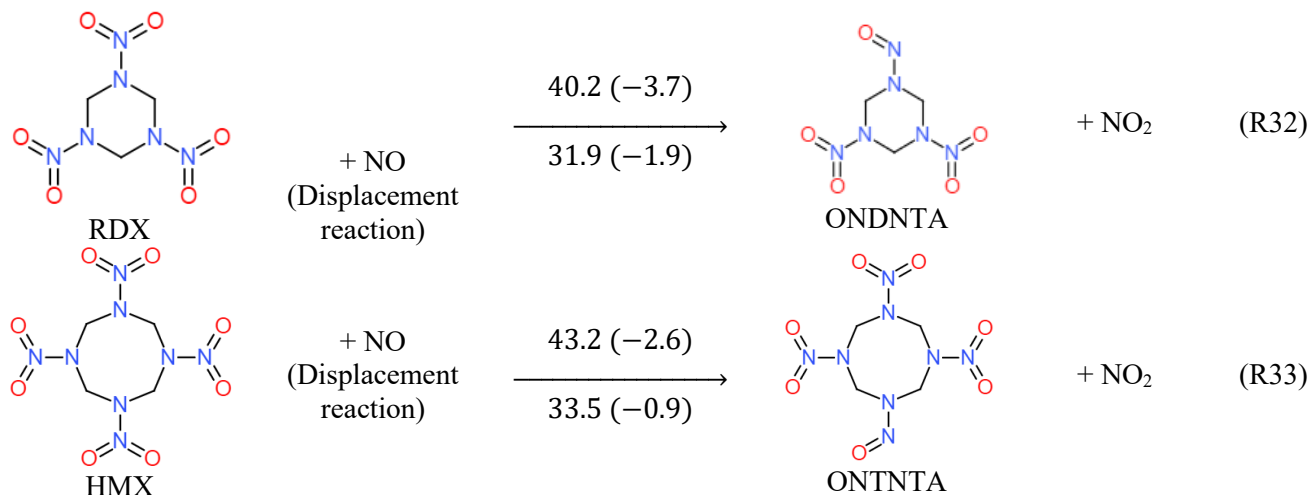


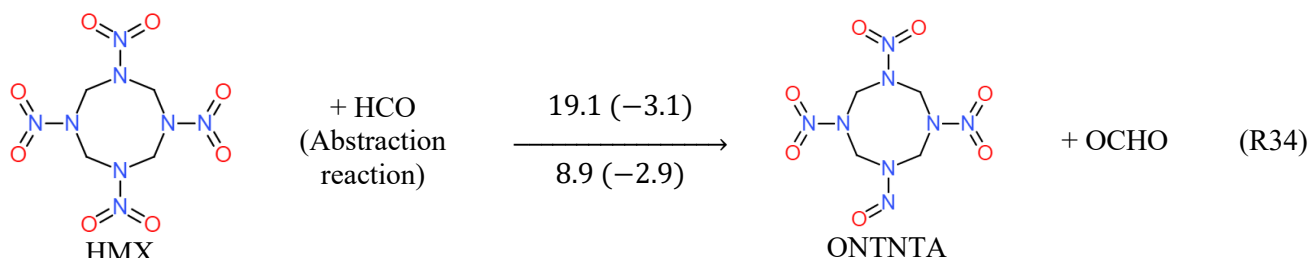
The ring-opening reaction (R27) leads to scission of the C-N bond of the ring followed by oxygen from the  $-\text{NO}_2$  group attacking the carbon atom which forms a 10-member ring structure INT249\_RO1. Formaldehyde and  $\text{N}_2\text{O}$  are released from INT249\_RO1 via a highly exothermic reaction (R29) and ring closure occur forming INT175 ( $\text{RDX}_{\text{HONO}}$ ). Similar oxygen attack occurs in INT249\_RO2 followed by the release of  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{NCHO}$  via reaction (R30) along with the formation of INT148, which subsequently decomposes to two methylene-nitramine molecules, i.e.,  $\text{CH}_2\text{NNO}_2$  via reaction (R31).

Since, the ring-opening reactions (R24), (R27) and (R28) have barriers much smaller than the barrier for the second HONO elimination reactions, and are followed by thermodynamically highly favorable reactions (R25), (R26) and (R29)-(R31), the former reactions are more likely to play an important role in liquid-phase decomposition of RDX and HMX. The species formed from ring-opening and subsequent reactions, such as  $\text{CH}_2\text{NNO}_2$ ,  $\text{CH}_2\text{NCHO}$ , and  $\text{CH}_2\text{O}$ , undergo further reactions to produce carbon-containing species, such as CO,  $\text{CO}_2$ , HCN, and HNCO observed very early in various experimental studies.

### 1.3.3 Pathway 3: Mono-nitroso analogs of RDX and HMX

Once the radical pool is initiated via the first two pathways and the concentration of NO and  $\text{NO}_2$  increases, further decomposition of RDX and HMX can occur through reactions such as (R32) – (R34). These produce ONDNTA and ONTNTA (mono-nitroso analogs of RDX and HMX respectively). Similar to their parent nitramines, ONDNTA and ONTNTA can decompose via N- $\text{NO}_2$  homolysis and HONO-elimination pathway including early ring-opening reactions.

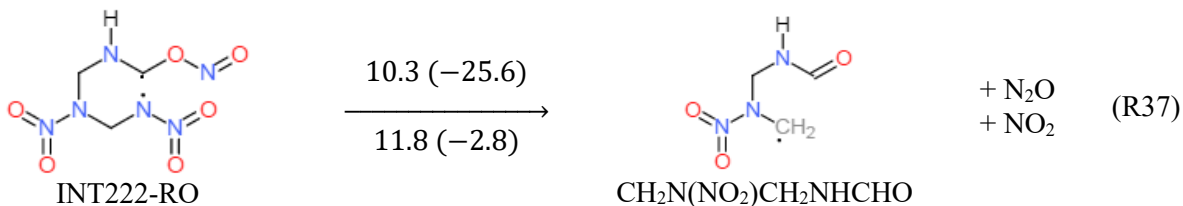
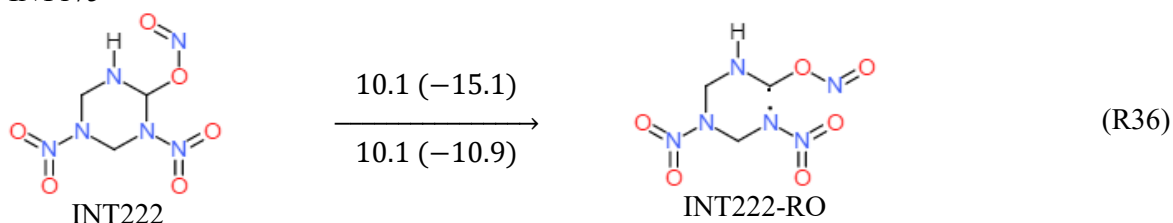
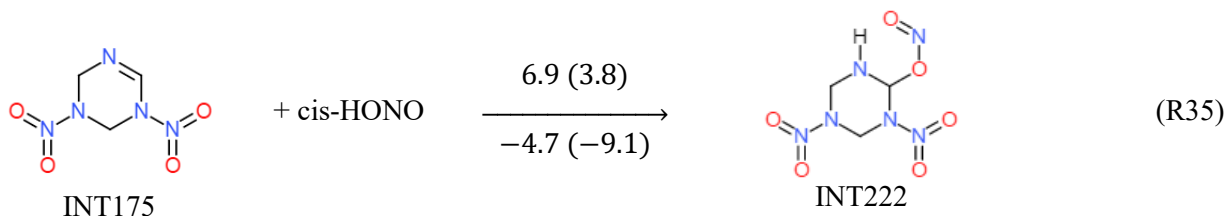


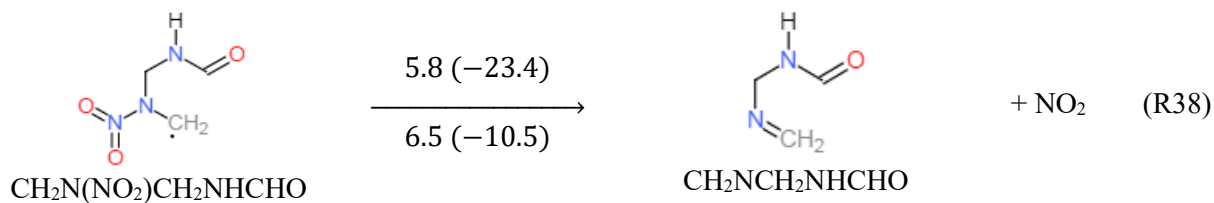


#### 1.3.4 Pathway 4: Autocatalytic prompt oxidation via HONO and ONNO<sub>2</sub> addition

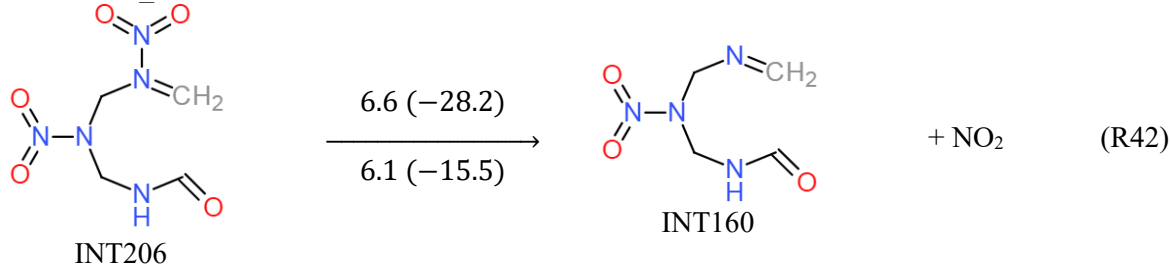
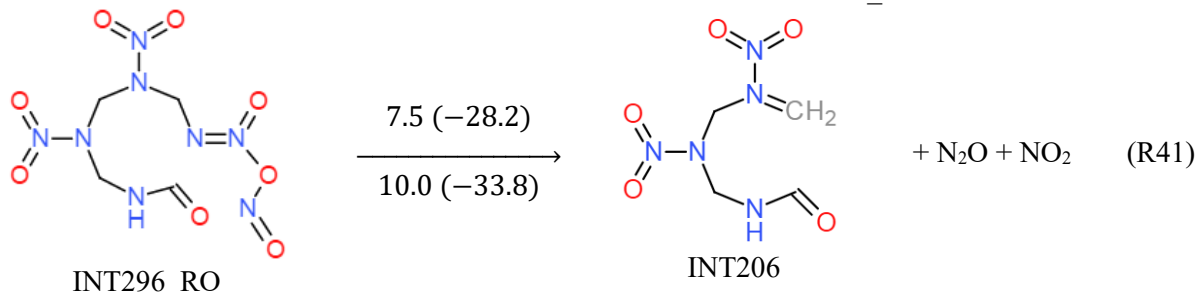
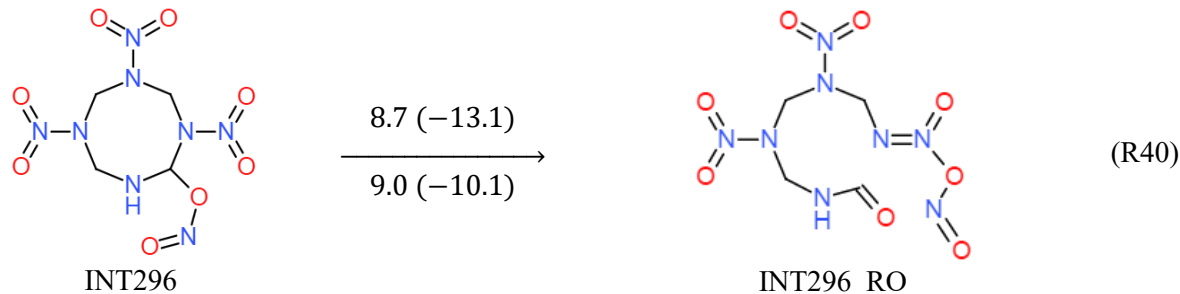
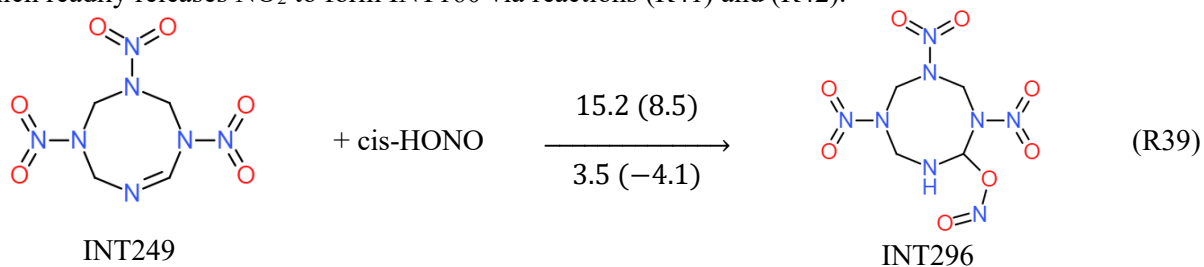
The fate of the HONO formed from HONO-elimination reactions strongly depends on the cage effect. The decomposition indeed begins with HONO elimination and forms INT175 (in RDX) and INT249 (in HMX). But due to reduced molecular mobility because of the cage effect, HONO may not be able to diffuse away from INT175 and INT249. It can react back with these intermediates, and the decomposition of the resulting intermediate can compete with the HONO elimination pathway. This reaction pathway was proposed for simple -NO<sub>2</sub> containing energetic materials such as methylnitrate, methylnitramine and nitroethane by Melius [35] and was termed as ‘prompt oxidation’ pathway. Decomposition of RDX and HMX through this pathway in the liquid phase is investigated here.

In case of RDX, HONO can react with INT175 and produce RDX, i.e., the reverse of the HONO elimination reaction (R16). But while reacting with INT175, it can flip around and react via reaction (R35) to form INT222 which is an isomer of RDX. But in INT222, there is a swapping of nitro group and hydrogen between carbon (fuel) and nitrogen (oxidizer), i.e., nitro gets attached to carbon in nitrite form as -ONO while hydrogen gets attached to the nitrogen. This converts RDX to a more oxidized form which is thermodynamically more stable by 9.1 kcal/mol as evident by reaction (R35). The resulting INT222 readily undergoes ring-opening reaction (R36) with the free energy of activation ~10 kcal/mol, which is much lower than other initial steps of decomposition. The ring-opened intermediate INT222-RO decomposes to amides such as CH<sub>2</sub>N(NO<sub>2</sub>)CH<sub>2</sub>NHCHO and CH<sub>2</sub>NCH<sub>2</sub>NHCHO via reactions (R37) and (R38), respectively. Various amides have been observed experimentally by Brill et al. [36–38].





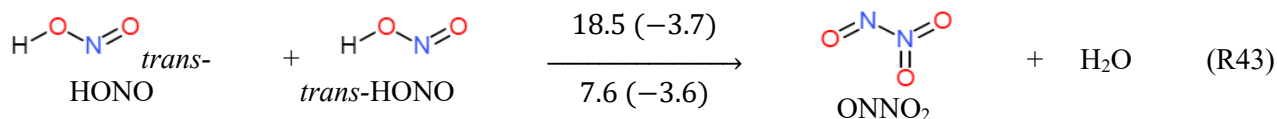
In case of HMX, HONO reacts with INT249 and produce INT296 which is an isomer of HMX. Again, in INT296, there is a swapping of nitro group and hydrogen between carbon (fuel) and nitrogen (oxidizer) similar to that of INT222. This converts HMX to a more oxidized form, which is exothermic by 4.1 kcal/mol as evident by reaction (R39). The resulting INT296 readily undergoes ring-opening reaction (R40) with the free energy of activation of 8.7 kcal/mol, which is much lower than other initial steps of decomposition. The ring-opened intermediate INT296\_RO decomposes to an intermediate amide INT206 which readily releases  $\text{NO}_2$  to form INT160 via reactions (R41) and (R42).



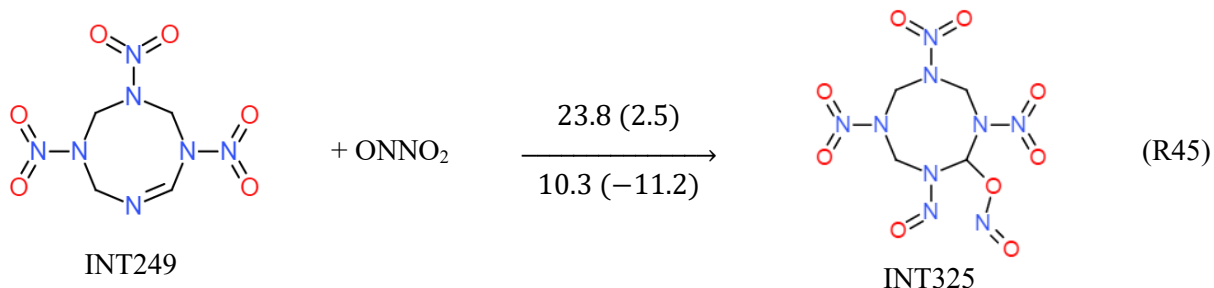
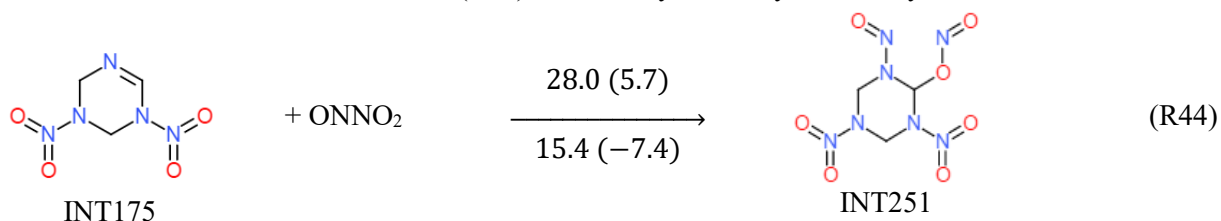
The release of  $\text{N}_2\text{O}$  and  $\text{NO}_2$  very early explains the exothermicity observed in the experiments. These amides are proposed to form a non-volatile residue (NVR) in slow thermolysis experiments of Behrens, or they further decompose to lower-molecular-weight amides, as well as  $\text{HCN}$ ,  $\text{CH}_2\text{O}$ , and  $\text{N}_2\text{O}$ .

Similar HONO addition reactions are also possible for intermediates, formed from various initial reactions, such as  $\text{CH}_2\text{NCHNNO}_2$ ,  $\text{CH}_2\text{NNO}_2$ , and  $\text{CH}_2\text{NCHO}$ . These reactions lead to the formation of  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{HNO}$ , and  $\text{HNCO}$ , while HONO acts as an autocatalytic species.

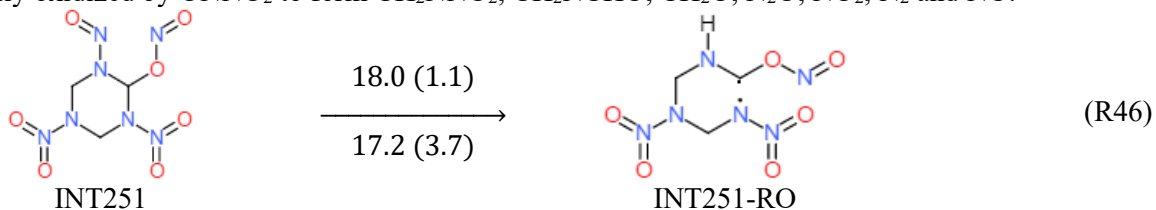
HONO also undergoes self-reactions in various combinations of *cis*- and *trans*-configurations, and forms  $\text{H}_2\text{O}$  and  $\text{ONNO}_2$  with a forward free energy barrier of about 20 kcal/mol.  $\text{ONONO}$  can also be formed from the HONO self-reactions but it is readily converted to the more stable isomer  $\text{ONNO}_2$ , and can possibly dissociate to  $\text{NO}_2^-$  and  $\text{NO}^+$  in the liquid phase. In our calculations, the formation of ions is not favored, and  $\text{ONNO}_2$  tend to remain undissociated in liquid-phase. In the gas-phase, however,  $\text{ONNO}_2$  readily dissociates into  $\text{NO}$  and  $\text{NO}_2$ .

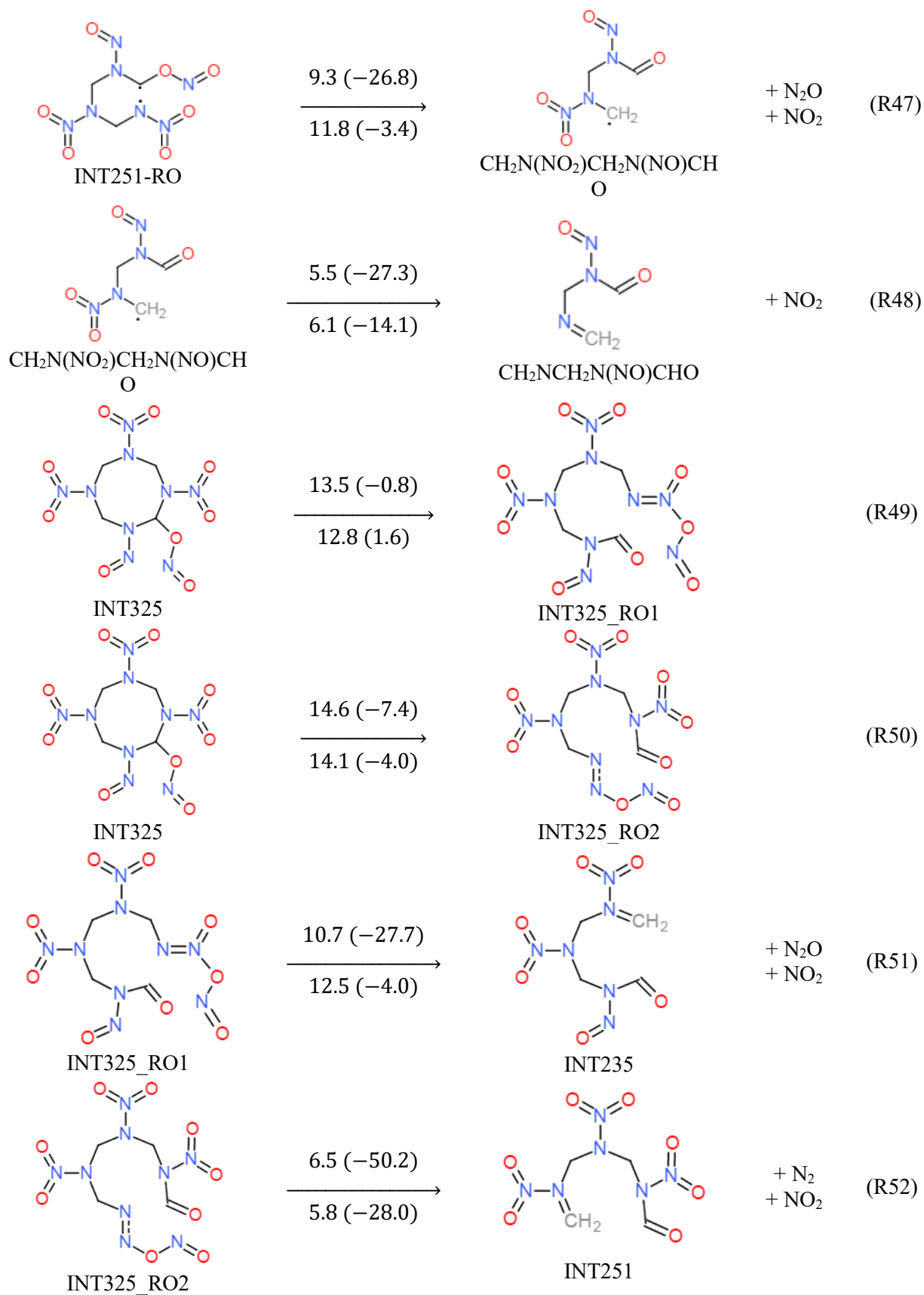


Similar to HONO addition reactions, C-N double bond in INT175 can be attacked by  $\text{ONNO}_2$  leading to the formation of INT251 via reaction (R44) where  $-\text{ONO}$  is attached to carbon and  $-\text{NO}$  is attached to nitrogen. Similar to INT222, INT251 is also a more oxidized form and the reaction (R44) is thermodynamically favored by 7.4 kcal/mol. In case of HMX, C-N double bond in INT249 can also be attacked by  $\text{ONNO}_2$  leading to the formation of INT325 via reaction (R45). Similar to INT296, INT325 is also a more oxidized form, and reaction (R45) is thermodynamically favored by 11.2 kcal/mol.



INT251 decomposes via ring-opening reaction (R46) followed by decomposition to amides  $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO})\text{CHO}$  and  $\text{CH}_2\text{NCH}_2\text{N}(\text{NO})\text{CHO}$  via (R47) and (R48), respectively. In INT251 and INT325, the  $-\text{C}-\text{N}-$  bonds of the carbon having  $-\text{ONO}$  group on it are very weak. INT325 readily undergoes ring-opening reactions (R49) and (R50) with barriers 13.5 kcal/mol and 14.6 kcal/mol, respectively. The intermediates produced from ring-opening reactions release  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$  via highly exothermic reactions (R51) and (R52) along with the formation of amides INT235 and INT251. These amides are promptly oxidized by  $\text{ONNO}_2$  to form  $\text{CH}_2\text{NNO}_2$ ,  $\text{CH}_2\text{NCHO}$ ,  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{N}_2$  and  $\text{NO}$ .

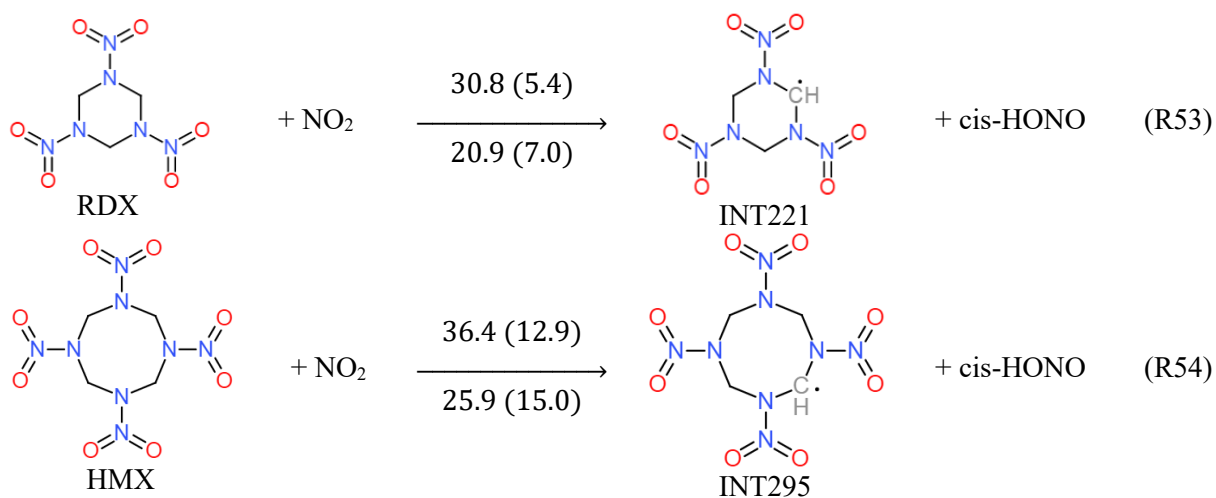




ONNO<sub>2</sub> can also accelerate the decomposition of the intermediates formed from various initiation reactions. The C-N double bonds in the intermediates CH<sub>2</sub>NCHNNO<sub>2</sub>, CH<sub>2</sub>NNO<sub>2</sub> and CH<sub>2</sub>NCHO are attacked by ONNO<sub>2</sub> via a five-member transition state and an intermediate complex is formed where -ONO gets attached to the carbon atom while NO gets attached to the nitrogen atom. Subsequently, the C-N bond becomes very weak and breaks apart forming amide group >N-C(O)-R. The products formed from these reactions include CO, HNO, HNCN, and HOCN, while ONNO<sub>2</sub> acts as an autocatalytic species.

### 1.3.5 Pathway 5: Autocatalytic hydrogen abstraction via NO<sub>2</sub>

Various radical intermediates, such as NO<sub>2</sub>, NO, HCO etc., can abstract hydrogen from RDX and HMX. Instead of successive HONO elimination to ultimately form TAZ (RDX-<sub>3</sub>HONO) and INT108 (HMX-<sub>4</sub>HONO), we have found an alternate route to TAZ and INT108 via hydrogen abstraction. NO<sub>2</sub> readily abstracts a hydrogen atom and forms INT221 (RDX-<sub>H</sub>) and INT295 (HMX-<sub>H</sub>) as shown by reaction (R53) and (R54) respectively. Once a hydrogen is abstracted from the carbon, N-NO<sub>2</sub> bond on the adjacent nitrogen becomes very weak resulting in the release of NO<sub>2</sub> and formation of C=N. These two-step reactions lead to the same products INT175 and INT249 as obtained via first HONO elimination reactions from RDX and HMX respectively. This two-step process is repeated successively, suggesting that TAZ and INT108 could be formed. Analogous reactions of ONDNTA and ONTNTA were also investigated and found to have similar barriers.



## 1.4 Conclusions

Based on the liquid-phase calculations presented here and the gas-phase results reported in the literature, we believe the major channel for decomposition of RDX and HMX in gas-phase could be N-NO<sub>2</sub> bond homolysis, however, in liquid phase; these are more likely to begin decomposition via HONO elimination. The subsequent ring-opening reactions, prompt oxidation reactions and autocatalytic hydrogen abstraction reactions presented here have barriers much lower than the successive HONO elimination reactions, and hence these reactions could be very fast. The release of N<sub>2</sub>O and N<sub>2</sub> makes these pathways exothermic as well. Additionally, these reactions could also play an important role in gas phase. The proposed reactions explain the likely mechanism of formation of N<sub>2</sub>O and CH<sub>2</sub>O from the same pathway. The regeneration of NO<sub>2</sub>, HONO and ONNO<sub>2</sub> also makes the proposed reactions very important and explains the “autocatalytic-like” reactions observed experimentally. Furthermore, these pathways explain the formation of amides observed experimentally. These elementary reactions are used to develop a detailed liquid-phase chemical kinetics mechanism of RDX and HMX.

## CHAPTER 2

### IMPROVEMENT AND VALIDATION OF A DETAILED REACTION MECHANISM FOR THERMAL DECOMPOSITION OF RDX IN LIQUID PHASE

#### 2.1 Introduction

The objective of the current study is to expand and validate the liquid-phase decomposition mechanism of RDX proposed by Patidar and Thynell [10] by using experimental results from confined rapid thermolysis. In the expanded mechanism, many secondary reactions were identified to link intermediate species to the final decomposition products detected in the experiments. Specifically, several important reactions among the smaller molecular weight species, such as CO, CO<sub>2</sub>, CH<sub>2</sub>O, NO, NO<sub>2</sub>, CH<sub>2</sub>NH, HONO, HCOOH, etc., were added to the mechanism. For its validation, the developed liquid-phase reaction mechanism for RDX is included in a transient model simulating the confined rapid thermolysis experiment, covering the temperature range from 538 to 568 K. A sensitivity analysis is performed to identify the most important reactions, which also yields a reduced reaction mechanism.

#### 2.2 Experimental details

To study the thermal decomposition of RDX in the liquid phase, we employ results from confined rapid thermolysis [39] which is sensitive to condensed phase decomposition. In this experiment, a sub-milligram sample is rapidly heated to a set temperature where decomposition occurs. The spectral transmittance of the evolved gases is recorded by an FTIR spectrometer operating at a 2.6 cm<sup>-1</sup> wavenumber resolution. A spectrum of the transmittance is recorded every 50 ms, covering the spectral range from 600 to 3750 cm<sup>-1</sup>. The evolved decomposition products enter a cool atmosphere, which is purged by with an inert gas (N<sub>2</sub>); thus gas-phase reactions among the evolved decomposition products are very limited and neglected. The schematics of the thermolysis region with position of RDX sample is shown in Figure 2-1.

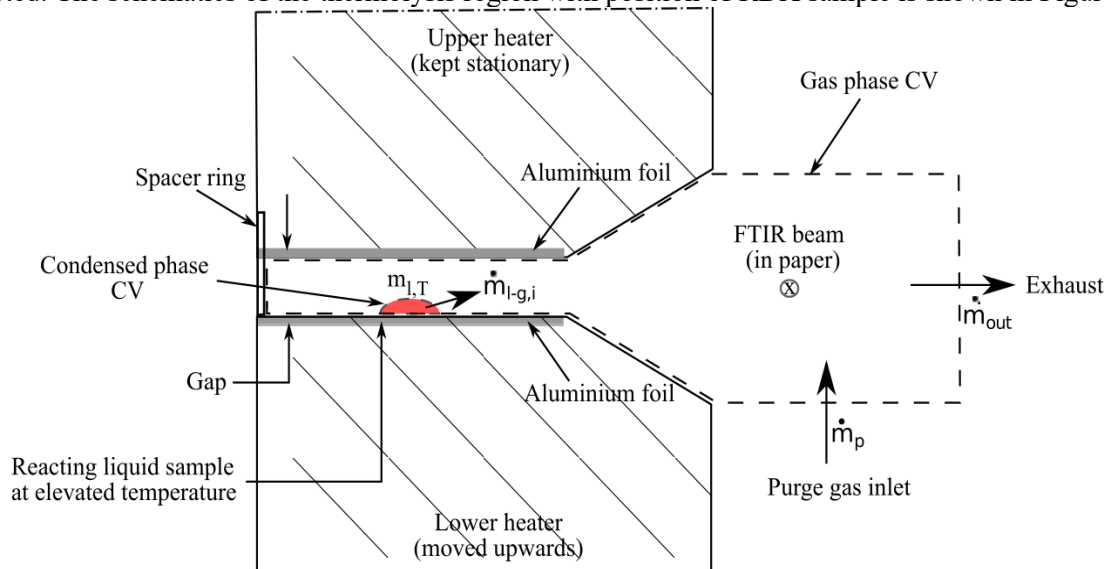


Figure 2-1. Schematics of the thermolysis chamber and the accessories required for species detection in gas phase.

#### 2.3 Data reduction procedure

Multiple confined rapid thermolysis experiments were performed at each set temperature and at atmospheric pressure. The spectrums recorded in these experiments contain information about the concentration of all IR active species that were present in the gas-phase region. In order to quantify the species concentration, each spectrum was analyzed separately using a data-reduction model described in [40]. The required radiative properties of the IR active species were taken from the HITRAN database [41].

Table 2-1 shows the list of identified species, where the spectral ranges were obtained from the NIST webbook [42].

Table 2-1. Wavenumber range used for different molecules in data reduction model.

| Molecule          | Spectral Range (cm <sup>-1</sup> ) | Molecules with overlapping bands | Comments                                          |
|-------------------|------------------------------------|----------------------------------|---------------------------------------------------|
| NO <sub>2</sub>   | 1565–1655                          | H <sub>2</sub> O                 | Only band tail of CH <sub>2</sub> O overlaps      |
| NO                | 1800–1950                          | H <sub>2</sub> O                 | Only band tail of CH <sub>2</sub> O overlaps      |
| CO                | 2000–2150                          | —                                | —                                                 |
| N <sub>2</sub> O  | 2150–2250                          | —                                | CO is ignored (weak absorber)                     |
| CO <sub>2</sub>   | 2275–2400                          | —                                | —                                                 |
| CH <sub>2</sub> O | 2675–3100                          | NO <sub>2</sub>                  | —                                                 |
| HCN               | 3200–3400                          | —                                | —                                                 |
| H <sub>2</sub> O  | 3600–3750                          | CO <sub>2</sub>                  | CO <sub>2</sub> combinations bands are very small |

## 2.4 Experimental results

The set temperature of the RDX decomposition varied from 538 K to 568 K in the gaps of 10 K. Several experiments were performed for each set temperature to determine the experimental uncertainty.

### 2.4.1 IR spectrum of the gas-phase species

Figure 2-2 shows a single transmittance spectrum with bands corresponding to different product species. These species evolved during RDX decomposition for a set temperature of 558 K. The spectrum was obtained at  $t = 4.84$  s from the start of the decomposition process. The different bands present in the spectrum indicate the presence of N<sub>2</sub>O, NO<sub>2</sub>, NO, HCN, CH<sub>2</sub>O, CO<sub>2</sub>, CO, and H<sub>2</sub>O in significant concentrations. These species match with the earlier identified products of RDX decomposition by Schroeder [2] and Oyumi and Brill [43]. According to Beer's law, the band height depends upon the species concentration and its molar absorptivity. CO and NO are less IR-active due to a low value of their permanent dipole moments, and hence their bands are weak. Many other similar species can be present in the gas phase and are not identified here. For the current study, we only focus on the evolution of these eight species.

### 2.4.2 Concentration of gas-phase species

The relative mole fractions of decomposition products identified using transmittance spectrum were calculated using the data reduction model described in section 2.3. The model was simulated for each of the acquired spectrums to provide species relative mole fractions at corresponding time instants. These relative mole fraction values at different time instants were combined to create profiles for the entire 7 s interval of an experiment. These relative mole fraction profiles were obtained for set temperatures of 538 K, 548 K, 558 K, and 568 K. Figure 2-3 shows the relative mole fraction profiles of all the eight identified product species for the set temperature of 568 K. Even though the set temperature varies from 538 to 568 K, the species evolution rates vary significantly.

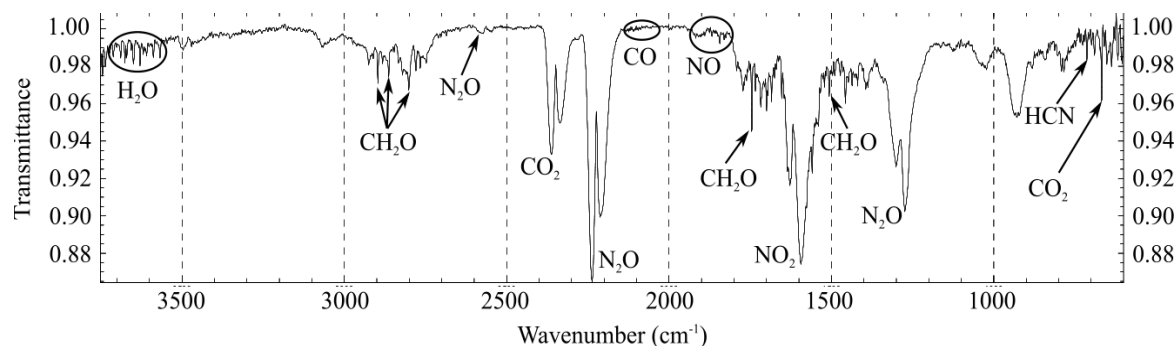


Figure 2-2. IR spectrum of species in gas-phase region evolved during RDX decomposition for a set temperature of 558 K and 1 atm pressure.

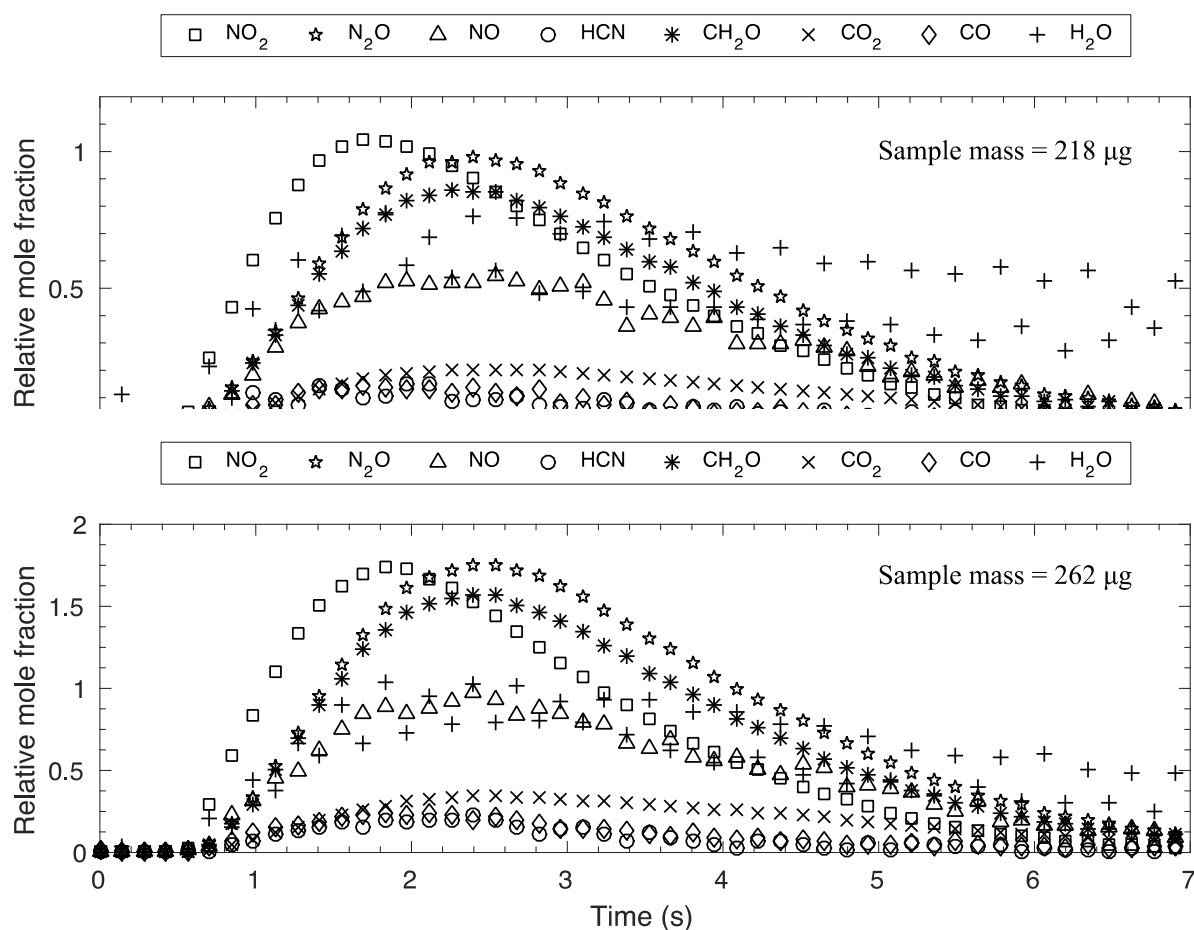


Figure 2-3. Temporal species evolution for two experiments with slightly different sample masses at a set temperature of 568 K and 1 atm pressure.

To get a qualitative estimate of the uncertainty in the experimentally obtained relative mole fraction profiles three experiments were performed at each of the set temperatures. For these experiments, all other experimental parameters such as purge gas flow rate and pressure were kept constant except sample mass. Since the sample mass in the CRT experiments was in micrograms, it was not possible to exactly take the same amount every time. The variation in experimental relative mole fraction profiles for two experiments performed at a set temperature of 568 K is shown in Figure 2-3. For these two experiments, the initial mass

of RDX sample was slightly different (218  $\mu\text{g}$  and 262  $\mu\text{g}$ ). The sample with more mass is expected to release more gaseous products upon decomposition. However, the evolution of different species relative to each other is expected to remain largely the same. Figure 2-3 shows that for the sample with 262  $\mu\text{g}$  initial mass the relative mole fractions of evolved species are slightly higher. The relative mole fraction profiles corresponding to the two initial sample masses are, however, not exactly same. For the sample with 218  $\mu\text{g}$  of initial mass of RDX,  $\text{NO}_2$  peak is higher than  $\text{N}_2\text{O}$  peak but for the sample with 262  $\mu\text{g}$  of initial mass  $\text{N}_2\text{O}$  peak is slightly higher than  $\text{NO}_2$  peak. Similar variations are obtained for rest of the species as well at other temperatures. These results suggest that the experimentally obtained relative mole fractions have an uncertainty of approximately 10%. From Figure 2-3, it can also be observed that the relative mole fraction value for  $\text{H}_2\text{O}$  fluctuates much more than other species. These fluctuations are not physically possible. It suggests that the data reduction model results for  $\text{H}_2\text{O}$  are much less reliable compared to other species. In general, these large variations in  $\text{H}_2\text{O}$  concentration are caused by its fine line structure, which is very difficult to resolve. For example, in the works by Brill and co-workers [43,44], the evolution of  $\text{H}_2\text{O}$  is not estimated; only the initial appearance of  $\text{H}_2\text{O}$  is given. To improve the quality of the predictions, it is necessary to increase the spectral resolution, but it comes at the expense of a decreased time resolution and increased noise in the spectra.

Figure 2-3 also shows that  $\text{NO}_2$  emerges quickly in the initial phase of decomposition, reaches its peak value and then decreases.  $\text{NO}$  seems to roughly follow  $\text{NO}_2$  evolution trend although the peaks are somewhat shifted. This suggests that most major pathways of their production are common. Similarly, the relative mole fraction profiles for  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  follow almost the same trend. Both species emerge at a slightly lower rate than  $\text{NO}_2$  during the initial decomposition phase, reaches peak value and then decreases. The peaks for these two species occur after the peak of  $\text{NO}_2$ . The evolution profiles of  $\text{CO}_2$  and  $\text{CO}$  are almost overlapping for all the experiments. The concentrations of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{HCN}$  are small compared to other species.

The effect of the set temperature on RDX decomposition process in liquid phase was also studied. Relative mole fraction profiles obtained for set temperatures in the range 538 to 568 K were compared. It was observed that with increase in set temperature, the peaks in the relative mole fraction profiles of all the species become higher and emerge earlier in the decomposition event. Also, the  $\text{NO}_2$  mole fraction relative to  $\text{N}_2\text{O}$  increases as the set temperature increases. Similar trend of  $\text{NO}_2/\text{N}_2\text{O}$  ratio was obtained by Brill and co-workers [44,45] in their experimental work on explosives and propellants, including, RDX and HMX.

## 2.5 Model for decomposition of RDX

The overall computational model consists of three key components, 1) liquid-phase reaction mechanism, 2) conservation equations for mass and species in the liquid-phase region, and 3) conservation equations for mass and species in the gas-phase region. Each one is described in following sub-sections.

### 2.5.1 Liquid-phase reaction mechanism

The detailed liquid-phase decomposition mechanism of RDX was initially developed by Patidar and Thynell [10]. The mechanism was further augmented in the current study by adding several secondary reactions by following the same approach that was utilized by Patidar and Thynell [10].

### 2.5.2 Analysis of liquid-phase region

The liquid-phase model is formulated based on the conservation equations of mass and species. The control volume (CV) for this model is defined by the boundaries of the sample present in the liquid phase, shown in Figure 2-1. The CV is sandwiched between two heaters 300  $\mu\text{m}$  apart. For such a small CV, it is reasonable to ignore the small concentration gradients for the species within the liquid sample. Hence, the transient mathematical model is zero-dimensional.

The temporal evolution of a species inside this CV can be attributed to its net production rate via chemical reactions and rate of evaporation. The net evaporation rate of species  $i$  can be expressed as,  $\dot{m}_{lg,i} = m_{l,i}k_{lg,i}$  where,  $m_{l,i}$  is its mass in liquid phase and  $k_{lg,i}$  is its liquid-to-gas conversion rate constant.  $k_{lg,i}$  can be expressed in a modified Arrhenius form. The net mass production rate of species  $i$  due to all elementary reactions can be expressed as,  $\dot{m}_{rxn,l,i} = (\dot{\omega}_{l,i}W_i/\rho_l)m_{l,T}$  where,  $\dot{\omega}_{l,i}$  is the net molar

production rate per unit volume,  $W_i$  is the species molecular weight,  $\rho_l$  is the liquid-phase density, and  $m_{l,T}$  is total mass of the liquid phase. For the experimentally measured sample temperature range, the density of the liquid sample is assumed constant. Hence, the set of mass conservation equations which governs the temporal evolution of species mass fraction  $Y_{l,i}$  in the liquid phase is given by,

$$\frac{d}{dt}(Y_{l,i}) = \frac{\dot{\omega}_{l,i}W_i}{\rho_l} - Y_{l,i}k_{lg,i} + Y_{l,i} \sum_{j=1}^{n_g-1} Y_{l,j}k_{lg,j}, \quad i = 1, 2, \dots, n_l \quad (2-1)$$

where,  $n_l$  and  $n_g$  are the total number of species in liquid and gas phase, respectively.

$\dot{\omega}_{l,i}$  can be evaluated by considering rate law and species stoichiometry for each of the elementary reactions of species  $i$ . The effective rate constant  $k_{eff}$  for an elementary reaction is evaluated using kinetics-based ( $k_{kin}$ ) and diffusion-based ( $k_{diff}$ ) rate constants,

$$\frac{1}{k_{eff}} = \frac{1}{k_{kin}} + \frac{1}{k_{diff}}. \quad (2-2)$$

The kinetics-based rate constants are evaluated using the thermodynamic formulation of conventional transition state theory [20]. For an elementary reaction, it can be expressed as

$$k_{kin,f}(T) = \sigma_s \tau_{tun} \frac{k_B T}{h c_{ref}^{n-1}} \exp\left(-\frac{\Delta G_f^\ddagger}{R_u T}\right) \quad (2-3)$$

where,  $k_B$  is the Boltzmann constant,  $h$  the Planck's constant,  $R_u$  the universal gas constant,  $n$  the order of the reaction, and  $c_{ref}$  is the standard state concentration taken as 1M.  $\sigma_s$ ,  $\tau_{tun}$ , and  $\Delta G_f^\ddagger$  are the symmetry factor, the tunneling factor, and the forward Gibbs free energy barrier for the reaction, respectively. Tunneling factor is calculated using the Wigner approach [25]. Kinetics-based rate constant for the backward reaction can be expressed similarly by using Gibbs free energy in the backward direction  $\Delta G_b^\ddagger$ . The kinetics-based rate constant accounts for the energy required to cross the activation barrier but does not consider the finite time required for the molecules to diffuse through the solution. The rate at which molecules diffuse to react with one another depends on their size and solution viscosity. Unlike in gas phase, diffusion plays a significant role in the liquid-phase decomposition process. As viscosity of the solution increases, the diffusion of molecules within the solution decreases. As a result, the reaction rate is limited by the diffusion process for otherwise kinetically fast reactions. For kinetically slow reactions, diffusion has a negligible or no effect at all.

The mathematical treatment used here for consideration of diffusion represents an extension of theory for bimolecular reactions with neutral species provided by Strehlow [46]. For a general elementary reaction of the form,  $A + B + \dots \leftrightarrow P + Q + \dots$ , diffusion of the reactants to form a reactant complex can be approximated by sequential combination of these species. Similarly, the diffusive dissociation of product complex to form all the products can be approximated by its sequential dissociation. The diffusion rate constants for these intermediate steps are given by [46],

$$k_{diff,c} = 4\pi N_A R(D_P + D_Q) \text{ and } k_{diff,d} = 4\pi R(D_P + D_Q)/V. \quad (2-4)$$

$k_{diff,c}$  is diffusion rate constant for combination of species  $P$  and  $Q$ , whereas  $k_{diff,d}$  is the diffusion rate constant for dissociation of  $PQ$ .  $N_A$  is Avogadro number,  $R$  is encounter radius,  $V$  is volume corresponding to encounter radius, and  $D$  is diffusion coefficient. Diffusion coefficient is inversely proportional to molecule radius  $r$  and is given by  $D = k_B T / 6\pi\eta r$  where  $\eta$  is dynamic viscosity of the solution. The net diffusion rate constants in forward and backward directions can be obtained by applying quasi-static assumption. The radius of each molecule is approximated according to the method used in computing its volume within the Gaussian program package. The dynamic viscosity of the solution is approximated by dynamic viscosity of RDX at the solution temperature. For RDX, dynamic viscosity value was calculated at various temperatures using equilibrium molecular dynamics calculation and then fitted to a cubic polynomial for 475-675 K range,  $\eta = (-0.002551883266 T^3 + 5.1897440080 T^2 - 3531.527767 T + 807165.85) \times 10^{-6}$  Pa-s.

### 2.5.3 Analysis of gas-phase region

Similar to the liquid-phase, the gas-phase model is also based on the conservation equations of mass and species. The gas-phase CV is shown in Figure 2-1. Decomposition products which evaporate from the liquid-phase mix with the purge gas in this CV. Uniform mixing of the species is assumed. The gaseous mixture leaves the CV instantly to the large volume of the thermolysis chamber. For this open CV, a constant pressure of 1 atm is reasonable. At inlet, the purge gas is at room temperature and hence, temperature of the decomposition products decreases as they mix with it. It is suitable to assume that chemical reactions cease to occur in gas-phase CV. For high flow rate of purge gas temperature inside the CV remains almost constant. Ideal gas law is also assumed to be applicable for the gaseous mixture.

Under these model assumptions, the mass conservation equation for species  $i$  in terms of its mole fraction  $X_{g,i}$  in gas-phase region with  $n_g$  species is given by,

$$\frac{d}{dt}(X_{g,i}) = \frac{R_u T}{P V_g W_i} \left[ m_{l,T} Y_{l,i} k_{lg,i} - \left( \sum_{j=1}^{n_g-1} \frac{m_{l,T} Y_{l,j} k_{lg,j}}{W_j} + \frac{\dot{m}}{W_P} \right) X_{g,i} W_i \right], \quad (2-5)$$

$i = 1, 2, \dots, n_g - 1$

where,  $P$  and  $V_g$  are pressure and volume of the gas-phase CV, respectively.

The mass conservation equation for the purge gas in terms of its mole fraction  $X_{g,P}$  is given by,

$$\frac{d}{dt}(X_{g,P}) = \frac{R_u T}{P V_g W_P} \left[ \dot{m}_P - \left( \sum_{j=1}^{n_g-1} \frac{m_{l,T} Y_{l,j} k_{lg,j}}{W_j} + \frac{\dot{m}}{W_P} \right) X_{g,P} W_P \right] \quad (2-6)$$

where,  $W_P$  is molecular weight of purge gas.

Note that energy conservation equation is not required in the model. Experimentally obtained temperature variation is provided as input to the model. A constant temperature of 200°C is considered for gas phase. Equations (2-1), (2-5), and (2-6) together form a system of first-order differential equations. With the availability of a comprehensive reaction mechanism, these differential equations are solved simultaneously to obtain the temporal variation of species mole fractions in both liquid-phase and gas-phase regions. The decomposition mechanism for RDX has reactions with a wide range of reaction rates which makes the system of first-order differential equations stiff. This stiff system of nonlinear equations is solved using the DVODE routines developed by Brown et al. [47].

## 2.6 Computational results and comparison with experiments

Using the method explained in section 2.5.1, a total of 500 elementary liquid-phase reactions describing decomposition of RDX were identified. These reactions include 321 species and have molecularity between 1 and 3. Along with these reactions, the developed reaction mechanism also consists of the data required for estimating reaction rates. For each of the reactions, symmetry factors for forward and backward directions are listed to take into account the increase in reaction rates due to symmetry in molecular structures. For calculation of tunneling factor using the Wigner approach [25], the imaginary frequency of the transition state is listed. Other calculated properties include free energy, enthalpy and entropy of all the species and transition states.

### 2.6.1 Parameter optimization

Using the detailed reaction mechanism, the computational model was simulated for various set temperatures at a constant gas-phase pressure of 1 atm. The variation of evaporation rates of different species with temperature is not available in the literature, and hence liquid-to-gas conversion rates were optimized using experimental results of CRT. Out of the 321 species present in the liquid phase, 24 species were considered to evaporate. These species were selected on the basis of molecular weight and relative concentration in the liquid phase. The liquid-to-gas conversion rates can be expressed in modified Arrhenius form. The initial guesses for the pre-exponential factors and the activation energies for evaporation were based on a previous study on HAN by Lee and Litzinger [48]. The fitted values obtained by the optimization process for the crucial species are provided in Table 2-2.

Table 2-2. Optimized parameters of modified Arrhenius form for calculating liquid-to-gas conversion rates.

| Evaporating species | Pre-exponential, $A$ ( $s^{-1}$ ) | $n$ | Activation energy, $E_p$ (kcal/mol) |
|---------------------|-----------------------------------|-----|-------------------------------------|
| NO <sub>2</sub>     | $4.226 \times 10^{13}$            | 1   | $3.755 \times 10^4$                 |
| N <sub>2</sub> O    | $2.7 \times 10^2$                 | 0   | $6.2 \times 10^3$                   |
| NO                  | $6.133 \times 10^{11}$            | 1   | $3.393 \times 10^4$                 |
| HCN                 | $2.7 \times 10^2$                 | 0   | $8.644 \times 10^3$                 |
| CH <sub>2</sub> O   | $3.9 \times 10^5$                 | 0   | $6.904 \times 10^3$                 |
| CO <sub>2</sub>     | $2.7 \times 10^3$                 | 0   | $1.4 \times 10^3$                   |
| CO                  | $1.0 \times 10^3$                 | 0   | $6.934 \times 10^3$                 |
| H <sub>2</sub> O    | $3.9 \times 10^5$                 | 0   | $1.3856 \times 10^4$                |
| <i>cis</i> -HONO    | $3.9 \times 10^5$                 | 0   | $1.35 \times 10^4$                  |
| <i>trans</i> -HONO  | $3.9 \times 10^5$                 | 0   | $1.4 \times 10^4$                   |
| RDX                 | $3.9 \times 10^5$                 | 0   | $2.467 \times 10^4$                 |

The parameters specified in the reaction mechanism also have inherent error ranges associated with them. The error ranges depend upon the level of theory used for the quantum mechanics calculations, but more importantly on the solvation model itself. The calculated forward and backward free energy barriers in liquid phase have an estimated uncertainty up to 4-5 kcal/mol. Using the computational model, these free energy barrier values were optimized with the guidance from the experimental results of CRT. Sensitive reactions were identified by performing sensitivity analysis and their free energy barriers were modified. These values were modified by a maximum of 3.8 kcal/mol. Optimized free energy barriers for sensitive reactions are provided in Table 2-3. For reaction R41, a single optimal value of forward free energy barrier satisfying equation (2-3) could not be found. Instead, the forward rate constant was obtained in modified Arrhenius form and is provided with Table 2-3.

### 2.6.2 Validation of the detailed reaction mechanism

Using the optimized model parameters, the simulations were performed for the four set temperatures for which experimental data are available. Figure 2-4 shows the relative mole fractions of evolved gases in gas-phase region obtained experimentally and computationally for a set temperature of 538 K. In the experimental results, non-zero values of the relative mole fractions are only obtained after approximately 0.5 seconds. This delay in the evolution of gases is caused by the slow initiation of RDX decomposition at 538 K, finite rate of increase of temperature, and the time required for gases to leave the thermolysis region. The computational model takes into account the RDX decomposition rate and temporal variation of sample temperature but assumes that the gaseous products instantly escape from the thermolysis region. Hence, the peaks in evolution profiles are slightly shifted early in time in the computational result.

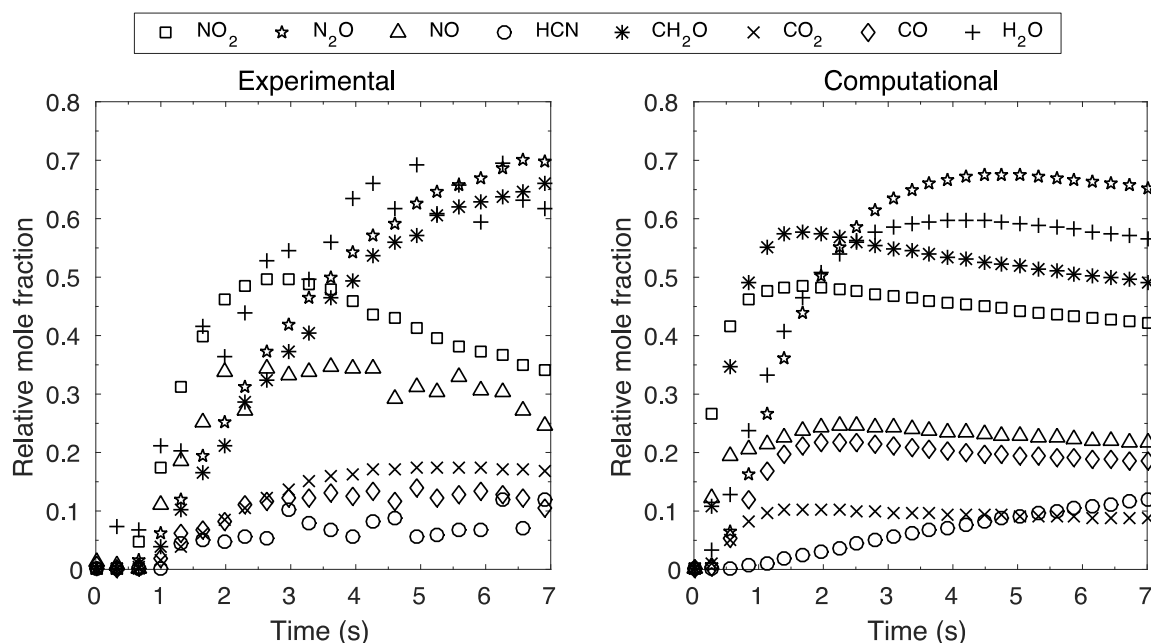


Figure 2-4. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 538 K.

For a given set temperature, the magnitude of the relative mole fractions depends upon the initial mass of RDX sample. Hence, the trend of relative mole fractions should be compared instead of the absolute values. The experimental results shown in Figure 2-4 reveal that the relative mole fraction of  $\text{NO}_2$  increases rapidly during the initial decomposition phase and then decreases. This trend is successfully captured by the computational model with our reaction mechanism. However, the model predicts slightly early peak in  $\text{NO}_2$  profile compared to experimental result. The experimentally obtained profiles of  $\text{NO}$  and  $\text{NO}_2$  are similar with lower relative mole fraction values for  $\text{NO}$ . This similarity in  $\text{NO}$  and  $\text{NO}_2$  profiles is also captured by the computational model. In both experimental and computational results, the initial evolution of  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  is slow compared to  $\text{NO}_2$ . For the later part of the decomposition process, however, their relative mole fractions are higher compared to  $\text{NO}_2$ . The computational evolution profile of  $\text{H}_2\text{O}$  lies within the experimental fluctuation range. The relative mole fractions of  $\text{HCN}$ ,  $\text{CO}_2$ , and  $\text{CO}$  are small compared to other identified species in the experiments. A reasonable agreement in the evolution trends of these species is obtained by the computational model.  $\text{HCN}$  relative mole fraction almost matches perfectly whereas  $\text{CO}$  and  $\text{CO}_2$  are predicted slightly higher and lower, respectively. The deviation can be justified by the uncertainty in the experimental results. The computational model also predicts the mass fraction of RDX remaining at the end of 7 second period in liquid-phase region. For the set temperature of 538 K, the decomposition process is slow and 83.39 percent of RDX compared to its initial mass remains at the end of 7 seconds.

Figure 2-5, Figure 2-6 and Figure 2-7 show the comparison between experimental and computational model results for set temperatures of 548 K, 558 K, and 568 K, respectively. The peaks in relative mole fraction profiles occur earlier in time as the set temperature increases. The computational model is able to capture this shift in peaks. The increase in decomposition rate with temperature can be realized by comparing the amount of RDX left in liquid phase after 7 seconds. The percentages of RDX remaining compared to its initial mass for the set temperatures of 548 K, 558 K, and 568 K are 72.42, 56.6, and 36.8, respectively. Similar to the results for the 538 K set temperature, the experimental trends of relative mole fraction profiles are captured with reasonable accuracy. Although, in general, the predictive capability of the computational model decreases with increase in set temperature. This is likely caused by

an increase in experimental uncertainties at higher temperatures, where the gas evolution becomes very rapid.

With the help of this model, we compute the time required for 95 % decomposition of RDX and define it as decomposition time. Results show that decomposition time decreases by a factor of 0.56 when set temperature increases by 10 K. The variation of decomposition time with set temperature is fits well to an exponential function and is given by,

$$t_{decomposition} = 1.987992 * 10^{15} \exp(-5.666675 * 10^{-2} T). \quad (2-7)$$

The exponential variation of decomposition time with set temperature suggests that RDX decomposition in condensed phase can be defined by a unimolecular global decomposition reaction. The global pre-exponential factor is found to be  $6.4172 * 10^{12} \text{ s}^{-1}$  with the global activation energy of 35.45 kcal/mol. The set  $E_{global} - \ln A_{global}$  is consistent with the compensation regression line for RDX provided by Brill et al. [49]. This further validates the detailed reaction mechanism and the rate kinetics parameters.

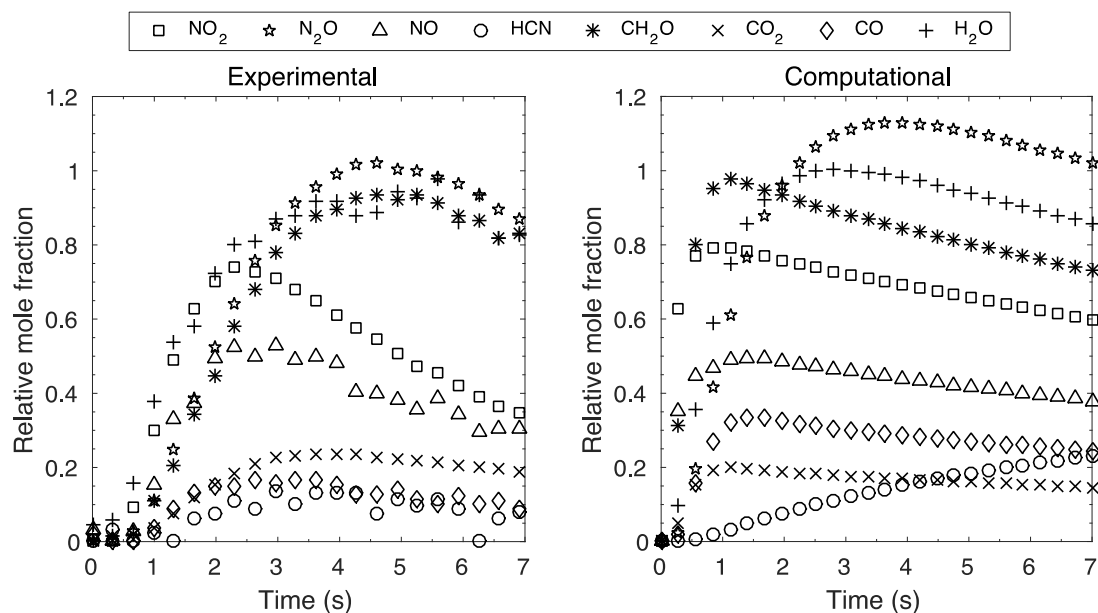


Figure 2-5. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 548 K.

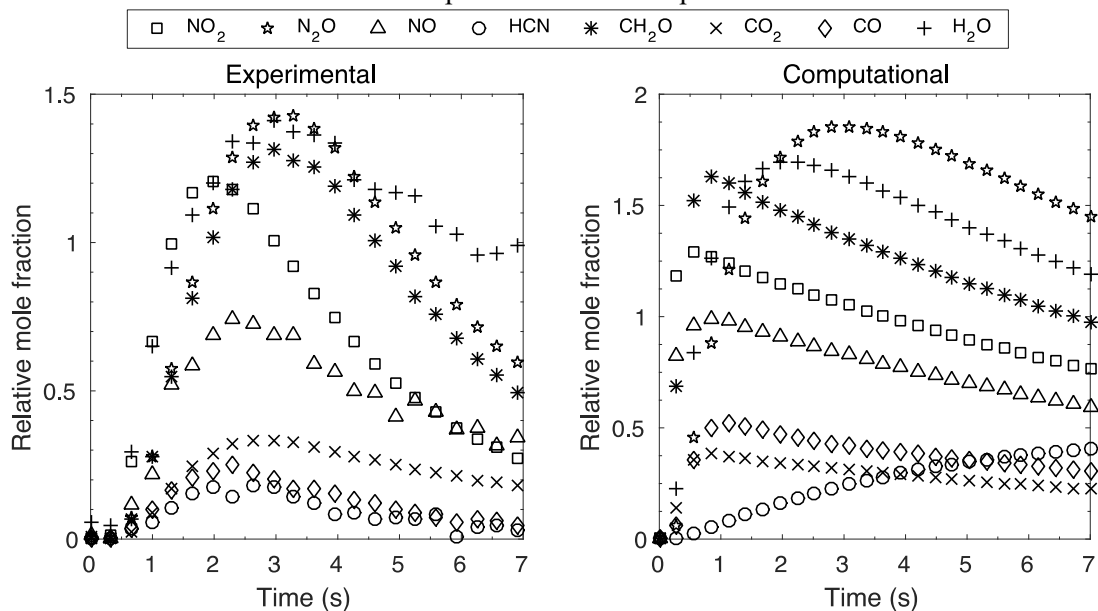


Figure 2-6. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 558 K.

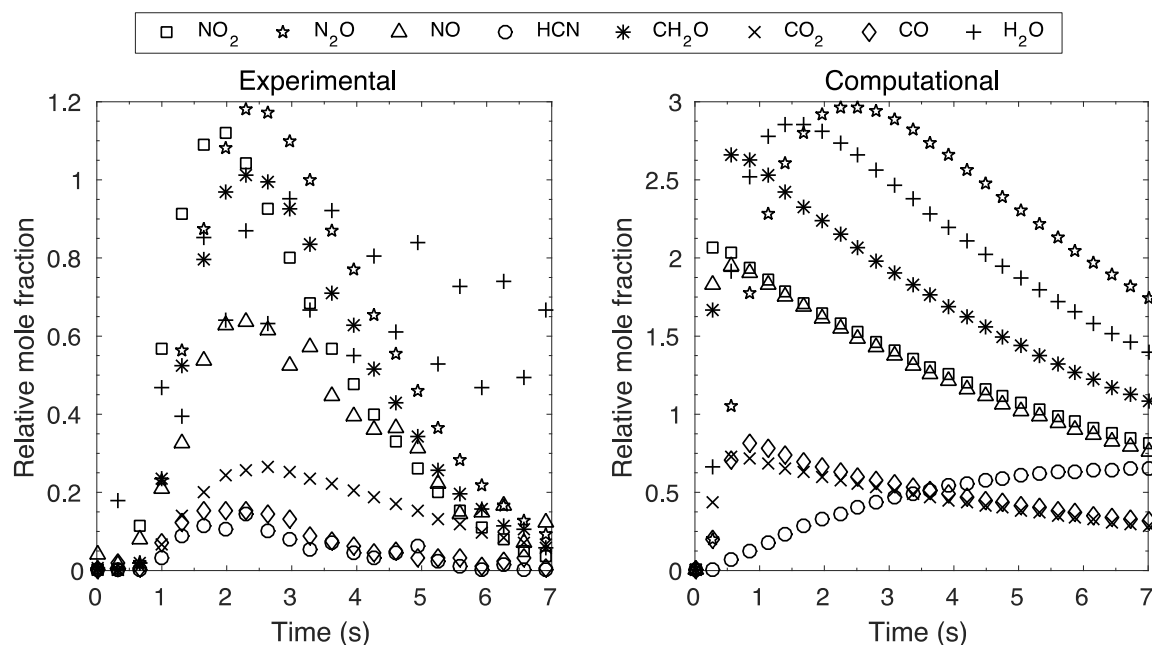


Figure 2-7. Experimental and computational species evolution profiles in gas phase for RDX decomposition at a set temperature of 568 K.

### 2.6.3 Reaction mechanism reduction

The results of sensitivity analysis were used to remove unimportant reactions in order to develop a reduced mechanism. The computationally obtained species evolution profiles remain largely unchanged when using the reduced mechanism; the deviation is limited to about 1%. The reduced mechanism is provided in Table 2-3. Reactions R1–R34 constitute a set of significant pathways which describes decomposition of RDX into its decomposition products. The important secondary reactions between smaller molecular weight species are listed as R35–R56. The reactions without transition states are marked with an asterisk ( $R^*$ ). For such reactions, enthalpy of activation is used instead of Gibbs free energy of activation in equation (2-3) for rate calculation. The enthalpy of activation and Gibbs free energy of activation in both forward and backward directions are provided in Table 2-3, in kcal/mol. The reduced mechanism represents isothermal decomposition of a small amount of RDX with rapid evolution of products into the surrounding purge gas. As such, the reduced mechanism is not likely to represent the situation of combustion of RDX, in which the temperature varies at high rates and product species have an insufficient time to enter bubbles in a foam layer.

Table 2-3. Reduced reaction mechanism for RDX decomposition in liquid phase. All quantities are in kcal/mol.

| Id                                           | Reaction                                                                                 | $\Delta H_f$ | $\Delta H_b$ | $\Delta G_f$ | $\Delta G_b$ |
|----------------------------------------------|------------------------------------------------------------------------------------------|--------------|--------------|--------------|--------------|
| Initiation pathways                          |                                                                                          |              |              |              |              |
| R1                                           | $\text{RDX} \leftrightarrow \text{INT175a} + \text{trans-HONO}$                          | 39.40        | 52.75        | 39.08        | 65.51        |
| R2                                           | $\text{RDX} + \text{NO} \leftrightarrow \text{ONDNTA} + \text{NO}_2$                     | 31.87        | 33.76        | 40.96        | 43.86        |
| R3                                           | $\text{RDX} + \text{NO}_2 \leftrightarrow \text{INT221a} + \text{cis-HONO}$              | 20.88        | 12.60        | 34.55        | 23.97        |
| R4                                           | $\text{RDX} + \text{CH}_2\text{N} \leftrightarrow \text{INT221a} + \text{CH}_2\text{NH}$ | 15.20        | 15.60        | 24.27        | 25.04        |
| Reaction which merge two initiation pathways |                                                                                          |              |              |              |              |
| R5                                           | $\text{INT221a} \leftrightarrow \text{INT175a} + \text{NO}_2$                            | 2.66         | 22.98        | 2.95         | 35.64        |
| Secondary pathways                           |                                                                                          |              |              |              |              |
| R6                                           | $\text{INT175a} \leftrightarrow \text{INT128a} + \text{trans-HONO}$                      | 39.22        | 50.49        | 39.77        | 63.76        |
| R7                                           | $\text{INT128a} \leftrightarrow \text{TAZ} + \text{trans-HONO}$                          | 31.78        | 62.60        | 32.87        | 74.93        |

|                                              |                                                                                      |       |       |       |       |
|----------------------------------------------|--------------------------------------------------------------------------------------|-------|-------|-------|-------|
| R8                                           | INT175a + NO <sub>2</sub> ↔ INT174a + <i>cis</i> -HONO                               | 18.61 | 17.95 | 32.35 | 28.36 |
| R9                                           | INT175a + <i>cis</i> -HONO ↔ INT222a                                                 | 4.89  | 4.41  | 17.30 | 3.14  |
| R10                                          | INT222a ↔ INT222a_RO                                                                 | 10.09 | 21.00 | 13.90 | 25.16 |
| R11                                          | INT222a_RO ↔ INT132a + N <sub>2</sub> O + NO <sub>2</sub>                            | 11.78 | 14.56 | 14.09 | 35.89 |
| R12                                          | INT132a ↔ INT86a + NO <sub>2</sub>                                                   | 6.50  | 16.96 | 6.57  | 29.18 |
| R13                                          | INT86a + ONNO <sub>2</sub> ↔ INT162b                                                 | 8.31  | 28.58 | 17.83 | 31.49 |
| R14                                          | INT162b ↔ INT132d + CH <sub>2</sub> O                                                | 21.60 | 6.26  | 19.34 | 19.70 |
| R15                                          | INT132d ↔ CH <sub>2</sub> NHCHO + NO <sub>2</sub> + N <sub>2</sub>                   | 3.04  | 28.75 | 3.20  | 50.70 |
| R16                                          | CH <sub>2</sub> NHCHO + NO <sub>2</sub> ↔ CH <sub>2</sub> NH + <i>cis</i> -HONO + CO | 0     | 12.91 | 5.40  | 32.76 |
| R17                                          | CH <sub>2</sub> NHCHO + NO <sub>2</sub> ↔ CH <sub>2</sub> NCHO + <i>trans</i> -HONO  | 0     | 22.99 | 0     | 22.53 |
| R18                                          | CH <sub>2</sub> NCHO + NO <sub>2</sub> ↔ CH <sub>2</sub> NCO + <i>cis</i> -HONO      | 14.32 | 18.86 | 21.54 | 29.68 |
| R19*                                         | CH <sub>2</sub> NCO + NO <sub>2</sub> ↔ INT102h                                      | 0     | 36.95 | 0     | 25.29 |
| R20                                          | INT102h ↔ CH <sub>2</sub> NNO + CO <sub>2</sub>                                      | 2.00  | 22.22 | 3.45  | 32.69 |
| R21*                                         | CH <sub>2</sub> NNO ↔ CH <sub>2</sub> N + NO                                         | 19.46 | 0     | 8.41  | 0     |
| R22                                          | INT175a + ONNO <sub>2</sub> ↔ INT251a                                                | 15.36 | 22.79 | 28.79 | 22.28 |
| R23                                          | INT251a ↔ INT251a_RO                                                                 | 17.15 | 13.47 | 18.81 | 16.94 |
| R24                                          | INT251a_RO ↔ INT161a + N <sub>2</sub> O + NO <sub>2</sub>                            | 11.76 | 15.13 | 10.15 | 36.08 |
| R25                                          | INT161a ↔ INT115a + NO <sub>2</sub>                                                  | 6.11  | 20.19 | 6.32  | 32.76 |
| R26                                          | INT175a ↔ INT101a + CH <sub>2</sub> NNO <sub>2</sub>                                 | 37.85 | 13.34 | 36.57 | 26.98 |
| R27*                                         | CH <sub>2</sub> NNO <sub>2</sub> ↔ CH <sub>2</sub> N + NO <sub>2</sub>               | 30.67 | 0     | 15.00 | 0     |
| R28                                          | CH <sub>2</sub> NNO <sub>2</sub> ↔ HCN + <i>trans</i> -HONO                          | 29.23 | 50.03 | 33.17 | 57.42 |
| R29                                          | CH <sub>2</sub> NNO <sub>2</sub> + <i>cis</i> -HONO ↔ INT121a                        | 16.54 | 29.98 | 26.16 | 32.49 |
| R30                                          | INT121a ↔ INT121b                                                                    | 9.00  | 10.80 | 10.02 | 11.30 |
| R31                                          | INT121b ↔ INT90a + HNO                                                               | 28.50 | 30.38 | 29.10 | 41.98 |
| R32                                          | CH <sub>2</sub> NNO <sub>2</sub> + ONNO <sub>2</sub> ↔ INT150a                       | 13.49 | 20.93 | 27.09 | 21.15 |
| R33                                          | INT150a ↔ CH <sub>2</sub> O + INT120b                                                | 12.73 | 6.25  | 13.73 | 20.58 |
| R34                                          | INT120b ↔ N <sub>2</sub> O + ONONO                                                   | 19.67 | 47.96 | 20.69 | 57.67 |
| Important reactions between smaller species: |                                                                                      |       |       |       |       |
| R35                                          | <i>trans</i> -HONO + <i>trans</i> -HONO ↔ ONNO <sub>2</sub> + H <sub>2</sub> O       | 7.58  | 11.21 | 16.19 | 25.09 |
| R36                                          | NO + NO ↔ ONNO                                                                       | 3.55  | 0     | 13.85 | 0     |
| R37                                          | NO <sub>2</sub> + NO <sub>2</sub> ↔ ONONO <sub>2</sub>                               | 0     | 0     | 7.95  | 0     |
| R38                                          | NO <sub>2</sub> + NO <sub>2</sub> ↔ O <sub>2</sub> NNO <sub>2</sub>                  | 0     | 0     | 1.30  | 0     |
| R39                                          | NO + NO <sub>2</sub> ↔ ONNO <sub>2</sub>                                             | 0     | 0     | 1.11  | 3.00  |
| R40                                          | NO + NO <sub>2</sub> ↔ ONONO                                                         | 0     | 0     | 8.89  | 3.00  |
| R41**                                        | <i>trans</i> -HONO ↔ <i>cis</i> -HONO                                                | 11.08 | 9.77  | 11.84 | 9.73  |
| R42                                          | CH <sub>2</sub> NH + NO <sub>2</sub> ↔ CH <sub>2</sub> N + <i>cis</i> -HONO          | 11.47 | 2.80  | 22.07 | 12.93 |
| R43                                          | CH <sub>2</sub> NH + NO <sub>2</sub> ↔ CH <sub>2</sub> N + <i>trans</i> -HONO        | 16.31 | 8.95  | 26.09 | 18.26 |
| R44                                          | CH <sub>2</sub> N + NO <sub>2</sub> ↔ HCN + <i>cis</i> -HONO                         | 0     | 47.15 | 0     | 38.73 |
| R45                                          | HNO <sub>2</sub> + CH <sub>2</sub> N ↔ NO <sub>2</sub> + CH <sub>2</sub> NH          | 0     | 10.63 | 8.16  | 23.14 |
| R46                                          | <i>trans</i> -HONO + <i>cis</i> -HONO ↔ ONNO <sub>2</sub> + H <sub>2</sub> O         | 7.13  | 12.06 | 14.88 | 25.90 |
| R47                                          | <i>cis</i> -HONO + <i>cis</i> -HONO ↔ ONONO + H <sub>2</sub> O                       | 6.78  | 4.74  | 14.38 | 18.94 |
| R48                                          | ONONO ↔ ONNO <sub>2</sub>                                                            | 4.04  | 12.33 | 5.08  | 15.86 |
| R49                                          | CH <sub>2</sub> O + NO <sub>2</sub> ↔ <i>cis</i> -HONO + HCO                         | 14.13 | 2.84  | 23.78 | 12.61 |
| R50                                          | HCOOH + NO <sub>2</sub> ↔ HOCO + <i>cis</i> -HONO                                    | 21.00 | 1.23  | 31.75 | 12.30 |
| R51                                          | HNO + NO <sub>2</sub> ↔ NO + <i>cis</i> -HONO                                        | 0     | 27.10 | 8.47  | 34.89 |
| R52                                          | CH <sub>2</sub> N + NO ↔ HCN + HNO                                                   | 0     | 19.77 | 0     | 15.31 |
| R53                                          | HOCO + NO ↔ CO + <i>trans</i> -HONO                                                  | 0     | 15.80 | 0     | 15.06 |
| R54*                                         | HCO + NO <sub>2</sub> ↔ INT75c                                                       | 0     | 45.61 | 0     | 33.26 |

|     |                                                  |       |       |       |       |
|-----|--------------------------------------------------|-------|-------|-------|-------|
| R55 | INT75c $\leftrightarrow$ CO + <i>trans</i> -HONO | 22.92 | 32.00 | 22.65 | 42.36 |
| R56 | HCO + NO $\leftrightarrow$ CO + HNO              | 0     | 26.00 | 0     | 25.23 |

$\Delta H_f$  and  $\Delta G_f$  are enthalpy and free energy difference between transition state and reactants, respectively.

$\Delta H_b$  and  $\Delta G_b$  are enthalpy and free energy difference between transition state and products, respectively.

\* For these reactions,  $\Delta H_f$  and  $\Delta H_b$  were considered as forward and backward activation barriers, respectively.

\*\* Optimized forward rate constant for R41:  $k_{kin,f}(T) = 2.32 \times 10^{42} \times (T^{-12.28}) \text{ s}^{-1}$ .

#### 2.6.4 Discussion of the reaction mechanism

The overall reaction mechanism for liquid phase has four initiation steps, (P1) HONO elimination, (P2) NO<sub>2</sub> homolytic cleavage, (P3) hydrogen abstraction, and (P4) substitution of nitro group with nitroso group. Based on the values of the forward and reverse activation barriers, Patidar and Thynell [10] proposed HONO elimination as the dominant liquid-phase initiation step. Using the computational model, sensitivity analysis was performed. Results show that, concentrations of decomposition product species are most sensitive to HONO elimination step. A small change in the reaction rate parameters of HONO elimination step produces large variations in the product composition. Other pathways were found to be comparatively much less sensitive. This suggests that HONO elimination is indeed the dominant initiation step for decomposition in the liquid phase. Similar result for gas-phase decomposition was obtained by Chakraborty et al. [50].

Our proposed dominant initiation step satisfies all the characteristics of rate controlling mechanistic step obtained using deuterium kinetic isotope effect (DKIE) based studies [51,52]. Shackelford et al. [51] found that rate controlling step for RDX decomposition has a covalent carbon-hydrogen bond rupture. Oxley et al. [52] found that RDX dominant decomposition reaction is unimolecular, and has intramolecular hydrogen transfer. Since, HONO elimination is a unimolecular reaction with transfer of a hydrogen from carbon to oxygen of the same molecule we believe that it is the rate controlling step discussed by Shackelford et al. [51] and Oxley et al. [52]. Oxley et al. [52] also found that mononitroso derivatives are present in much less concentrations during liquid-phase decomposition of RDX. Mononitroso derivatives are formed by the initiation step (P4) which, according to our sensitivity analysis results, is not important in liquid phase. It should be noted that our result on significance of the initiation step (P4) defer from previous study by Behrens and Bulusu [32]. We believe, the difference in results is due to the occurrence of gas-phase decomposition reactions in the reaction cell used by them. It is also of interest to note that unlike in gas phase where NO<sub>2</sub> homolytic cleavage is a dominant step [43,53–56], liquid-phase decomposition doesn't initiate with it. In a recent study on RDX decomposition pathways, a well-defined transition state for NO<sub>2</sub> homolytic cleavage in gas phase was located using coupled cluster theory [57]. Based on the activation barrier values, HONO elimination was proposed as a preferred initiation step over NO<sub>2</sub> homolytic cleavage.

The reduced reaction mechanism has four significant pathways for the decomposition of INT175a (which is produced from the HONO elimination initiation step): (P1.1) HONO addition followed by ring opening, (P1.2) ring opening of INT175a, (P1.3) ONNO<sub>2</sub> addition, and (P1.4) successive HONO elimination. Figure 2-8 shows the Gibbs free energy profiles for these pathways. Molecular structures of different intermediates formed along these pathways are shown in Figure 2-9. Sensitivity analysis shows that pathway (P1.1) is responsible for formation of most of the decomposition products in the liquid phase. Pathway (P1.3) has second lowest barrier but due to the insufficient concentration of ONNO<sub>2</sub>, it becomes much less important. Pathway (P1.2) and pathway (P1.4) have relatively higher barriers and do not contribute towards formation of significant amount of decomposition products.

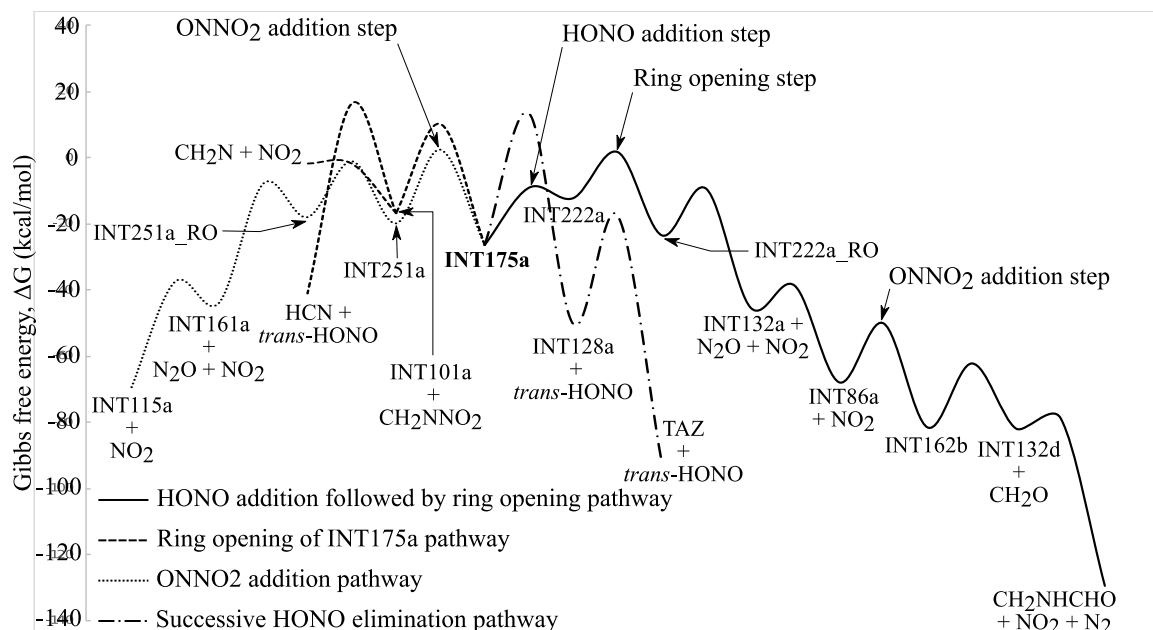


Figure 2-8. Important pathways for decomposition of INT175a, an intermediate produced by HONO elimination from RDX.

Hence, based on our computational model and sensitivity analysis results, we believe, liquid-phase decomposition of RDX occurs predominantly via a single pathway, unlike found previously by Behrens and Bulusu [32]. The decomposition process initiates via unimolecular HONO elimination from RDX molecule, followed by HONO addition in a different configuration. The intermediate thus formed (INT222a) undergoes a ring opening step followed by two successive unimolecular dissociation steps releasing  $\text{NO}_2$  and  $\text{N}_2\text{O}$ . At this stage, ONNO<sub>2</sub> addition takes place which is followed by two successive unimolecular dissociation steps forming  $\text{CH}_2\text{NHCHO}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{N}_2$ . Further dissociation of  $\text{CH}_2\text{NHCHO}$  occurs via two successive hydrogen-abstraction steps followed by  $\text{NO}_2$  addition and two successive unimolecular dissociation steps. The various smaller molecular weight species formed along this primary decomposition pathway react with each other to form final decomposition products in experimentally observed composition.

Attempts have also been made to identify competitive pathways where the initiation step is a bimolecular reaction involving RDX. It is driven by the need to simulate reactions during detonation, where the pressure may reach or exceed 20 GPa. For such pressures, Schweigert [58] has used combined molecular dynamics simulations and DFT calculations to identify the reaction



as having a rate constant greater than the HONO elimination step. At such high pressures, it is expected that rate constants for bimolecular reactions are, in general, larger than for unimolecular reactions [59,60]. The reason is that the activation volume decreases as the pressure increases for bimolecular reactions, whereas the opposite occurs for unimolecular reactions. For the above reaction (R57), we have identified a forward free energy barrier of 56.1 kcal/mol, which suggests that the reaction (R57) is not important for our low-pressure calculations. Symmetry could also play an important role, but it is highly doubtful that the rate becomes competitive with the HONO elimination step. The reaction does, however, satisfy the DKIE effect observed for RDX decomposition [51,52].

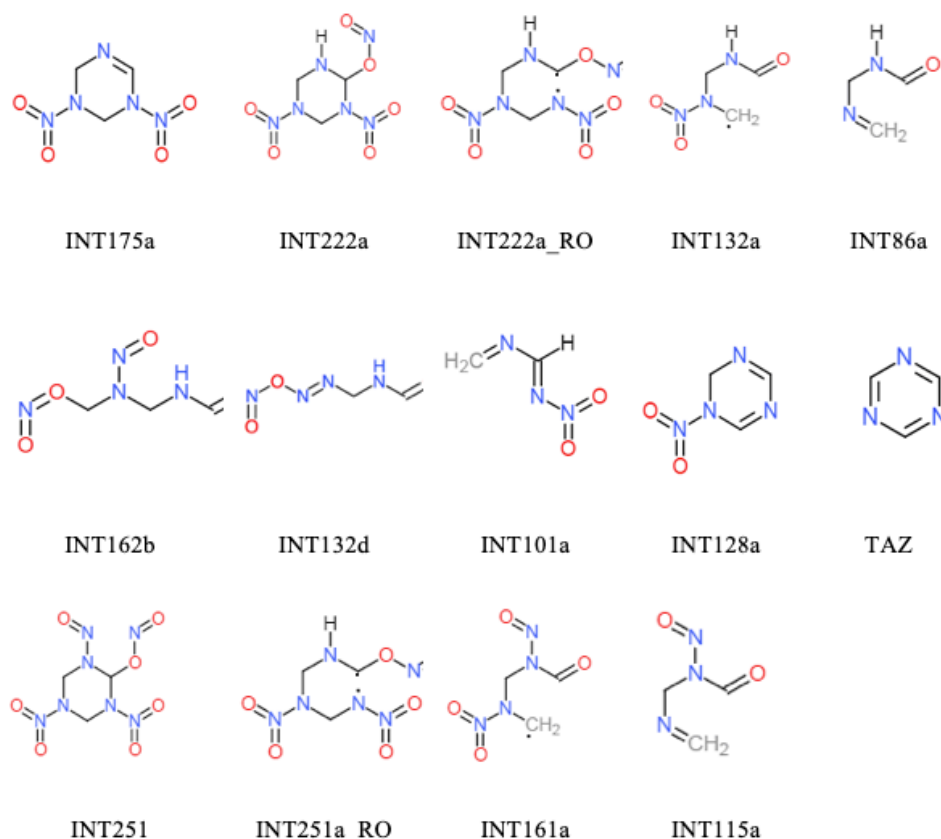


Figure 2-9. Molecular structures of important intermediates formed during RDX decomposition in liquid phase.

## 2.7 Summary and conclusions

In this study, an expanded version of recently developed reaction mechanism describing liquid-phase decomposition of RDX was validated using results from CRT. The developed mechanism consists of 321 species and 500 elementary reactions identified using DFT based calculations at B3LYP/6-311++G(d,p) level of theory and the CPCM solvation model. A computational model based on conservation equations was developed. The model uses the reaction mechanism as input and predicts the mole fractions of decomposition products in both liquid and gas-phase regions. Using the experimental data for gas phase, the reaction rate parameter values were optimized. With the optimized parameters, the computational model captures the experimentally observed trends, in general. This indicates that the proposed reaction mechanism includes most of the key decomposition reactions of RDX in liquid phase. Using sensitivity analysis, a reduced mechanism with 56 elementary reactions and 53 species was also generated.

Out of the four previously known liquid-phase initiation steps, HONO elimination was found to be a dominant decomposition step. Four important pathways were identified for decomposition of HONO elimination product of RDX, (P1.1) HONO addition followed by ring opening, (P1.2) ring opening of INT175a, (P1.3) ONNO<sub>2</sub> addition, and (P1.4) successive HONO elimination. Based on our computational model and sensitivity analysis results, we believe that in liquid-phase most of the RDX decomposes via HONO elimination step followed by pathway (P1.1). Also, unlike in gas phase, N-N homolytic cleavage is a minor decomposition pathway in liquid phase.

Finally, our results and proposed reduced mechanism are relevant to only low-pressure condition decomposition processes with fast heating rates as in CRT experiments. Additional bimolecular reaction pathways are likely to play a significant role under high pressure conditions pertinent to detonation.

## CHAPTER 3

### THERMOLYSIS EXPERIMENTS AND KINETIC MODELING OF HMX

#### 3.1 Introduction

In this chapter, we demonstrate synergetic application of quantum mechanics calculations, chemical kinetic modeling and thermolysis experiments to expand and validate a comprehensive mechanism for liquid-phase decomposition of energetic materials consisting of elementary reactions. HMX is chosen as the representative energetic material, but the methodology is applicable to other energetic materials as well. The first objective is to quantify species evolution rates during thermal decomposition of HMX using FTIR spectroscopy for low heating rates using TGA (thermogravimetric analysis) setup and for high heating rates using CRT (confined rapid thermolysis) setup. The second objective is to further expand and validate the HMX initiation mechanism presented in chapter 1.

#### 3.2 Experimental details and data reduction

Experimental details for both Slow thermolysis (TGA-FTIR setup) and fast thermolysis (CRT-FTIR setup) are given in [18].

#### 3.3 Computational details

##### 3.3.1 *Quantum mechanics calculations*

The initiation mechanism developed in our previous study [11] was further expanded and a comprehensive reaction mechanism was developed. Additional reactions of larger intermediates were added which eventually form simple final products observed experimentally. The comprehensive reaction mechanism includes 109 species and 157 elementary reactions.

#### 3.4 Detailed kinetic modeling for validation of the mechanism

The details of the gas-phase and liquid-phase kinetics modeling are given in [18].

#### 3.5 Experimental results

##### 3.5.1 *TGA and DSC data*

The TGA curves for the four heating rates are given in Figure 3-1(a) and the corresponding DSC curves are given in Figure 3-1(b). These results are the average of three repeatable experiments with similar sample masses. The  $\beta$ -HMX to  $\delta$ -HMX phase transformation is observed at around 190 °C as indicated by a slight endothermic peak in the DSC data as shown by Figure 3-2. As the temperature is further increased above 260 °C, the mass loss starts very slowly. On further heating, the melting of the sample is observed at 280°C as revealed by the endothermic peaks in Figure 3-1(b). These endothermic peaks shift to a slightly higher temperature at higher heating rates due to heat transfer limitations. Hence, 280°C is taken as the approximate melting temperature of HMX.

The melting of the sample is immediately followed by rapid mass loss and exothermic decomposition as shown by the TGA and DSC data. At 5 K/min, approximately 20% of the initial sample mass sublimates before the melting temperature of 280°C. At 10, 15 and 20 K/min, the corresponding values are approximately 8%, 5%, and 3% respectively. At low heating rates, the mass loss starts to occur at a lower temperature because more time is available for the sample to undergo sublimation and possibly solid-phase decomposition. At higher heating rates, the sample temperature reaches the liquefaction temperature of 280°C relatively quickly before any substantial sublimation and solid-phase decomposition could occur. Exothermicity of the decomposition is observed to increase with the heating rate as revealed in the DSC curves in Figure 3-1(b). Hence, these TGA and DSC results suggest that the decomposition of HMX occurs predominantly in the liquid phase.

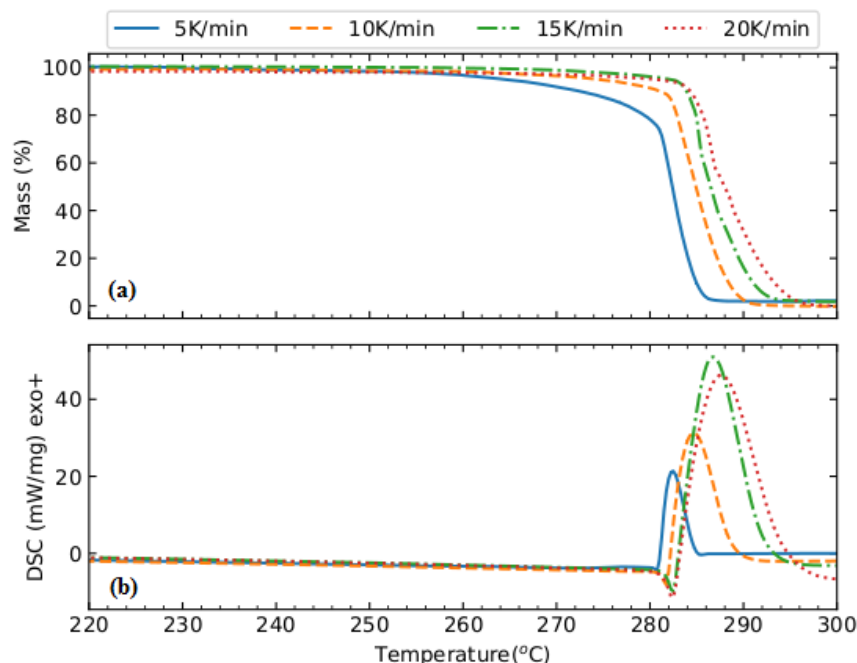


Figure 3-1. (a) TGA data and (b) DSC data.

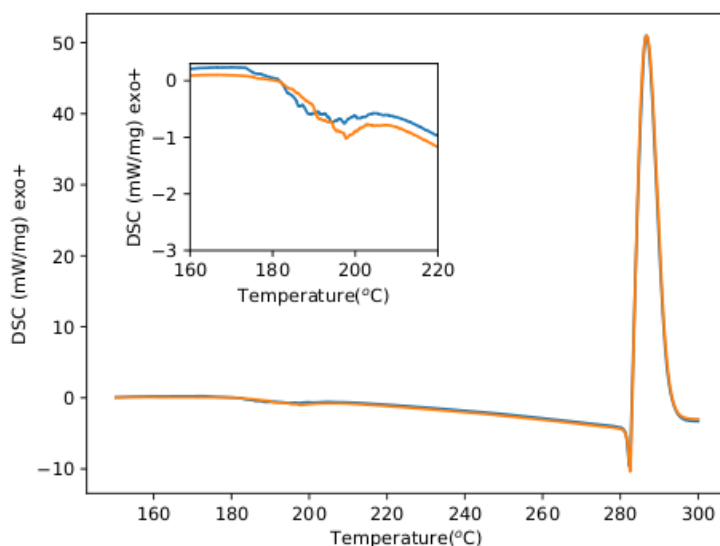


Figure 3-2. DSC data for two experimental runs at 15 K/min. Inset shows the endothermic peaks around 190 °C corresponding to  $\beta$ -HMX to  $\delta$ -HMX phase transformation.

### 3.5.2 Species evolution

Figure 3-3(a) shows a single transmittance spectrum in the case of TGA experiments for a heating rate of 20 K/min and a sample temperature of 285°C. For CRT experiments, a single transmittance spectrum is shown in Figure 3-3(b) which was obtained for a set temperature of 300°C at  $t = 10.08$  s. Various decomposition products identified in earlier studies [2,43], including  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$ , can be observed in the spectrum recorded in the present study. Signal intensities of the absorption bands of  $\text{CO}$  and  $\text{NO}$  are weak due to small permanent dipole moments.

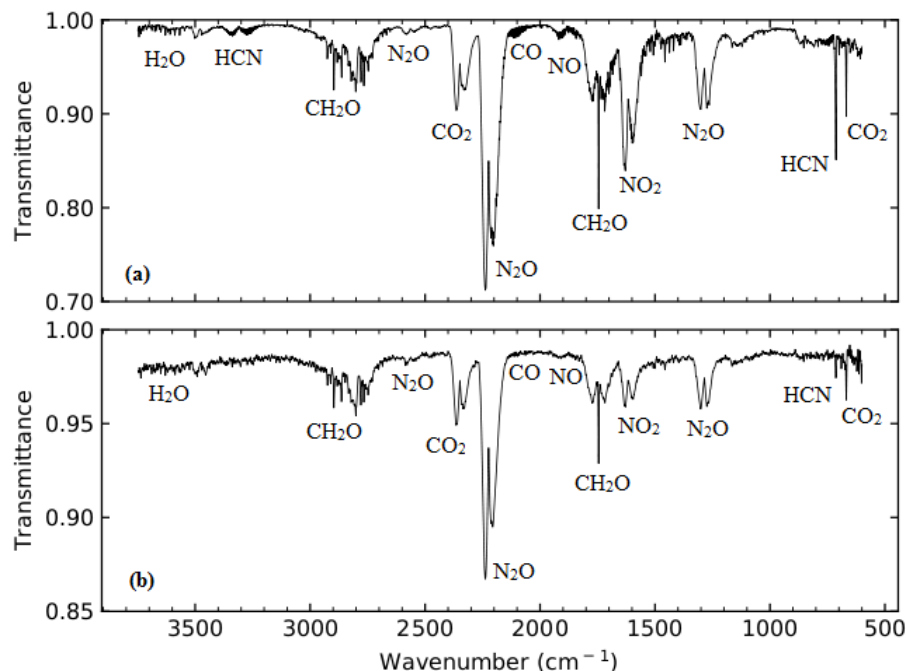


Figure 3-3. FTIR spectrum of the evolved gases (a) TGA setup (heating rate = 20 K/min and temperature = 285°C) and (b) CRT setup ( $T_{\text{set}} = 300^{\circ}\text{C}$  and  $t = 10.08$  s).

In addition to these species, thermal decomposition products in the gas phase may include other similar molecules. Here, temporal evolution profiles were obtained for only these eight species using the data reduction model previously described.

### 3.5.3 Effect of heating rate in TGA experiments

Species evolution profiles, obtained from FTIR spectroscopy and shown in Figure 3-4, reveal that  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  are major decomposition products followed by  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{CO}_2$  and  $\text{CO}$  in smaller concentrations. The rates of evolution of  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  are considerably higher compared to other species. The rapid evolution of species is observed only after the temperature reaches  $280^{\circ}\text{C}$  for all heating rates as shown in Figure 3-4. This indicates that the mass loss before melting of the sample mainly consists of sublimating HMX which condenses out in the transfer tube maintained at the maximum possible temperature of  $230^{\circ}\text{C}$ . At 5 K/min, the evolution of species ends with the complete mass loss at around  $285^{\circ}\text{C}$  since more time is available for the sample to decompose at lower temperatures just after liquefaction. As the heating rate is increased, temperature increases relatively quickly and hence the species evolution continues until a higher temperature is reached as revealed by the stretched profiles in Figure 3-4 (b) – (d).

### 3.5.4 Effect of set temperature in CRT experiments

In the CRT apparatus, the optical path length is not known with certainty. Hence, in the data reduction model, the path length is assumed to be 1 cm, which renders the concentration profiles as relative. Due to these reasons, the trend of relative mole fractions of species is compared unlike the absolute values used in TGA experiments where the path length is known exactly as 12.3 cm. Species evolution profiles for four set temperatures investigated in this study, as obtained from FTIR spectroscopy, are shown in Figure 3-5. It is again observed that  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  are the major decomposition products followed by  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{HCN}$  and  $\text{CO}$ . Significant fluctuations are observed in the mole fraction profile of  $\text{H}_2\text{O}$  which are attributed to the difficulty in resolving the fine line structure of  $\text{H}_2\text{O}$ .

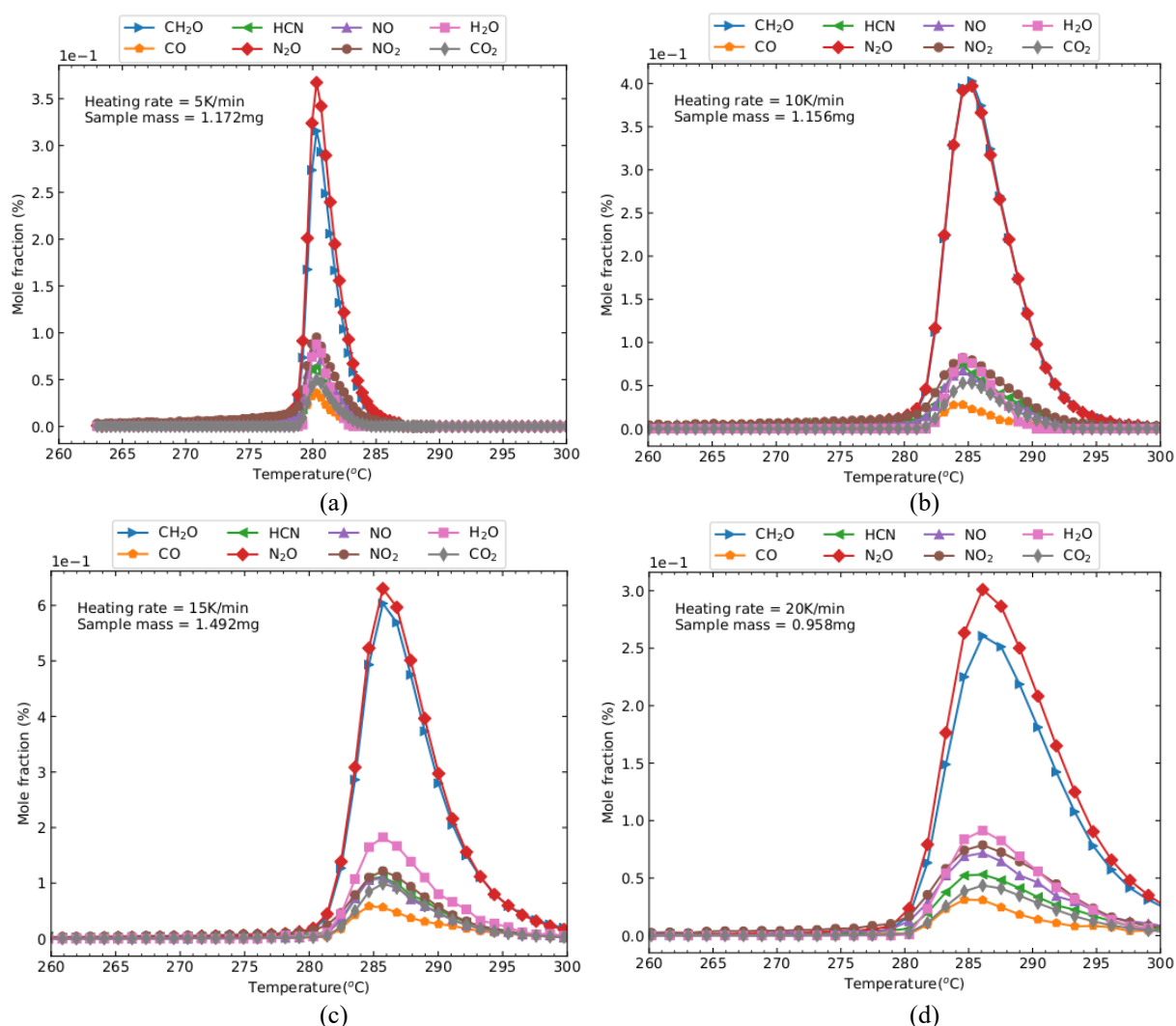


Figure 3-4. Variation of species mole fractions in the gas phase with temperature during HMX decomposition in TGA-FTIR setup (a) 5 K/min, (b) 10 K/min, (c) 15 K/min and (d) 20 K/min.

For high heating rate experiments in CRT-FTIR setup,  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  evolve at a much higher rate compared to other species. On increasing the set temperature, the decomposition rate increases as evident by a shift in the peaks of mole fraction profiles. At higher set temperatures, the relative mole fraction of  $\text{NO}_2$  is slightly higher indicating a shift towards high-temperature reaction pathways.  $\text{NO}_2$  is also consumed very quickly which indicates that it participates in secondary reactions. Maximum levels of  $\text{CO}_2$  and  $\text{NO}$  occur later in the decomposition process, which reveal that they are formed from secondary reactions. However,  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  remain the major decomposition products at all set temperatures investigated in the present study.

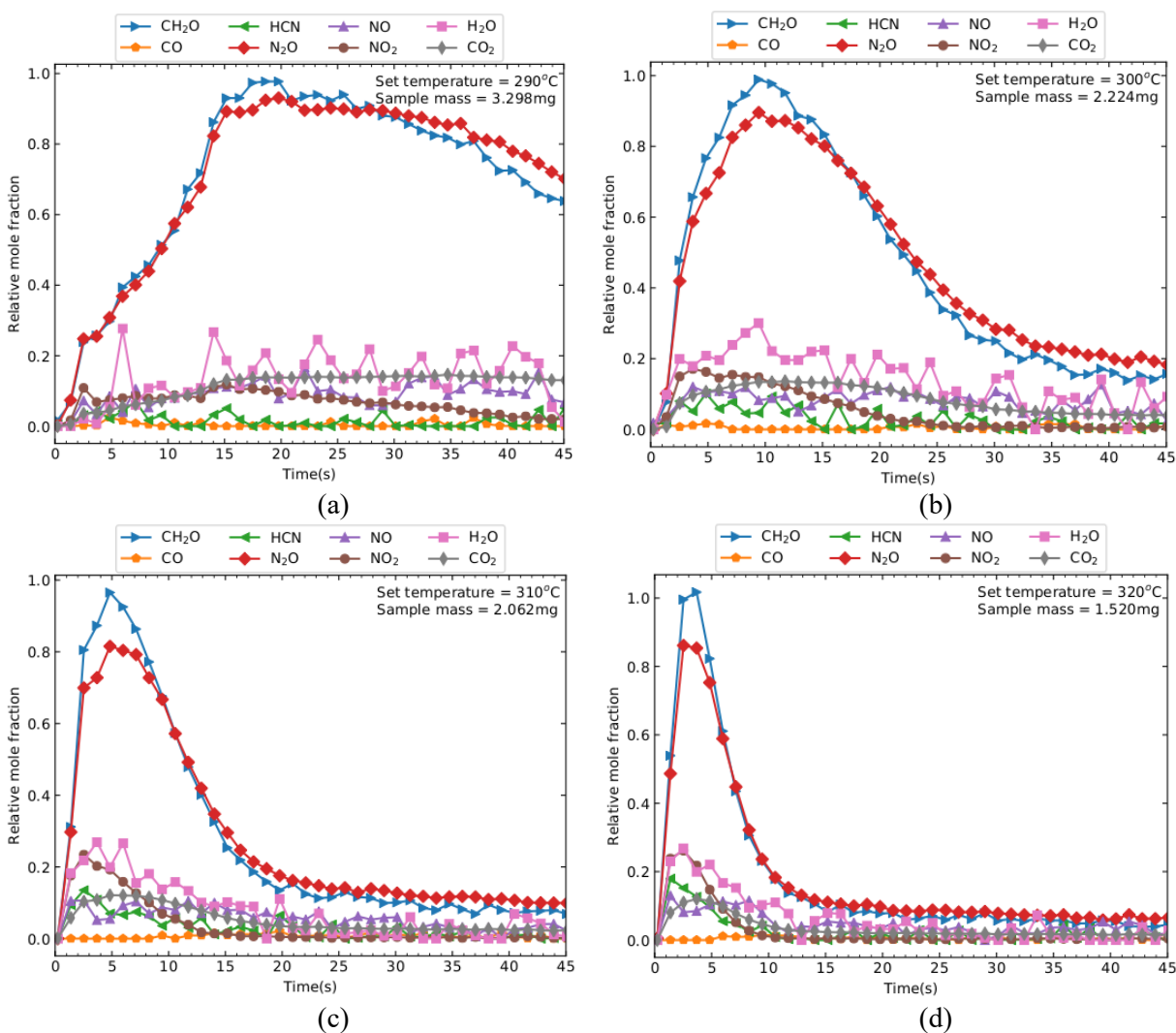


Figure 3-5. Species mole fractions profiles in the gas phase during HMX decomposition in CRT-FTIR setup at a set temperature of (a) 290°C, (b) 300°C, (c) 310°C and (d) 320°C.

### 3.6 Computational results

#### 3.6.1 Liquid-to-gas conversion rates

Results from TGA-DSC experiments are frequently used to obtain apparent activation parameters for thermal decomposition of energetic materials using isoconversional methods [61–63]. It is to be emphasized that the meaning of the term ‘activation energy’ in isoconversional methods differs significantly from its original definition and what is generally accepted in chemical kinetics. These isoconversional methods treat a complex multi-step process as a single-step process. Hence, the obtained activation energy may not have any mechanistic significance and should be treated as apparent activation energy only rather than free energy or enthalpic barrier. Since our objective is to develop and validate a detailed mechanism, describing the complex multi-step decomposition process using elementary reactions, isoconversional analysis is not performed to obtain global apparent activation energy.

However, the values of the apparent activation parameters obtained in these isoconversional analysis studies can be used to reproduce the mass loss curves. The liquid-to-gas conversion rates for species  $i$ , can be represented using  $\dot{m}_{i,vaporized} = k_{l-g,i} m_{i,c}$ , where  $k_{l-g,i}$  is the corresponding rate constant, which can be written in Arrhenius form with the activation energy and pre-exponential factor obtained from the isoconversional analysis. Brill et al. [49] have evaluated different Arrhenius parameters published in the literature for thermal decomposition of HMX and observed kinetic compensation effect where a linear

relationship exists between activation energy  $E_a$  and logarithm of pre-exponential factor, i.e.,  $\ln A$ . Various values of apparent Arrhenius parameters given by Brill et al. [49] are tested for liquid-to-gas conversion rates of species in our kinetic model using a methodology as described in the next section. The final values used for all species in the validated mechanism are  $E_a = 51.3$  kcal/mol and  $\ln A/s^{-1} = 43.3$ . The list of species evolving from liquid to gas includes  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{HONO}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{N}_2$ .

### 3.6.2 Mechanism development and validation methodology

The comprehensive reaction mechanism consists of 109 species and 157 elementary reactions. It is used in conjunction with the chemical kinetic model to simulate the TGA and CRT experiments. The liquid-phase reaction mechanism for HMX was developed and validated using the synergetic application of quantum mechanics calculations, kinetic modeling, and TGA and CRT experiments. The development of the reaction mechanism was guided by the experimental results. For example, we see in the experiments that  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  are the major decomposition products. Hence, we look into our database of thousands of reactions and add the reactions involving  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  in our mechanism. We then continue the process and add reactions of other species such as  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HCN}$ . The initial version did not have reactions for the formation of  $\text{CO}$  and  $\text{CO}_2$  but we see these species as well in the experiments. Hence, we also perform additional quantum mechanics calculations which lead to the formation of  $\text{CO}$  and  $\text{CO}_2$  and add those reactions to the mechanism. None of the input parameters required for the computational model are coming from our experimental data. The vaporization parameters are obtained from various Arrhenius parameters compiled by Brill et al. [49] and the kinetic parameters are obtained directly from quantum mechanics calculations. The experimental data are not used in any mathematical function within some optimization routine to obtain or tweak the kinetic parameters. The experimental data are merely used to guide the development of the mechanism. This is our mechanism development methodology. The experimental results are used only to validate the model. The liquid-to-gas conversion rates and the chemical kinetic parameters were validated by comparing the following results:

1. Mass loss data obtained from the TGA experiments
2. Species evolution profiles obtained from the TGA experiments
3. Species evolution profiles obtained from the CRT experiments

A sensitivity analysis provides information about what reactions need to be modified in order to obtain a better agreement with the experimental data. This is justified because the free energy values in solution are uncertain to a few kcal/mol and changes were made to 6 reactions out of 157; the largest change was 3 kcal/mol, which is within the uncertainty of the calculated free energy barriers.

### 3.6.3 Prediction of mass loss and species evolution profiles

The computational results for the mass loss are shown in Figure 3-6. The model predictions are in excellent agreement with the experimental mass loss curves for all heating rates considered in this study. Since the computational model is developed for the liquid-phase decomposition of HMX, sublimation is not included. Hence, in the computational results, the mass loss does not occur before the melting temperature of  $280^\circ\text{C}$ . The discrepancies in the mass loss for temperatures lower than  $280^\circ\text{C}$ , especially at low heating rates of 5 K/min and 10 K/min, are attributed to sublimation of HMX.

After the melting of the sample above  $280^\circ\text{C}$ , the computational model accurately captures the rate of mass loss for all heating rates. For example, the complete mass loss occurs at a temperature of  $285^\circ\text{C}$  for a heating rate of 5 K/min. The corresponding temperatures for heating rates of 10, 15, and 20 K/min are 290, 295, and  $300^\circ\text{C}$  respectively. The model also predicts 100% mass loss at these temperatures accurately for different heating rates.

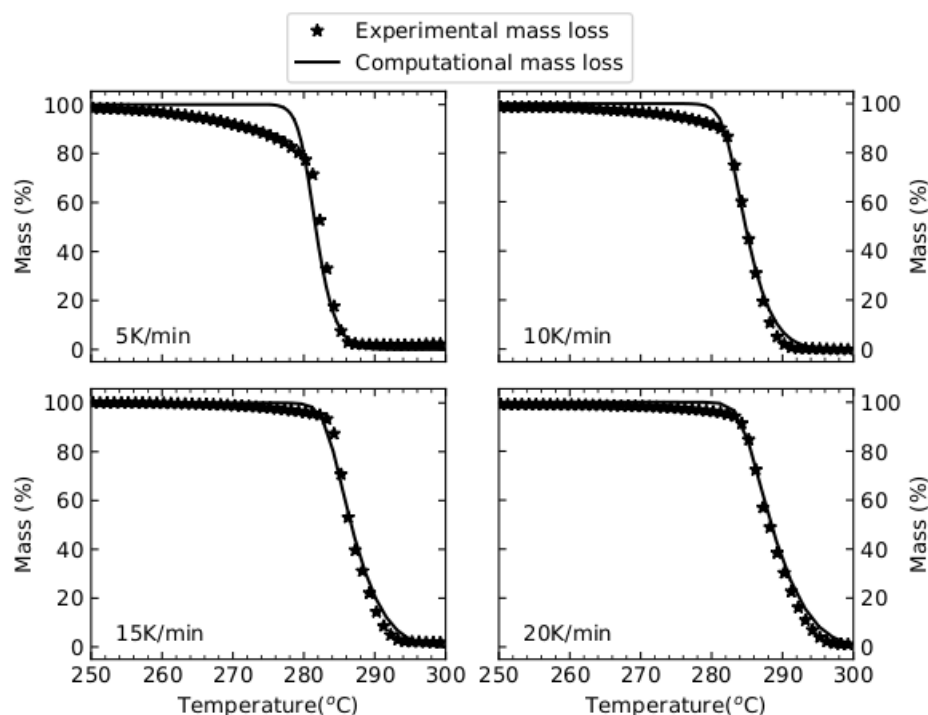


Figure 3-6. Mass loss curve for HMX decomposition at four heating rates.

The species evolution profiles predicted by the model for a heating rate of 15 K/min are shown in Figure 3-7(a) and compared against the corresponding experimental results shown in Figure 3-7(b). The model predicts  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  as the primary decomposition products. The peak mole fractions of  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  in the FTIR gas cell are also in excellent agreement with the experimental peak values. The evolution of  $\text{H}_2\text{O}$ ,  $\text{NO}$  and  $\text{CO}_2$  are also in good agreement with the experimentally obtained evolution profiles. However,  $\text{HCN}$  is formed in slightly larger quantities in the computational model as compared to the experimental results, whereas  $\text{NO}_2$  is formed in smaller quantities. A large fraction of  $\text{NO}_2$  is consumed in secondary reactions in our mechanism which explains the low mole fraction of  $\text{NO}_2$ . The computational model predicts the species evolution profiles for other heating rates with good accuracy as well.

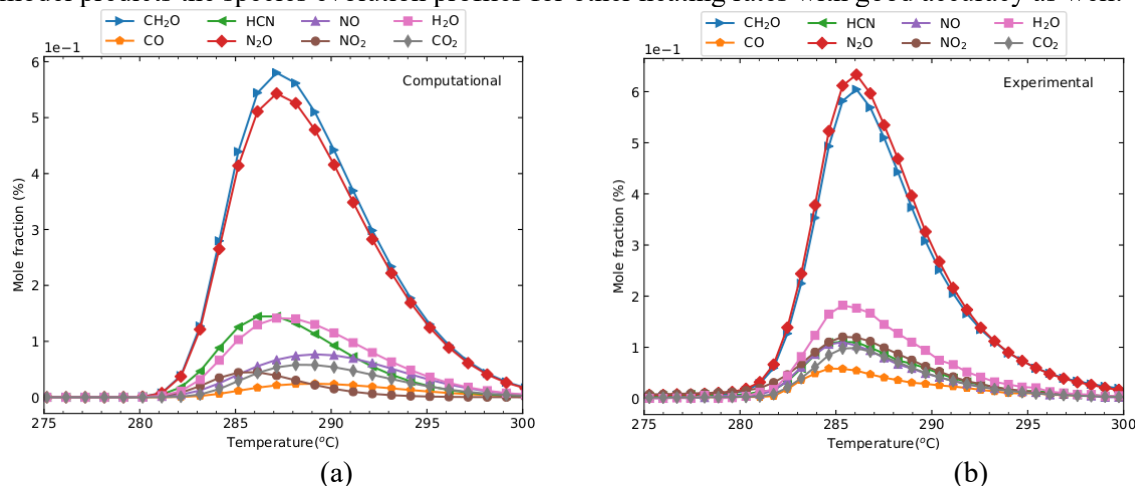


Figure 3-7. HMX decomposition for a heating rate of 15 K/min. Species mole fractions profiles in the gas phase (a) computational and (b) experimental.

The CRT simulation results for species relative mole fraction profiles at a set temperature of  $300^\circ\text{C}$  are shown in Figure 3-8(a) and compared against the corresponding experimental results shown in Figure

3-8(b). The model predicts  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  as the primary decomposition products for isothermal decomposition as well. The evolution of  $\text{NO}_2$  and  $\text{NO}$  is also captured reasonably well. The computational evolution profile of  $\text{H}_2\text{O}$  lies within the experimental fluctuation range.  $\text{HCN}$  is produced in larger concentration in the computational model as compared to the experimental results. On the other hand, smaller quantities of  $\text{CO}_2$  are predicted by the computational model.

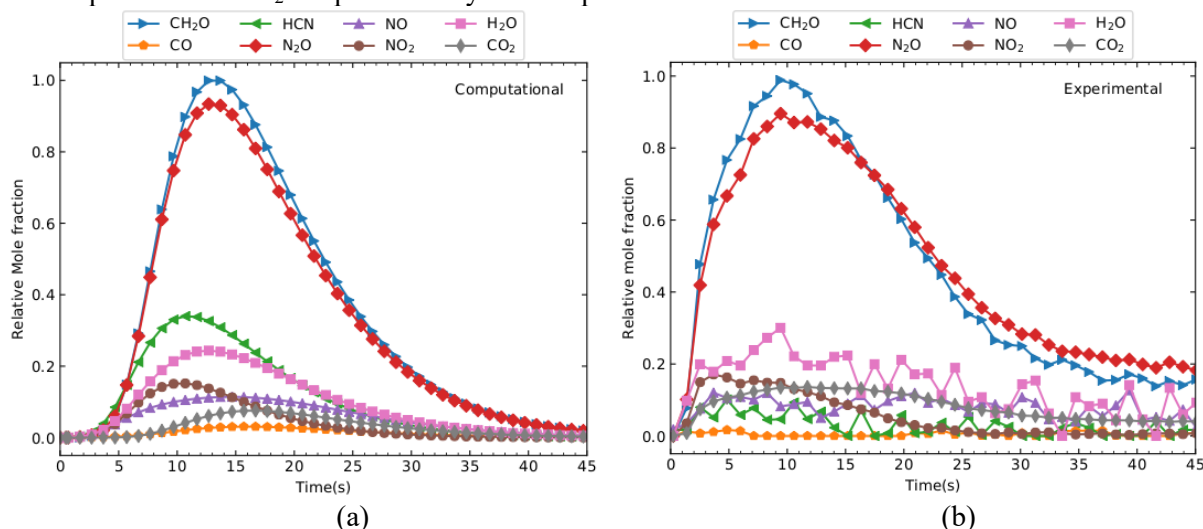


Figure 3-8. HMX decomposition in the liquid phase at 300°C. Temporal evolution of species relative mole fractions in the gas phase (a) computational and (b) experimental.

The computational and experimental results for the species mole fraction profiles are in reasonable agreement with each other for both types of experiments. This indicates that the initiation and subsequent reactions for the liquid-phase decomposition of HMX are reasonably captured by the comprehensive reaction mechanism developed and validated in the present study.

### 3.7 Sensitivity analysis

A sensitivity analysis is performed to identify important reactions in the liquid phase at various time instants during the thermal decomposition of HMX. The sensitivity coefficient  $S_{ij}$  was defined as shown in Eq. (3-1),

$$S_{ij} = \frac{A_j}{\Delta A_j} \frac{\Delta y_i}{y_i}, \quad i = 1, 2, \dots, N_{\text{species}}; j = 1, 2, \dots, N_{\text{reactions}} \quad (3-1)$$

where  $\Delta y_i$  represents the change in the mass fraction  $y_i$  of  $i^{\text{th}}$  species in the liquid phase and  $\Delta A_j$  represents the change in  $A$ -factor  $A_j$  of  $j^{\text{th}}$  reaction in the liquid-phase mechanism. Representative values of the sensitivity coefficients at a heating rate of 15 K/min and at a temperature of 283°C are shown in Figure 3-9.

The liquid phase decomposition of HMX can begin via four unimolecular initiation steps – (1) HONO elimination (2) N- $\text{NO}_2$  bond fission, (3) concerted ring fission (4) C-N bond scission of the ring. Early bimolecular reactions include hydrogen abstraction and nitroso formation pathways. A detailed comparison of these pathways with other studies in the literature was presented in our previous studies [10,11]. The analysis of the activation barriers for forward and backward reactions reveals that the decomposition of HMX in liquid phase begins with HONO elimination. This is in agreement with results for the gas-phase decomposition of RDX by Molt et al. [57] and for the solid-phase decomposition of  $\delta$ -HMX by Sharia et al. [64] who also found HONO elimination channel to be dominant. In most other studies, N- $\text{NO}_2$  bond fission has been considered a dominant step for the initiation of HMX decomposition. However, the barrier for the backward radical recombination reaction is negligible. Hence, this reaction is less significant in the liquid phase.

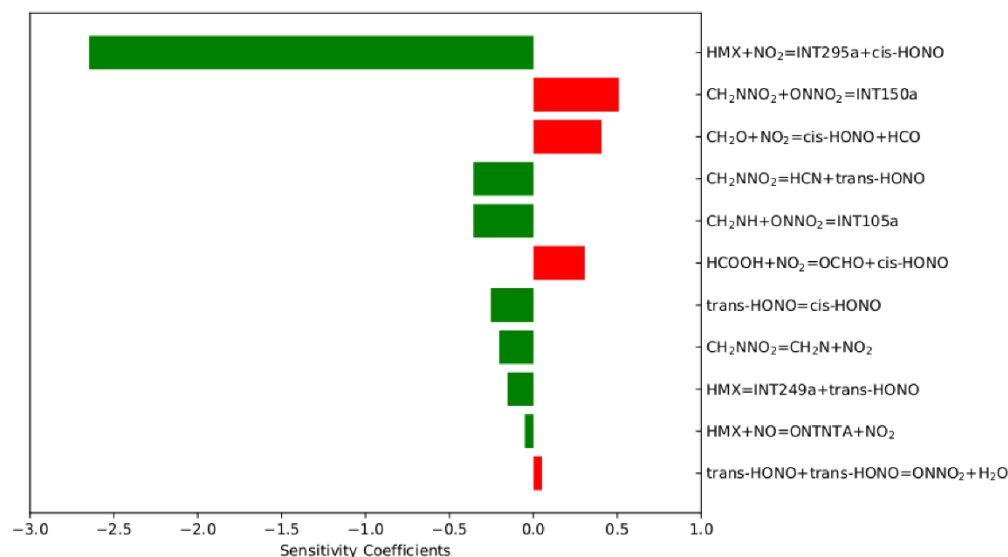


Figure 3-9. Sensitivity coefficients of forward rate constants on HMX mass fraction in the liquid phase at 15 K/min heating rate and 283°C during TGA simulations.

Decomposition of HMX begins with HONO elimination. HONO formed from the initiation step subsequently undergoes various self-reactions and forms  $\text{ONNO}_2$ ,  $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{H}_2\text{O}$ . Autocatalytic hydrogen abstraction pathway from HMX was found to be the most sensitive pathway at all time instants. During the initial stage of the decomposition, reactions of HMX and larger intermediate species such as INT249a ( $\text{HMX-HONO}$ ) were found to be more sensitive. As the mass fraction of HMX decreases in the liquid phase, reactions of smaller intermediate species such as  $\text{CH}_2\text{NNO}_2$  and  $\text{CH}_2\text{NH}$  becomes more sensitive.

The subsequent reactions of HONO formed from HONO-elimination and hydrogen abstraction reactions are governed by the cage effect [35,65] in the liquid phase. The first step during the liquid-phase decomposition of HMX is the HONO elimination reaction, which forms INT249a and HONO. However, the diffusion of HONO away from INT249a may be hindered by the cage effect. It reacts back with INT249a and the subsequent decomposition of INT249a occurs via autocatalytic prompt oxidation by HONO addition. As discussed in detail in our previous study [11], these prompt oxidation reactions are highly exothermic and they explain the simultaneous formation of  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  as observed experimentally. Similar prompt oxidation reactions were postulated for simple  $-\text{NO}_2$  containing energetic molecules [35]. Autocatalytic prompt oxidation of INT249 also occurs via  $\text{ONNO}_2$ . These prompt oxidation reactions of INT249 produces  $\text{CH}_2\text{NNO}_2$ ,  $\text{CH}_2\text{NHCHO}$ , and  $\text{CH}_2\text{NH}$  which subsequently decompose and contribute towards formation of a significant amount of final decomposition products i.e.  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ . A summary of important reaction pathways in the liquid-phase HMX is presented in Figure 3-10.

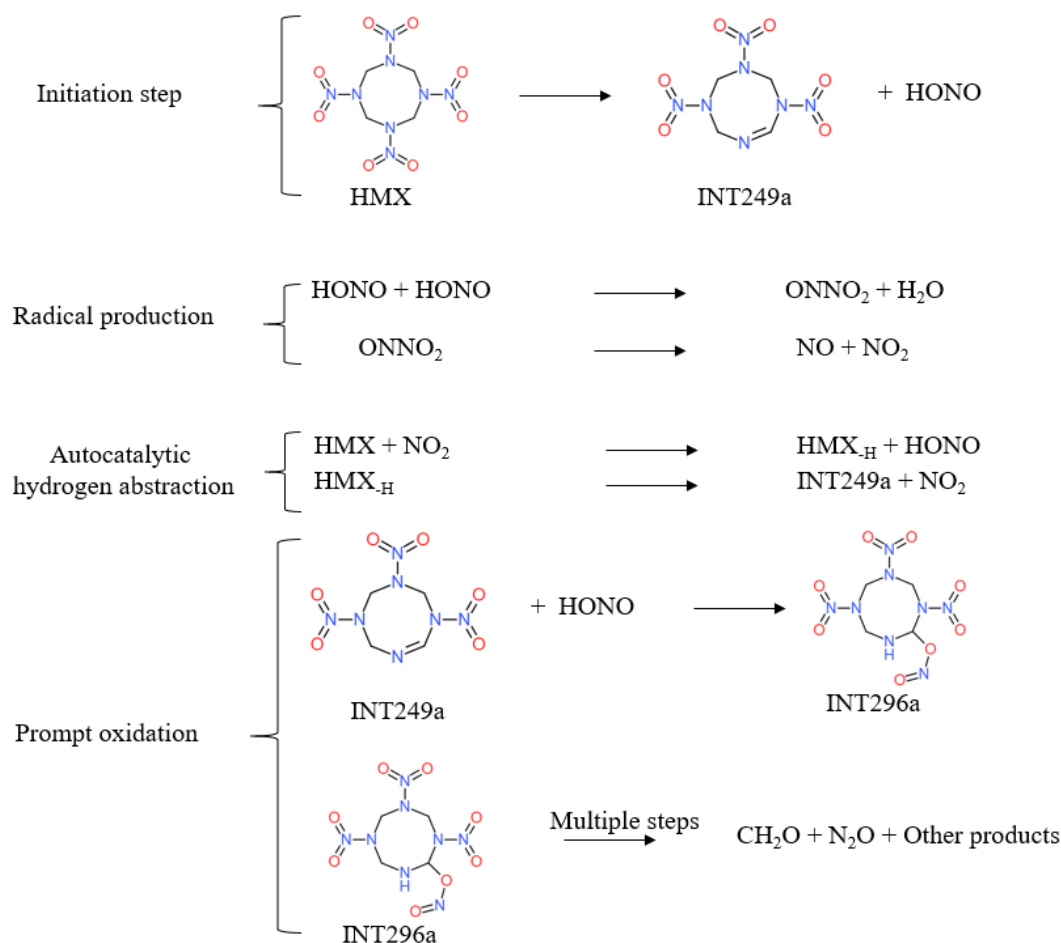


Figure 3-10. Summary of liquid-phase decomposition mechanism of HMX

### 3.8 Conclusions

Thermal decomposition of HMX was studied using TGA-FTIR setup for different low heating rates and using CRT-FTIR setup for high heating rates to isothermal conditions at different set temperatures. A phase transformation from  $\beta$ -HMX to  $\delta$ -HMX was observed around 190°C. DSC data show the endothermic melting at approximately 280°C. This was followed by rapid mass loss and exothermic decomposition. For heating rates of 10, 15 and 20 K/min, sublimation of HMX was very small and it decomposed predominately in the liquid phase. During both types of experiments,  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  were observed to be major decomposition products followed by smaller quantities of  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ . Using quantum mechanics calculations, the initiation mechanism for the liquid-phase decomposition of HMX was further augmented to yield 109 species and 157 reactions. The reaction mechanism was employed in a computational model to simulate TGA and CRT experiments. The mass loss curves predicted by the computational model are in excellent agreement with the TGA data. The species mole fraction profiles predicted by the computational model are also in good agreement with the experimental results obtained from FTIR spectral transmittance data. The computational model accurately predicts  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  as the primary decomposition products for both types of experiments. The evolution of other decomposition products formed in smaller quantities such as  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{HCN}$  were also captured reasonably well. This validates our comprehensive reaction mechanism for the liquid-phase decomposition of HMX.

## CHAPTER 4

### TRANSPORT PARAMETERS FOR COMBUSTION MODELING

#### 4.1 Introduction

Numerical simulations are becoming increasingly important in the study of the ignition, combustion and detonation behaviors of energetic materials. These simulations rely upon accurate treatment of diffusion of heat and species, as well as knowledge of chemical kinetic models of decomposition [10,11,66–68], combustion [69–75] and detonation [76–78]. With regard to diffusion of heat and species, models of decomposition and combustion require transport properties such as coefficients of diffusion, viscosities and thermal conductivities of species. Detonation models require equation of state describing properties at very high pressures.

In this chapter, three classes of widely used energetic materials – nitroalkanes, nitramines and nitrate esters representing the C-NO<sub>2</sub>, N-NO<sub>2</sub> and O-NO<sub>2</sub> functional groups, respectively, – are selected, and a generalized CHNO intermolecular potential is parametrized using ab initio calculations. The Lennard-Jones potential,

$$V(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right] \quad (4-1)$$

where  $\sigma_{ij}$  is collision diameter and  $\varepsilon_{ij}$  is the well depth, is commonly used for transport properties calculations in various combustion modeling suites such as CHEMKIN [79]. Hence, the Lennard-Jones parameters, i.e.,  $\sigma_{ij}$  and  $\varepsilon_{ij}$  are calculated here for various energetic organic molecules. For intermolecular interactions with these energetic molecules, four bath gases – He, Ne, Ar and N<sub>2</sub> – are chosen to reduce complexities in the electronic structure calculations and eliminate effects of dipole-dipole interactions. The pure gas Lennard-Jones parameters are then obtained using the usual combining rules [80], and the transport properties are calculated using kinetic theory of gases [81]. The accuracy of the proposed method in conjunction with the choice of the bath gas and the combining rule is evaluated by comparing the calculated transport properties – viscosity, thermal conductivity and diffusion coefficient – with experimentally measured values for nitromethane at different temperatures. In addition to Lennard-Jones parameters, transport properties also depend on dipole moment and polarizabilities, which can readily be obtained using low-level electronic structure methods. Hence, a transport properties database for nitramines combustion modeling, containing the Lennard-Jones parameters, dipole moments and polarizabilities in CHEMKIN format, is developed and provided in [82]. A comparative sensitivity analysis is also performed to investigate the importance of transport parameters relative to reaction rate parameters in combustion modeling of RDX.

#### 4.2 Theory and Computational methods

The one-dimensional minimization approach of Jasper and Miller [83] is used to calculate Lennard-Jones collision parameters for a target molecule  $T$  interacting with bath gas  $M$ , and is briefly described here. The total geometry of the interacting pair  $T+M$  depends on the internal coordinates of the target species  $\mathbf{R}_T$ , the internal coordinates of the bath gas  $\mathbf{R}_M$  (if any), the relative orientation of the target and bath,  $\mathbf{R}_\Omega$ , and their center-of-mass separation,  $r$ . Hence, the full-dimensional coordinates of the system can be written as  $\mathbf{R} \equiv (\mathbf{R}_T, \mathbf{R}_M, \mathbf{R}_\Omega, r)$ . The full-dimensional intermolecular potential is defined by subtracting the energies of the isolated species, i.e.,

$$V(\mathbf{R}) = E(\mathbf{R}) - E_T(\mathbf{R}_T) - E_M(\mathbf{R}_M) \quad (4-2)$$

where  $E(\mathbf{R})$  is the total energy of the interacting target-bath system,  $T+M$ , evaluated at  $\mathbf{R}$ ,  $E_T(\mathbf{R}_T)$  and  $E_M(\mathbf{R}_M)$  are energies of isolated target and bath-gas molecules respectively. In one-dimensional minimization approach followed here,  $N$  different orientations,  $\mathbf{R}_\Omega$ , are sampled uniformly and the intermolecular potential  $V(\mathbf{R}_T^{eq}, \mathbf{R}_M^{eq}, \mathbf{R}_\Omega^n, r)$  is minimized with respect to  $r$  for each orientation  $\mathbf{R}_\Omega^n$  for  $n=1$  to  $N$ , where target and bath geometries are set to calculated equilibrium geometries  $\mathbf{R}_T^{eq}$  and  $\mathbf{R}_M^{eq}$ , respectively. The desired Lennard-Jones parameters for each orientation are obtained conveniently from Eq. (4-3) and (4-4),

$$\varepsilon_n = -\min_r(V) \quad (4-3)$$

$$\sigma_n = 2^{-1/6} r_{min} \quad (4-4)$$

where  $r_{min}$  is the center-of-mass separation corresponding to the minimum of potential energy  $V$ . The effective Lennard-Jones parameters, which include anisotropy, are then calculated by averaging over all orientations.

$$\varepsilon = \frac{1}{N} \sum_{n=1}^N \varepsilon_n \quad (4-5)$$

$$\sigma = \frac{1}{N} \sum_{n=1}^N \sigma_n \quad (4-6)$$

One-dimensional minimization approach was shown to be more accurate than spherical averaging approach, especially for larger molecules with significant anisotropy [83]. It is also computationally more efficient as compared to full-dimensional trajectory-based method as investigated for hydrocarbon species by Jasper and Miller [83]. Hence, spherical averaging approach, which is computationally inexpensive but inaccurate, and full-dimensional trajectory-based approach, which is accurate but computationally demanding, are not considered in the present study.

The quality of the potential energy used will sensitively determine the accuracy of the method described above. For energetic organic molecules containing many heavy atoms, the level of electron correlation and the size of basis set that could be used is limited since a large number of orientations should be considered for each molecule interacting with different bath gases. Hence, the strategy adopted here first makes use of high-level ab initio calculations to evaluate the accuracy of various low-level quantum chemistry methods. The high-level method used here is counterpoise corrected QCISD(T) [84] with complete basis set (CBS) extrapolations based on aug-cc-pVDZ and aug-cc-pVTZ basis sets as shown by Eq. (4-7),

$$E_X = E_{CBS} + A X^{-3} \quad (4-7)$$

where  $X$  is cardinal number ( $X=2$  for double-zeta basis set and  $X=3$  for triple-zeta basis set),  $E_x$  is the energy with a basis set whose cardinal number is  $X$ ,  $E_{CBS}$  is the energy at the basis-set limit and  $A$  is fitting parameter. Solving Eq. (4-7) with  $X=2$  and  $X=3$  and eliminating the parameter  $A$  gives  $E_{CBS}$  as shown in Eq. (4-8),

$$E_{CBS} = \frac{27E_{X=3} - 8E_{X=2}}{19} \quad (4-8)$$

Once a computationally feasible yet accurate quantum chemistry method is chosen, a training set of six molecules was chosen, including two nitramines ( $\text{CH}_2\text{NNO}_2$  and  $\text{CH}_3\text{NHNO}_2$ ), two nitrate esters ( $\text{CH}_3\text{ONO}_2$  and  $\text{CH}_3\text{CH}_2\text{ONO}_2$ ) and two nitroalkanes ( $\text{CH}_3\text{NO}_2$  and  $\text{CH}_3\text{CH}_2\text{NO}_2$ ). The low-level quantum chemistry method was then used to calculate potential energy surfaces for the interaction of each of the molecule in training set with four different bath gases – He, Ne, Ar and  $\text{N}_2$  along 14 different spherically uniform orientations. The ab initio data are then used to parametrize an analytical site-site intermolecular potential which is then used to perform one-dimensional minimization calculations for Lennard-Jones parameters. All quantum chemistry calculations are performed using Gaussian 09 (version d01) [13].

### 4.3 Results and discussions

#### 4.3.1 Validation of low-level quantum chemistry methods

The accuracy of two lower-level quantum chemistry methods, i.e., second order Møller–Plesset perturbation theory (MP2) [85–88] and long-range corrected DFT functional  $\omega\text{B97X-D}$  [89], along with aug-cc-pVDZ and aug-cc-pVTZ basis sets, as well as CBS extrapolation based on these two basis sets, was evaluated by comparing the interaction energies along three  $\text{CH}_2\text{NNO}_2$ –He approaches and three  $\text{CH}_3\text{NO}_2$ –He approaches relative to QCISD(T)/CBS energies. The comparison is made using three error values: root-mean-squared error in the minimum energy,  $\varepsilon_{\min}$ , root-mean-squared error in center-of-mass separation corresponding to minimum energy,  $R_{\min}$ , and the mean unsigned error (MUE) for all 96 data points using six different directions of approach for the two molecules.

The average error in prediction of the well depth,  $\epsilon_{\min}$ , is 8.2  $\text{cm}^{-1}$  only for MP2/CBS relative to QCISD(T)/CBS energies and the error in center-of-mass separation at the minimum of energy is 0.12 Å. Corresponding errors for the DFT method  $\omega$ B97X-D/CBS are 16.9  $\text{cm}^{-1}$  and 0.35 Å, respectively. The MUE for all 96 data points is 15.8  $\text{cm}^{-1}$  only for MP2/CBS as compared to 68.8  $\text{cm}^{-1}$  for  $\omega$ B97X-D/CBS. CBS extrapolation, based on aug-cc-pVTZ and aug-cc-pVDZ basis sets, improves the accuracy of MP2 method whereas for DFT functional  $\omega$ B97X-D, the CBS extrapolation does not improve the accuracy. The detailed comparison is shown in Table 4-1.

Table 4-1. Errors for low-level quantum chemistry methods relative to counterpoise corrected QCISD(T)/CBS calculations for  $\text{CH}_2\text{NNO}_2\text{---He}$  and  $\text{CH}_3\text{NO}_2\text{---He}$  interactions along three approaches for each molecule

| Method                      | $\epsilon_{\min} (\text{cm}^{-1})$<br>(six orientations) | $R_{\min} (\text{\AA})$<br>(six orientations) | MUE ( $\text{cm}^{-1}$ )<br>(96 data points) |
|-----------------------------|----------------------------------------------------------|-----------------------------------------------|----------------------------------------------|
| MP2/CBS                     | 8.2                                                      | 0.12                                          | 15.8                                         |
| MP2/aug-cc-pVTZ             | 10.8                                                     | 0.16                                          | 27.1                                         |
| MP2/aug-cc-pVDZ             | 17.5                                                     | 0.28                                          | 54.1                                         |
| $\omega$ B97X-D/CBS         | 16.9                                                     | 0.35                                          | 68.8                                         |
| $\omega$ B97X-D/aug-cc-pVTZ | 17.0                                                     | 0.35                                          | 66.2                                         |
| $\omega$ B97DX/aug-cc-pVDZ  | 17.1                                                     | 0.35                                          | 59.9                                         |

Hence, MP2/CBS method is chosen for further calculations. Figure 4-1 shows the comparison of QCISD(T)/CBS interaction energies with MP2/CBS energies and  $\omega$ B97X-D/CBS energies for three approaches of He towards  $\text{CH}_2\text{NNO}_2$ . Corresponding comparison for  $\text{CH}_3\text{NO}_2 + \text{He}$  interactions is shown in Figure 4-2.

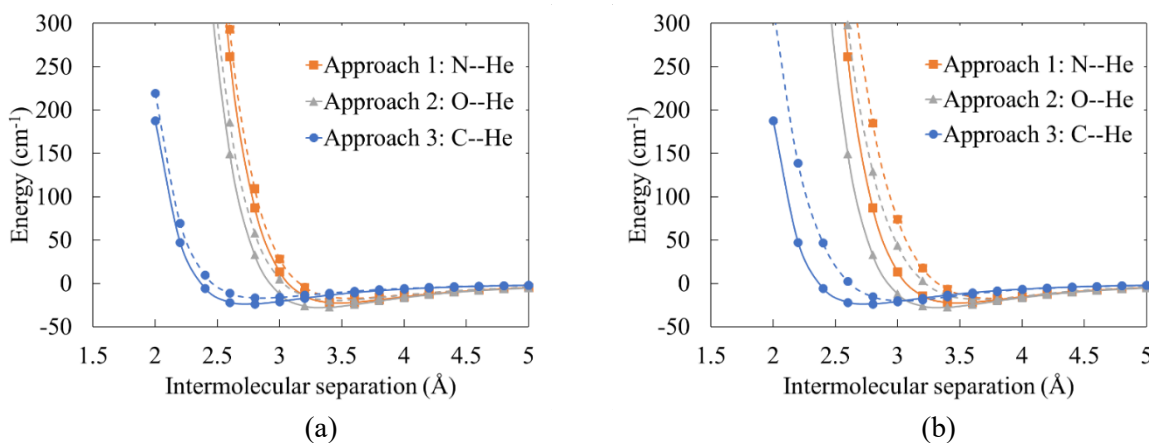


Figure 4-1.  $\text{CH}_2\text{NNO}_2 + \text{He}$  interaction potential for three approaches. Solid lines are QCISD(T)/CBS energies while the dashed lines are (a) MP2/CBS and (b)  $\omega$ B97X-D/CBS energies.

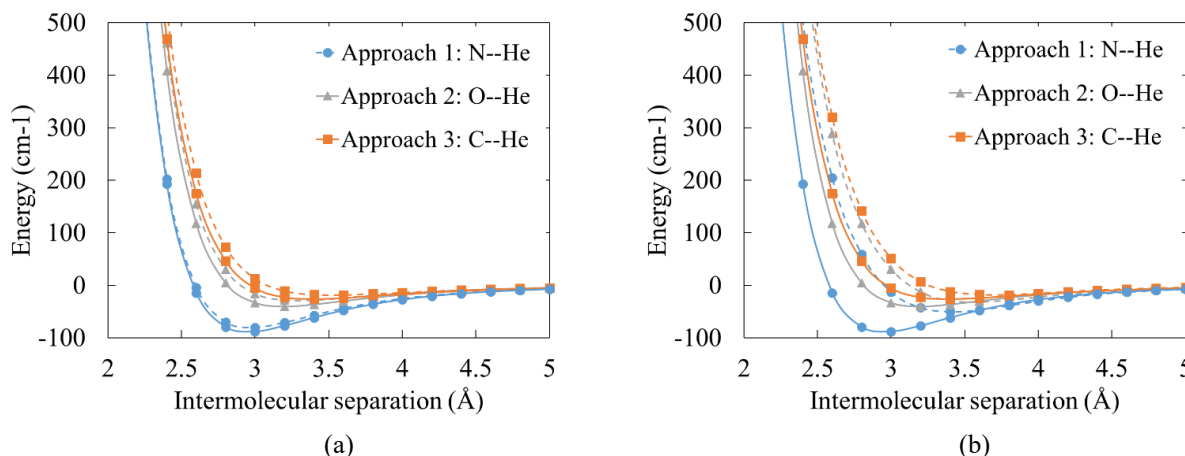


Figure 4-2.  $\text{CH}_3\text{NO}_2 + \text{He}$  interaction potential for three approaches. Solid lines are QCISD(T)/CBS energies while the dashed lines are (a) MP2/CBS and (b)  $\omega\text{B97X-D/CBS}$  energies.

#### 4.3.2 Separable approximation to potential energy surface

A training set of six molecules was chosen, including two nitramines ( $\text{CH}_2\text{NNO}_2$  and  $\text{CH}_3\text{NHNO}_2$ ), two nitrate esters ( $\text{CH}_3\text{ONO}_2$  and  $\text{CH}_3\text{CH}_2\text{ONO}_2$ ) and two nitroalkanes ( $\text{CH}_3\text{NO}_2$  and  $\text{CH}_3\text{CH}_2\text{NO}_2$ ). MP2/CBS method was then used to calculate potential energy surfaces for the interaction of each of the molecules in the training set with four different bath gases – He, Ne, Ar and  $\text{N}_2$ . For MP2/CBS calculations on these large molecules, 14 different spherically uniform orientations were chosen due to limited computational resources. Since we are interested in obtaining average Lennard-Jones parameters for energetic molecules, which have highly anisotropic intermolecular potentials, thousands of trajectories should be calculated which becomes computationally infeasible even with MP2/CBS. Hence, alternate approximate analytical potentials are investigated.

The full-dimensional intermolecular potential  $V(\mathbf{R})$  given by Eq. (4-2) is approximated as a sum of pairwise atom-atom interactions in Eq. (4-9),

$$V(\mathbf{R}) \approx \sum_{ij} V_{ij}(R_{ij}) \quad (4-9)$$

where  $i$  labels the atoms on target molecule,  $j$  labels the atom on bath gas molecule and  $R_{ij}$  is the distance between the two atoms. Two forms of  $V_{ij}$  were considered by Jasper and Miller [90] for  $\text{CH}_4$  interacting with different bath gases – Lennard-Jones potential and modified Buckingham potential – and it was found that modified Buckingham potential is more accurate than Lennard-Jones form. Hence the modified Buckingham potential (referred to as exp/6) was chosen in the present study as shown in Eq. (4-10)

$$V_{ij}(R_{ij}) = A_{ij} \exp(-R_{ij}/B_{ij}) - C_{ij}^6/(R_{ij}^6 + D_{ij}^6) \quad (4-10)$$

where  $A_{ij}$ ,  $B_{ij}$ ,  $C_{ij}$  and  $D_{ij}$  are fitted parameters for atom-atom interactions. i.e.,  $ij = \text{C-X, N-X, O-X and H-X}$  ( $\text{X} \equiv \text{He, Ne, Ar and N}_2$ ). The fitted potential energy surface is compared with MP2/CBS energies to investigate the accuracy of the separable pairwise approximation. For each of the four bath gases, parameters for exp/6 potential were obtained by fitting the MP2/CBS energies along 14 approaches for each of the six molecules in the training set. A more detailed description of the least-squares minimization procedure to obtain exp/6 potential parameters is given below:

1. Translate the coordinates of the target molecule such that the center of mass (COM) is at the origin of the coordinate system. Choose a starting distance between COM of target and bath molecules (we chose 8 Å and  $N=14$  orientations for QM calculations).
2. Imagine a sphere of radius 8 Å around the target molecule and distribute  $N=14$  points uniformly on that sphere.

3. Connect these points to the origin. This gives us 14 straight lines which we call “spherically uniform orientations”. These are representative orientations for the approach of bath molecule towards target molecule from all possible directions.
4. Perform QM calculations for each of the 14 directions of approach starting with center of mass separation being 8 Å and bringing the bath molecule closer to the target molecule.
5. Use the resulting QM data for these 14 orientations to fit the exp/6 potential.

The objective function for the least square minimization is defined as follows:

$$\chi^2 = \sum_{i=1}^6 \sum_{j=1}^{14} \sum_{k=1}^{21} \left[ \frac{V_{MP2}(\mathbf{R}_{ijk}) - V_{exp/6}(\mathbf{R}_{ijk})}{\sigma_{ijk}} \right]^2$$

where subscript  $i$  represents six different molecules in the training set, subscript  $j$  represents 14 different directions of approach for each molecule and subscript  $k$  represents 21 data points along each direction of approach resulting in total 1764 data points.  $V_{MP2}(\mathbf{R}_{ijk})$  represents the intermolecular potential energy given by Eq. (4-2) calculated using MP2/CBS method at the full-dimensional coordinates  $\mathbf{R}_{ijk}$  of the system.  $V_{exp/6}(\mathbf{R}_{ijk})$  is the intermolecular potential energy of the system given by Eq. (4-9).  $\sigma_{ijk}$  represents the weights for each data point which are assigned as 1 for all the data points. The coefficients  $A_{ij}$ ,  $B_{ij}$ ,  $C_{ij}$  and  $D_{ij}$  in Eq. (4-10) are then obtained by applying least-square minimization to the objective function  $\chi^2$  and are listed in Table 4-2.

Table 4-2. Exp/6 parameters for Eq. (4-10)

| Bath gas       | Atom-atom pair | A (Hartrees) | B (Å)  | C (Å)  | D (Å)  |
|----------------|----------------|--------------|--------|--------|--------|
| He             | C—He           | 0.1480       | 0.7950 | 1.2642 | 2.9071 |
|                | H—He           | 1.5603       | 0.3043 | 0.7444 | 2.2685 |
|                | N—He           | 17.4922      | 0.2621 | 0.6327 | 2.2012 |
|                | O—He           | 7.4972       | 0.2882 | 0.8048 | 2.6610 |
| Ne             | C—Ne           | 34.8023      | 0.2773 | 0.7343 | 2.2936 |
|                | H—Ne           | 0.3408       | 0.6503 | 1.2094 | 2.3817 |
|                | N—Ne           | 47.9763      | 0.2612 | 0.8087 | 2.1986 |
|                | O—Ne           | 42.9457      | 0.2604 | 0.8376 | 2.4547 |
| Ar             | C—Ar           | 59.7379      | 0.3094 | 1.0731 | 2.5329 |
|                | H—Ar           | 0.5667       | 0.7183 | 1.4541 | 2.6256 |
|                | N—Ar           | 56.7822      | 0.2956 | 1.0681 | 2.5103 |
|                | O—Ar           | 73.2496      | 0.2822 | 1.0173 | 2.5333 |
| N <sub>2</sub> | C—N            | 7.0581       | 0.3809 | 0.9073 | 2.1816 |
|                | H—N            | 0.1038       | 0.9000 | 1.3657 | 3.0207 |
|                | N—N            | 85.9890      | 0.2469 | 0.9096 | 2.0947 |
|                | O—N            | 54.1869      | 0.2751 | 0.8990 | 2.6454 |

The exp/6 form of intermolecular potential accurately describes the MP2/CBS energies for all the bath gases, with well depth errors,  $\epsilon_{min}$ , ranging from 3 – 18 cm<sup>-1</sup> and center-of-mass separation errors,  $R_{min}$ , ranging from 0.02 - 0.08 Å. The MUE for exp/6 potential is minimum for He (14.6 cm<sup>-1</sup>) followed by Ne (29.5 cm<sup>-1</sup>), Ar (43.3 cm<sup>-1</sup>) and N<sub>2</sub> (68.9 cm<sup>-1</sup>). The fitting errors are given in Table 4-3.

Table 4-3. Errors for exp/6 potential relative to counterpoise corrected MP2/CBS calculations for six molecules in the training set

| Bath gas       | $\epsilon_{min}$ (cm <sup>-1</sup> ) | $R_{min}$ (Å) | MUE (cm <sup>-1</sup> ) |
|----------------|--------------------------------------|---------------|-------------------------|
| He             | 3.01                                 | 0.08          | 14.61                   |
| Ne             | 5.71                                 | 0.08          | 29.46                   |
| Ar             | 13.30                                | 0.02          | 43.30                   |
| N <sub>2</sub> | 17.71                                | 0.05          | 68.68                   |

Figure 4-3 shows the comparison of MP2/CBS interaction energies with exp/6 energies for  $\text{CH}_2\text{NNO}_2 + \text{He}$  interactions along five different approaches out of 14 approaches used in the fitting procedure. Exp/6 potential reproduces MP2/CBS energies very accurately, including the van der Waals wells along different approaches as shown in inset in Figure 4-3.

The analytical exp/6 potential parameters were subsequently used to calculate the Lennard-Jones parameters for six molecules in the training set using the one-dimensional minimization approach with  $N=5000$  orientations. The results are compared against the Lennard-Jones parameters computed using MP2/CBS method as shown in Table 4-4. A convergence test was performed with respect to the choice of  $N$  for  $N=2000, 3000, 4000$  and  $5000$ , and Lennard-Jones parameters were found to converge within 0.05 %.

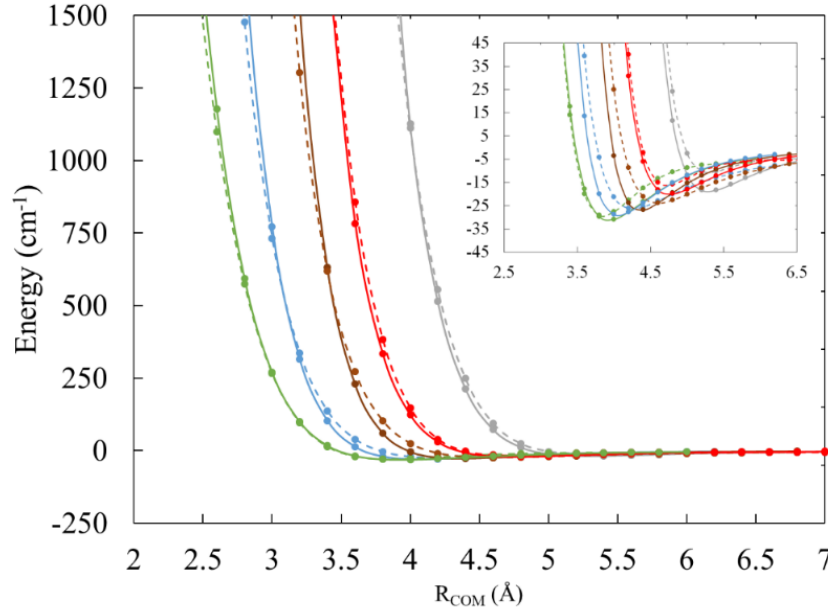


Figure 4-3.  $\text{CH}_2\text{NNO}_2 + \text{He}$  interaction potential for five different approaches. Solid lines are MP2/CBS energies while the dashed lines are exp/6 energies. Van der Waals wells are highlighted in the inset.

The Lennard-Jones parameters calculated using exp/6 potential and MP2/CBS potential were compared using collision rate coefficient  $z_{ij}$  as defined by Eq. (4-11)

$$z_{ij} = \pi \sigma_{ij}^2 \Omega^{(1,1)*} \bar{g}_{ij} \quad (4-11)$$

where  $\sigma_{ij}$  is the collision diameter for target-bath pair,  $\Omega^{(1,1)*}$  is reduced collision integral that depends on the intermolecular potential and  $\bar{g}_{ij} = (8k_B T / \pi \mu_{ij})^{1/2}$  is the average relative speed for collision of target  $i$  and bath  $j$ .  $k_B$  is Boltzmann's constant,  $T$  is temperature and  $\mu_{ij} = m_i m_j / (m_i + m_j)$  is the reduced mass for  $i, j$  collisions. The collision rate coefficient  $z_{ij}$  is used in the calculation of binary diffusion coefficient as shown by Eq. (4-12)

$$D_{ij} = \frac{3}{16} \frac{\bar{g}_{ij} (2\pi k_B^3 T^3 / \mu_{ij})^{1/2}}{p z_{ij}} \quad (4-12)$$

where  $p$  is the pressure. Collision rate coefficient, analogous to Eq. (4-11), can also be defined for the calculation of viscosity, where  $\Omega^{(1,1)*}$  is replaced by another reduced collision integral  $\Omega^{(2,2)*}$ , which also depends on the intermolecular potential and is readily available in tabular form. Collision integrals in the present study are obtained from high accuracy empirical interpolation formulas given by Kim and Monroe [91]. The collision rate coefficients at three temperatures for six molecules in the training set are given in Table 4-4. The collision rates, and hence the transport properties, as calculated using exp/6 potential and MP2/CBS potential differ by less than 10%.

Table 4-4. Lennard-Jones parameters and collision rates for molecules in training set

| Target                                           | Bath           | exp/6        |                                | MP2/CBS      |                                | $Z_{\text{exp}}/Z_{\text{MP2}}$ |        |        |
|--------------------------------------------------|----------------|--------------|--------------------------------|--------------|--------------------------------|---------------------------------|--------|--------|
|                                                  |                | $\sigma$ (Å) | $\epsilon$ (cm <sup>-1</sup> ) | $\sigma$ (Å) | $\epsilon$ (cm <sup>-1</sup> ) | 300 K                           | 1500 K | 3000 K |
| CH <sub>2</sub> NNO <sub>2</sub>                 | He             | 3.93         | 22.80                          | 3.79         | 28.20                          | 1.04                            | 1.04   | 1.04   |
|                                                  | Ne             | 3.95         | 55.98                          | 3.79         | 61.62                          | 1.06                            | 1.07   | 1.07   |
|                                                  | Ar             | 3.93         | 187.06                         | 3.93         | 200.34                         | 0.97                            | 0.99   | 0.99   |
|                                                  | N <sub>2</sub> | 4.34         | 149.55                         | 4.36         | 159.48                         | 0.96                            | 0.98   | 0.98   |
| CH <sub>3</sub> NHNO <sub>2</sub>                | He             | 3.83         | 37.19                          | 3.84         | 30.41                          | 1.03                            | 1.03   | 1.03   |
|                                                  | Ne             | 3.92         | 71.15                          | 3.88         | 65.21                          | 1.04                            | 1.03   | 1.03   |
|                                                  | Ar             | 3.95         | 214.30                         | 3.97         | 217.57                         | 0.98                            | 0.99   | 0.99   |
|                                                  | N <sub>2</sub> | 4.32         | 226.52                         | 4.41         | 181.08                         | 1.07                            | 1.00   | 1.00   |
| CH <sub>3</sub> ONO <sub>2</sub>                 | He             | 3.78         | 38.11                          | 3.72         | 33.81                          | 1.06                            | 1.05   | 1.05   |
|                                                  | Ne             | 3.89         | 66.86                          | 3.77         | 69.29                          | 1.05                            | 1.06   | 1.06   |
|                                                  | Ar             | 3.93         | 192.25                         | 3.89         | 214.33                         | 0.97                            | 1.00   | 1.00   |
|                                                  | N <sub>2</sub> | 4.36         | 171.30                         | 4.28         | 185.77                         | 1.00                            | 1.02   | 1.02   |
| CH <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub> | He             | 3.99         | 34.42                          | 3.97         | 31.39                          | 1.03                            | 1.02   | 1.02   |
|                                                  | Ne             | 4.09         | 77.67                          | 3.98         | 68.50                          | 1.09                            | 1.08   | 1.08   |
|                                                  | Ar             | 4.11         | 228.80                         | 4.14         | 221.97                         | 1.00                            | 0.99   | 0.99   |
|                                                  | N <sub>2</sub> | 4.53         | 208.13                         | 4.52         | 190.80                         | 1.05                            | 1.02   | 1.02   |
| CH <sub>3</sub> NO <sub>2</sub>                  | He             | 3.70         | 31.06                          | 3.65         | 31.34                          | 1.03                            | 1.03   | 1.03   |
|                                                  | Ne             | 3.81         | 59.79                          | 3.68         | 63.58                          | 1.06                            | 1.06   | 1.06   |
|                                                  | Ar             | 3.83         | 176.94                         | 3.79         | 199.30                         | 0.97                            | 1.00   | 1.00   |
|                                                  | N <sub>2</sub> | 4.25         | 168.18                         | 4.27         | 174.25                         | 0.97                            | 0.98   | 0.98   |
| CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>  | He             | 3.96         | 27.96                          | 3.96         | 26.84                          | 1.01                            | 1.01   | 1.01   |
|                                                  | Ne             | 4.05         | 70.79                          | 3.97         | 59.65                          | 1.09                            | 1.07   | 1.07   |
|                                                  | Ar             | 4.03         | 212.96                         | 4.10         | 195.63                         | 1.01                            | 0.98   | 0.98   |
|                                                  | N <sub>2</sub> | 4.46         | 203.29                         | 4.55         | 162.06                         | 1.07                            | 1.00   | 1.00   |

#### 4.3.3 Validation of the exp/6 potential energy surface

To validate the exp/6 potential, a test set of nine molecules was chosen containing three nitramines: dimethylnitramine (DMNA), 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), three nitrate esters: nitroglycerin, isopropyl nitrate (IPN), pentaerythritol tetranitrate (PETN), and three nitroalkanes: 1-nitropropane, 2-nitropropane and nitrobutane. Lennard-Jones parameters were calculated for all molecules in the test set using exp/6 potential and one-dimensional minimization approach. Since these molecules contain many heavy atoms, MP2/CBS calculations could not be performed. Instead MP2/aug-cc-pVDZ method was used to validate the results obtained using exp/6 potential as shown in Table 4-5.

The collision rate coefficients at three temperatures for nine molecules in the test set are also given in Table 4-5. It is to be noted that exp/6 potential was parametrized using MP2/CBS potential whose well depths are deeper than MP2/aug-cc-pVDZ potential. Hence, the Lennard-Jones well depth for test molecules calculated using MP2/aug-cc-pVDZ are smaller than corresponding values calculated using exp/6. Similarly, collision diameters are larger for MP2/aug-cc-pVDZ method as compared to MP2/CBS potential and exp/6 potential. Even though Lennard-Jones parameters calculated using these two potentials differ from each other significantly, the collision rates, and hence the transport properties, as calculated using exp/6 potential and MP2/aug-cc-pVDZ potential differ by less than 20%. Experimental measurements cannot fix the values of Lennard-Jones parameters individually, instead the two values lie on a two-dimensional curve all of which can produce the experimental measurements within a given uncertainty. Hence, the differences observed in the individual parameters in the present study do not necessarily indicate

poor performance of the method. The predicted collision rates are in good overall agreement with each other.

Table 4-5. Lennard-Jones parameters and collision rates for molecules in test set

| Target         | Bath           | exp/6        |                                | MP2/aug-cc-pVDZ |                                | $Z_{\text{exp}}/Z_{\text{MP2}}$ |       |       |
|----------------|----------------|--------------|--------------------------------|-----------------|--------------------------------|---------------------------------|-------|-------|
|                |                | $\sigma$ (Å) | $\epsilon$ (cm <sup>-1</sup> ) | $\sigma$ (Å)    | $\epsilon$ (cm <sup>-1</sup> ) | 300K                            | 1500K | 3000K |
| DMNA           | He             | 4.03         | 34.60                          | 4.14            | 25.18                          | 1.00                            | 1.00  | 1.00  |
|                | Ne             | 4.11         | 78.97                          | 4.14            | 47.04                          | 1.12                            | 1.07  | 1.07  |
|                | Ar             | 4.13         | 241.66                         | 4.25            | 169.32                         | 1.12                            | 1.02  | 1.00  |
|                | N <sub>2</sub> | 4.52         | 244.11                         | 4.61            | 165.70                         | 1.16                            | 1.04  | 1.03  |
| RDX            | He             | 4.75         | 43.50                          | 4.67            | 43.79                          | 1.03                            | 1.03  | 1.03  |
|                | Ne             | 4.70         | 100.93                         | 4.70            | 79.99                          | 1.08                            | 1.04  | 1.04  |
|                | Ar             | 4.81         | 317.00                         | 4.85            | 259.94                         | 1.09                            | 1.03  | 1.02  |
|                | N <sub>2</sub> | 5.22         | 245.79                         | 5.19            | 333.11                         | 0.86                            | 0.94  | 0.96  |
| HMX            | He             | 5.03         | 49.50                          | 4.96            | 45.15                          | 1.05                            | 1.04  | 1.04  |
|                | Ne             | 4.99         | 109.92                         | 4.98            | 82.19                          | 1.10                            | 1.05  | 1.05  |
|                | Ar             | 5.09         | 340.25                         | 5.17            | 270.12                         | 1.10                            | 1.03  | 1.01  |
|                | N <sub>2</sub> | 5.55         | 270.96                         | 5.47            | 365.85                         | 0.88                            | 0.95  | 0.97  |
| Nitroglycerin  | He             | 4.76         | 46.22                          | 4.67            | 39.24                          | 1.07                            | 1.07  | 1.07  |
|                | Ne             | 4.72         | 101.51                         | 4.75            | 69.92                          | 1.11                            | 1.05  | 1.05  |
|                | Ar             | 4.85         | 301.53                         | 4.93            | 224.58                         | 1.13                            | 1.04  | 1.02  |
|                | N <sub>2</sub> | 5.28         | 228.09                         | 5.16            | 321.93                         | 0.87                            | 0.97  | 0.98  |
| IPN            | He             | 4.24         | 33.76                          | 4.33            | 24.43                          | 1.02                            | 1.01  | 1.01  |
|                | Ne             | 4.21         | 86.42                          | 4.33            | 46.30                          | 1.11                            | 1.04  | 1.04  |
|                | Ar             | 4.28         | 256.63                         | 4.47            | 160.63                         | 1.15                            | 1.01  | 0.99  |
|                | N <sub>2</sub> | 4.70         | 240.53                         | 4.80            | 174.76                         | 1.12                            | 1.02  | 1.01  |
| PETN           | He             | 5.25         | 55.66                          | 5.18            | 41.00                          | 1.11                            | 1.09  | 1.09  |
|                | Ne             | 5.18         | 119.28                         | 5.23            | 72.36                          | 1.15                            | 1.07  | 1.06  |
|                | Ar             | 5.32         | 345.87                         | 5.45            | 232.16                         | 1.17                            | 1.05  | 1.02  |
|                | N <sub>2</sub> | 5.79         | 243.64                         | 5.67            | 342.55                         | 0.87                            | 0.96  | 0.98  |
| 1-nitropropane | He             | 4.23         | 26.88                          | 4.24            | 21.98                          | 1.03                            | 1.03  | 1.03  |
|                | Ne             | 4.12         | 82.16                          | 4.21            | 42.61                          | 1.13                            | 1.06  | 1.06  |
|                | Ar             | 4.20         | 248.16                         | 4.37            | 155.81                         | 1.15                            | 1.01  | 1.00  |
|                | N <sub>2</sub> | 4.62         | 235.28                         | 4.69            | 163.36                         | 1.16                            | 1.04  | 1.03  |
| 2-nitropropane | He             | 4.25         | 28.09                          | 4.25            | 22.44                          | 1.04                            | 1.04  | 1.04  |
|                | Ne             | 4.16         | 80.74                          | 4.24            | 42.93                          | 1.13                            | 1.06  | 1.06  |
|                | Ar             | 4.20         | 243.60                         | 4.38            | 154.04                         | 1.14                            | 1.01  | 0.99  |
|                | N <sub>2</sub> | 4.63         | 235.87                         | 4.85            | 155.70                         | 1.11                            | 0.99  | 0.98  |
| Nitrobutane    | He             | 4.69         | 27.43                          | 4.44            | 22.72                          | 1.15                            | 1.15  | 1.15  |
|                | Ne             | 4.20         | 92.36                          | 4.43            | 44.62                          | 1.09                            | 1.01  | 1.01  |
|                | Ar             | 4.33         | 279.33                         | 4.53            | 160.80                         | 1.20                            | 1.03  | 1.00  |
|                | N <sub>2</sub> | 4.75         | 266.39                         | 4.80            | 187.44                         | 1.17                            | 1.06  | 1.04  |

#### 4.3.4 Gas-phase transport properties of $\text{CH}_3\text{NO}_2$

Chemical kinetic and combustion modeling typically use transport properties via tabulated values for pure-gas (self-interaction) Lennard–Jones parameters, which are then converted to binary Lennard–Jones parameters via simple combining rules [80]. In the present study, binary Lennard–Jones parameters are directly calculated from first principles. To generate a transport properties database compatible with existing combustion modeling software, pure-gas Lennard–Jones parameters must be obtained from the binary Lennard–Jones parameters calculated here by reversing the combining rules.

Using tabulated parameters for the four bath gases in conjunction with the commonly used Lorentz-Berthelot combining rules [92,93] (arithmetic mean for collision diameter:  $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$  and geometric mean for well depth:  $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ ), the inferred pure gas values of  $\sigma$  for  $\text{CH}_3\text{NO}_2$  vary from 4.33 to 4.87 Å and the inferred pure gas values of  $\varepsilon/k_B$  vary from 198 to 599 K. The pure-gas Lennard-Jones parameters were used to calculate the temperature dependent viscosity of  $\text{CH}_3\text{NO}_2$  given by standard kinetic theory expression [81],

$$\eta = \frac{5}{16} \frac{\sqrt{\pi m k_B T}}{\pi \sigma^2 \Omega^{(2,2)*}} \quad (4-13)$$

where  $m$  is the molar mass of the gas,  $\sigma$  is pure-gas Lennard-Jones collision diameter,  $\Omega^{(2,2)*}$  is the reduced collision integral which depends on pure-gas Lennard-Jones parameters  $\sigma$  and  $\varepsilon$ . Table 4-6 shows the comparison of experimental viscosity [94] with calculated viscosity using pure-gas Lennard-Jones parameters obtained from different choices of bath gases.

Table 4-6. Comparison of experimental and calculated viscosity of  $\text{CH}_3\text{NO}_2$  using Lorentz-Berthelot combining rules and individual bath gases

| Temperature<br>(K) | Viscosity (micropoise) |                                                |             |             |                |
|--------------------|------------------------|------------------------------------------------|-------------|-------------|----------------|
|                    | Experimental<br>[94]   | Bath gas for pure-gas Lennard-Jones parameters |             |             |                |
|                    |                        | He                                             | Ne          | Ar          | N <sub>2</sub> |
| 400                | 103.2                  | 153.8                                          | 146.7       | 126.8       | 90.6           |
| 500                | 131.9                  | 184.8                                          | 176.9       | 159.3       | 114.1          |
| 600                | 159.8                  | 213.0                                          | 204.4       | 190.7       | 137.5          |
| 700                | 186.7                  | 239.1                                          | 229.7       | 220.9       | 160.4          |
| 800                | 212.8                  | 263.4                                          | 253.4       | 249.7       | 182.6          |
| 900                | 238.1                  | 286.3                                          | 275.7       | 277.1       | 204.0          |
| 1000               | 262.4                  | 308.1                                          | 296.9       | 303.3       | 224.6          |
| <b>MUE (%)</b>     | <b>-</b>               | <b>30.2</b>                                    | <b>25.1</b> | <b>18.4</b> | <b>13.8</b>    |

Using He as a bath gas produces largest discrepancy between experimental and theoretical viscosities at different temperatures with MUE being 30.2% followed by Ne (MUE = 25.1%), Ar (MUE = 18.4%) and N<sub>2</sub> (MUE = 13.8%). This indicates that the results are very sensitive to the choice of the bath gas, and Lennard-Jones parameters do not obey simple combining rules. Hence, alternate approaches should be considered.

In the novel strategy proposed here, instead of choosing a preferred bath gas, the pure-gas Lennard-Jones parameters are obtained from all four bath gases. A single set of pure-gas Lennard-Jones parameters are calculated by least-square minimization to reproduce the binary Lennard-Jones parameters for all four bath gases. Three combining rules are considered with this method – Lorentz-Berthelot rules [92,93], Waldman-Hagler rules [95] and Kong rules [96]. The values of pure-gas Lennard-Jones parameters obtained using this method in conjunction with the three combining rules are shown in Table 4-7.

The viscosities calculated using these values of Lennard-Jones parameters, as shown in Table 4-7, are in excellent agreement with the experimental values at all temperatures. Even the simplest Lorentz-Berthelot combining rule predicts viscosities with MUE error of 2.2% when all four bath gases are used to obtain the pure-gas Lennard-Jones parameters. The accuracy further improves on using sixth-power mean rules given by Waldman and Hagler [95] with MUE of just 0.69%. However, the very sophisticated Kong rules [96] does not improve the accuracy significantly.

Table 4-7. Comparison of experimental and calculated viscosity of CH<sub>3</sub>NO<sub>2</sub> using all four bath gases with different combining rules

| Temperature<br>(K) | Viscosity (micropoise) |                                                                                       |                                                                                    |                                                                          |
|--------------------|------------------------|---------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------|
|                    | Experimental<br>[94]   | Combining rule used                                                                   |                                                                                    |                                                                          |
|                    |                        | Lorentz-Berthelot<br>$\sigma = 4.71 \text{ \AA}$<br>$\epsilon/k_B = 466.10 \text{ K}$ | Waldman-Hagler<br>$\sigma = 4.23 \text{ \AA}$<br>$\epsilon/k_B = 750.89 \text{ K}$ | Kong<br>$\sigma = 4.18 \text{ \AA}$<br>$\epsilon/k_B = 926.84 \text{ K}$ |
| 400                | 103.2                  | 109.1                                                                                 | 105.3                                                                              | 97.7                                                                     |
| 500                | 131.9                  | 136.9                                                                                 | 132.0                                                                              | 121.6                                                                    |
| 600                | 159.8                  | 163.8                                                                                 | 159.4                                                                              | 146.3                                                                    |
| 700                | 186.7                  | 189.5                                                                                 | 186.7                                                                              | 171.5                                                                    |
| 800                | 212.8                  | 214.0                                                                                 | 213.7                                                                              | 196.8                                                                    |
| 900                | 238.1                  | 237.2                                                                                 | 240.2                                                                              | 222.0                                                                    |
| 1000               | 262.4                  | 259.4                                                                                 | 265.9                                                                              | 246.8                                                                    |
| <b>MUE (%)</b>     | <b>-</b>               | <b>2.21</b>                                                                           | <b>0.69</b>                                                                        | <b>7.19</b>                                                              |

Thermal conductivity of CH<sub>3</sub>NO<sub>2</sub> at different temperatures is calculated using Eq. (4-14) as described in detail in the CHEMKIN transport package [97].

$$\lambda = \frac{\eta}{W} (f_{trans}.C_{v,trans.} + f_{rot}.C_{v,rot.} + f_{vib.}C_{v,vib.}) \quad (4-14)$$

where  $\eta$  is viscosity,  $W$  is molecular weight and  $f_{trans.}$ ,  $f_{rot.}$  and  $f_{vib.}$ , are given by Eq. (4-15) to (4-17).

$$f_{trans.} = \frac{5}{2} \left( 1 - \frac{2}{\pi} \frac{C_{v,rot}}{C_{v,trans}} \frac{A}{B} \right) \quad (4-15)$$

$$f_{rot.} = \frac{\rho D}{\eta} \left( 1 + \frac{2}{\pi} \frac{A}{B} \right) \quad (4-16)$$

$$f_{vib.} = \frac{5}{2} - \frac{\rho D}{\eta} \quad (4-17)$$

$$A = \frac{\rho D}{\eta} \quad (4-18)$$

$$B = Z_{rot} + \frac{2}{\pi} \left( \frac{5}{3} \frac{C_{v,rot}}{R} \frac{\rho D}{\eta} \right) \quad (4-19)$$

The density  $\rho$  comes from the equation of state for the ideal gas, i.e.,  $\rho = PW/RT$ , where  $P$  is the pressure,  $T$  is the temperature and  $R$  is the universal gas constant.  $D$  is the self-diffusion coefficient given by Eq. (4-12) and  $Z_{rot}$  is the rotational relaxation collision number, a parameter that is assumed to be available at 298K with the temperature dependence given by Eq. (4-20). The components of heat capacity at constant volume  $C_v$ , i.e.,  $C_{v,trans.}$ ,  $C_{v,trans.}$  and  $C_{v,trans.}$  are given by Eq. (4-22) to (4-24).

$$Z_{rot.}(T) = Z_{rot.}(298 \text{ K}) \frac{F(298 \text{ K})}{F(T)} \quad (4-20)$$

$$F(T) = 1 + \frac{\pi^2}{2} \left( \frac{\epsilon/k_B}{T} \right)^{\frac{1}{2}} + \left( \frac{\pi^2}{4} + 2 \right) \left( \frac{\epsilon/k_B}{T} \right) + \pi^{3/2} \left( \frac{\epsilon/k_B}{T} \right)^{\frac{3}{2}} \quad (4-21)$$

$$C_{v,rot.} = \frac{3R}{2} \quad (4-22)$$

$$C_{v,trans.} = \frac{3R}{2} \quad (4-23)$$

$$C_{v,vib.} = C_v - 3R \quad (4-24)$$

Thermal conductivity depends not only on Lennard-Jones parameters but also on thermodynamic properties and temperature dependent rotational relaxation collision numbers. Hence, it is difficult to predict thermal conductivity as evident by the results shown in Table 4-8. Nonetheless, the simple kinetic theory

formulation predicts thermal conductivity to within 15% using Lorentz-Berthelot as well as Waldman-Hagler combining rules. Since viscosity is also used in the calculation of thermal conductivity, the error in viscosity using Kong's combining rule is propagated and thermal conductivity is predicted with a 20% MUE.

Table 4-8. Comparison of experimental and calculated thermal conductivity of  $\text{CH}_3\text{NO}_2$  using all four bath gases with different combining rules

| Temperature (K) | Thermal conductivity (W/m-K) |                     |                |        |
|-----------------|------------------------------|---------------------|----------------|--------|
|                 | Experimental [94]            | Combining rule used |                |        |
|                 |                              | Lorentz-Berthelot   | Waldman-Hagler | Kong   |
| 400             | 0.0148                       | 0.0128              | 0.0123         | 0.0114 |
| 500             | 0.0209                       | 0.0185              | 0.0179         | 0.0165 |
| 600             | 0.0275                       | 0.0245              | 0.0240         | 0.0221 |
| 700             | 0.0348                       | 0.0308              | 0.0306         | 0.0282 |
| 800             | 0.0426                       | 0.0371              | 0.0373         | 0.0345 |
| 900             | 0.0509                       | 0.0433              | 0.0441         | 0.0410 |
| 1000            | 0.0599                       | 0.0494              | 0.0509         | 0.0476 |
| MUE (%)         | -                            | 13.25               | 13.81          | 20.22  |

Binary diffusion coefficients of  $\text{CH}_3\text{NO}_2$  and  $\text{N}_2$  are also calculated using Eq. (4-12) and the results are shown in Table 4-9. Lennard-Jones parameters obtained using exp/6 potential are directly used, and since the combining rules are not needed, the results can be used to validate the exp/6 potential. However, the experimental data for binary diffusion coefficients of these energetic molecules with  $\text{N}_2$  or other bath gases are not available. Hence, the results are compared against experimental values of the binary diffusion coefficient for  $\text{CH}_3\text{NO}_2$  in air. The discrepancies in the calculated and experimental binary diffusion coefficients can result from inadequacies in the exp/6 potential as well as from neglecting the other components of air. Additional calculations are performed to obtain diffusion coefficients for  $\text{CH}_3\text{NO}_2 + \text{O}_2$  and subsequently for  $\text{CH}_3\text{NO}_2 + \text{air}$ . For these calculations, pure-gas LJ parameters for  $\text{O}_2$  are taken from CHEMKIN transport database and Lorentz-Berthelot combining rules are used to obtain binary LJ parameters for  $\text{CH}_3\text{NO}_2 + \text{O}_2$ . Then the mixture-averaged diffusion coefficients for  $\text{CH}_3\text{NO}_2 + \text{air}$  are obtained based on the formulation used in CHEMKIN. The mean unsigned error (MUE) between calculated and experimental values decreases to 16.8% (for  $\text{CH}_3\text{NO}_2 + \text{Air}$ ) from previous value of 18.5% (for  $\text{CH}_3\text{NO}_2 + \text{N}_2$ ) as shown in Table 4-9. Hence, other components of air (mainly  $\text{O}_2$ ) does have some influence on the diffusion coefficients but the inadequacies of exp/6 potential in conjunction with the kinetic theory formulation have a greater impact.

Table 4-9. Comparison of calculated binary diffusion coefficient of  $\text{CH}_3\text{NO}_2$  in air with experimental values for  $\text{CH}_3\text{NO}_2$  in air

| Temperature (K) | Experimental (with Air) [94] | Binary diffusion coefficient ( $\text{cm}^2/\text{s}$ ) |                                 |                                       |
|-----------------|------------------------------|---------------------------------------------------------|---------------------------------|---------------------------------------|
|                 |                              | Calculated (with $\text{N}_2$ )                         | Calculated (with $\text{O}_2$ ) | Calculated (mixture-averaged for air) |
| 200             | 0.0478                       | 0.0419                                                  | 0.0450                          | 0.0425                                |
| 300             | 0.1196                       | 0.0938                                                  | 0.1018                          | 0.0953                                |
| 400             | 0.2063                       | 0.1629                                                  | 0.1785                          | 0.1660                                |
| 500             | 0.3077                       | 0.2469                                                  | 0.2726                          | 0.2519                                |
| 600             | 0.4239                       | 0.3441                                                  | 0.3823                          | 0.3514                                |
| 700             | 0.5548                       | 0.4533                                                  | 0.5060                          | 0.4634                                |
| 800             | 0.7006                       | 0.5737                                                  | 0.6427                          | 0.5870                                |
| 900             | 0.8611                       | 0.7047                                                  | 0.7917                          | 0.7213                                |
| 1000            | 1.0364                       | 0.8458                                                  | 0.9522                          | 0.8661                                |

| MUE (%) | - | 18.5 | 9.8 | 16.8 |
|---------|---|------|-----|------|
|---------|---|------|-----|------|

#### 4.4 Application

##### 4.4.1 *Transport properties database for combustion modeling of nitramines*

Using the exp/6 potential in the one-dimensional minimization approach, Lennard-Jones parameters were obtained for all 92 species present in most recent gas-phase chemical kinetics mechanism of nitramines [33,68]. Pure-gas Lennard-Jones parameters were then obtained from least-square optimization to reproduce binary Lennard-Jones parameters for the four bath gases He, Ne, Ar, and N<sub>2</sub>. In addition to Lennard-Jones parameters, dipole moments and polarizabilities are also calculated at B3LYP/6-311++G(d,p) level of theory [98,99].

##### 4.4.2 *Comparative sensitivity analysis of transport vs. reaction rate parameters*

Gas-phase chemical kinetics mechanisms along with transport properties database have been used in one-dimensional combustion models to predict the burn-rate of solid propellants [69,72–75]. The temperature gradient near the surface of the burning propellant controls the heat feedback from the gas phase to the surface and hence controls the burn-rate. Anderson and Conner [75] tested two detailed gas-phase mechanisms for RDX and performed sensitivity analysis to identify the most sensitive reactions which control the temperature gradient at the surface. Several studies have shown that the uncertainties in transport parameters are as important in flame modeling as those in the reaction rates [100,101]. Hence, the study of Anderson and Conner [75] is extended here and sensitivity analysis is performed to identify important molecular transport parameters which controls the temperature gradient at the surface.

The one-dimensional, steady-state semi-empirical combustion model described in more detail in [74] is implemented in the open-source chemical kinetics software Cantera [102] and is briefly described here. It is assumed that two phases are present – a condensed phase and a gas phase. Experimentally derived pyrolysis law is used to relate the surface temperature to the gaseous mass flux leaving the surface of the burning propellant. The surface temperature and mass flux, along with the assumption that no reactions occur in the condensed phase and pure RDX evaporates into the gas-phase, define a one-dimensional, premixed, laminar flame problem. The temperature gradient at the surface is obtained from the gas-phase flame structure by solving the premixed flame problem. The heat feedback from the gas phase into the condensed phase is then obtained from the temperature gradient at the surface which is then used to calculate the mass flux evaporating from the surface. An algorithm iterates mass flux to converge the condensed phase heat flux requirement for the given burn-rate to the heat feedback from the gas phase flame. The converged mass flux is then converted to burn-rate via density of the solid propellant. The simulation parameters and pyrolysis law for RDX are given in Ref. [74]. Caltech nitramines mechanism [33,68] consisting of 89 species and 457 reactions is used along with the transport properties database developed in the present study.

Since the objective is to investigate the importance of transport parameters relative to reaction rates, only the results of the sensitivity analysis are presented. The predicted burn-rates are in close agreement with to the results obtained by Anderson and Conner [75] and are not repeated here, since the combustion model and chemical kinetics mechanism used are the same. For a converged burn-rate and hence the surface temperature, sensitivities of the temperature at the second grid point to all the reaction rates were obtained via brute force method. Table 4-10 shows the normalized sensitivity coefficients for the temperature at second grid point with respect to a reaction rate,  $S_T(k)$ , as defined by Eq. (4-25)

$$S_T(k) = \frac{k}{T_{max}} \frac{dT}{dk} \quad (4-25)$$

where  $k$  is the nominal rate constant,  $dT$  is the change in temperature at the second grid point due to  $dk$  change in the rate constant and  $T_{max}$  is the maximum temperature in the calculation domain.

Table 4-10. List of the top 15 normalized reaction temperature sensitivities for RDX at 1 atm for the second grid point

| Reaction                                                             | Normalized sensitivity coefficient $S_T(k)$ | Relative sensitivity |
|----------------------------------------------------------------------|---------------------------------------------|----------------------|
| $\text{HNC} + \text{OH} = \text{H} + \text{HNCO}$                    | 2.71E-04                                    | 100.00               |
| $\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$                   | 1.90E-04                                    | 70.18                |
| $\text{N} + \text{NO} = \text{N}_2 + \text{O}$                       | 1.68E-04                                    | 62.08                |
| $\text{NNH} + \text{O} = \text{NH} + \text{NO}$                      | 1.16E-04                                    | 42.68                |
| $\text{H} + \text{HNCO} = \text{CO} + \text{NH}_2$                   | 1.07E-04                                    | 39.65                |
| $\text{NH}_2 + \text{O} = \text{H} + \text{HNO}$                     | -7.74E-05                                   | -28.59               |
| $\text{NCO} + \text{M} = \text{CO} + \text{N} + \text{M}$            | 6.29E-05                                    | 23.24                |
| $\text{NH} + \text{OH} = \text{H} + \text{HNO}$                      | -6.02E-05                                   | -22.24               |
| $\text{N}_2\text{O} (+\text{M}) = \text{N}_2 + \text{O} (+\text{M})$ | 5.68E-05                                    | 20.98                |
| $\text{HCN} + \text{O} = \text{H} + \text{NCO}$                      | 5.45E-05                                    | 20.15                |
| $\text{HONO} + \text{OH} = \text{H}_2\text{O} + \text{NO}_2$         | -4.25E-05                                   | -15.69               |
| $\text{NCO} + \text{NO}_2 = \text{CO} + 2 \text{NO}$                 | -4.05E-05                                   | -14.98               |
| $\text{NH} + \text{NO} = \text{H} + \text{N}_2\text{O}$              | 3.90E-05                                    | 14.41                |
| $\text{HCN} + \text{OH} = \text{H} + \text{HOCN}$                    | 3.80E-05                                    | 14.05                |
| $\text{NNH} + \text{O} = \text{H} + \text{N}_2\text{O}$              | 3.70E-05                                    | 13.68                |

Next, the sensitivities of the temperature at the second grid point with respect to transport parameters were considered. Brown and Revzan [101] have observed large sensitivities with respect to Lennard-Jones collision diameter of various species followed by well depth. Dipole moment, polarizability and rotational relaxation collision number do not have significant sensitivity coefficients. Hence, the normalized sensitivity coefficients were calculated for collision diameters and well depths.

As shown in Table 4-11, the sensitivity coefficient is largest for the collision diameter of RDX and is larger than the corresponding sensitivity coefficient for the most sensitive reaction ( $\text{HNC} + \text{OH} = \text{H} + \text{HNCO}$ ) by a factor of 2.68. Sensitivity coefficients for H and  $\text{H}_2\text{O}$  are also larger by a factor of 1.58 and 1.25, respectively. Temperature at the second grid point above the surface is also relatively sensitive to the collision diameters of species present in relatively large concentrations near the surface, such as INT175 ( $\text{RDX}_{\text{-HONO}}$ ),  $\text{C}_3\text{N}_3\text{H}_3$  ( $\text{RDX}_{\text{-3HONO}}$ ), and decomposition products, i.e.,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HONO}$ , etc.

Temperature at the second grid point shows smaller sensitivity to well depth as compared to the collision diameter and reaction rate sensitivities. The results are shown in Table 4-12. List of the top 12 normalized temperature sensitivities for RDX at 1 atm for the second grid point with respect to Lennard-Jones well depth. Large sensitivity with respect to collision diameter  $\sigma$  is observed due to  $1/\sigma^2$  dependence of the transport properties. On the other hand, smaller sensitivity to well depth  $\varepsilon$  is expected because it is used indirectly in the calculations of collision integrals via scaling of the energy which does not have strong temperature dependence. Sensitivity coefficients at 1 atm presented above were also calculated for 10 atm. The ratio of collision diameter sensitivity vs. kinetic sensitivity, i.e.,  $S_T(\sigma_{\text{RDX}})/S_T(k_{\text{HNC}+\text{OH}=\text{H}+\text{HNCO}})$  increases from 2.68 to 3.65. Similarly, the ratio of well depth sensitivity to kinetic sensitivity, i.e.,  $S_T(\varepsilon_{\text{RDX}})/S_T(k_{\text{HNC}+\text{OH}=\text{H}+\text{HNCO}})$  increases from 0.62 to 0.78. This indicates that the importance of transport parameters increases as pressure increases.

Table 4-11. List of the top 15 normalized temperature sensitivities for RDX at 1 atm for the second grid point with respect to Lennard-Jones collision diameters

| Species                                      | Normalized sensitivity coefficient $S_T(\sigma)$ | Relative sensitivity | $S_T(\sigma)/S_T(k)^a$ |
|----------------------------------------------|--------------------------------------------------|----------------------|------------------------|
| RDX                                          | 7.54E-04                                         | 100.00               | 2.68                   |
| H                                            | -4.46E-04                                        | -59.09               | -1.58                  |
| H <sub>2</sub> O                             | -3.53E-04                                        | -46.76               | -1.25                  |
| N <sub>2</sub>                               | -2.43E-04                                        | -32.26               | -0.86                  |
| NO                                           | 2.18E-04                                         | 28.87                | 0.77                   |
| HONO                                         | 1.81E-04                                         | 24.04                | 0.64                   |
| CO                                           | -1.70E-04                                        | -22.51               | -0.60                  |
| NO <sub>2</sub>                              | 1.27E-04                                         | 16.77                | 0.45                   |
| C <sub>3</sub> N <sub>3</sub> H <sub>3</sub> | 1.23E-04                                         | 16.29                | 0.44                   |
| OH                                           | -1.03E-04                                        | -13.64               | -0.37                  |
| H <sub>2</sub>                               | 6.35E-05                                         | 8.42                 | 0.23                   |
| INT175                                       | 6.34E-05                                         | 8.40                 | 0.23                   |
| CO <sub>2</sub>                              | -5.00E-05                                        | -6.62                | -0.18                  |
| O                                            | -3.12E-05                                        | -4.14                | -0.11                  |
| N <sub>2</sub> O                             | 2.31E-05                                         | 3.06                 | 0.08                   |

$S_T(k)^a$  = Normalized sensitivity coefficient for HNC + OH = H + HNCO

Table 4-12. List of the top 12 normalized temperature sensitivities for RDX at 1 atm for the second grid point with respect to Lennard-Jones well depth

| Species                                      | Normalized sensitivity coefficient $S_T(\epsilon)$ | Relative sensitivity | $S_T(\epsilon)/S_T(k)^a$ |
|----------------------------------------------|----------------------------------------------------|----------------------|--------------------------|
| RDX                                          | 1.74E-04                                           | 100.00               | 0.62                     |
| H <sub>2</sub> O                             | -6.97E-05                                          | -39.98               | -0.25                    |
| H                                            | -4.76E-05                                          | -27.32               | -0.17                    |
| NO                                           | 4.55E-05                                           | 26.11                | 0.16                     |
| HONO                                         | 4.55E-05                                           | 26.09                | 0.16                     |
| C <sub>3</sub> N <sub>3</sub> H <sub>3</sub> | 4.48E-05                                           | 25.73                | 0.16                     |
| NO <sub>2</sub>                              | 1.60E-05                                           | 9.16                 | 0.06                     |
| OH                                           | -1.53E-05                                          | -8.76                | -0.05                    |
| INT175                                       | 1.45E-05                                           | 8.32                 | 0.05                     |
| N <sub>2</sub>                               | -1.22E-05                                          | -7.00                | -0.04                    |
| H <sub>2</sub>                               | 1.12E-05                                           | 6.40                 | 0.04                     |
| CO                                           | -6.40E-06                                          | -3.67                | -0.02                    |

$S_T(k)^a$  = Normalized sensitivity coefficient for HNC + OH = H + HNCO

Transport properties of only H and H<sub>2</sub> were often considered to be important in flame modeling, however, our results indicate that the transport properties of other species are also important, and their sensitivities are more significant than reaction rate sensitivities. It is to be noted that significant as used here implies influential in determining the value of a dependent variable. Uncertainties in the parameters were not considered in the present analysis but we note that the uncertainty in rate constants by a factor of 3 to 4 is not uncommon, and that uncertainties in collision diameters tend to be on the order of a small percentage. A parameter with large sensitivity and uncertainty would have a larger impact on model fidelity than one with large sensitivity and small uncertainty. However, our objective is to include the transport parameters in a more rigorous way as opposed to estimating and using a common value for all the species for which

data are not available. Hence, transport parameters must be considered more rigorously in addition to rate constant parameters while developing or validating reaction mechanisms for energetic materials.

#### 4.5 Summary and Conclusions

Intermolecular potential energy surfaces were developed for the interactions of various organic energetic molecules with four bath gases – He, Ne, Ar and N<sub>2</sub>. High-level ab initio calculations, i.e., counterpoise corrected QCISD(T) with complete basis set (CBS) extrapolations based on aug-cc-pVDZ and aug-cc-pVTZ basis sets, were used to validate results obtained using computationally more efficient MP2/CBS method and  $\omega$ B97X-D/CBS method. MP2/CBS method is in close agreement with QCISD(T)/CBS method and performs significantly better than the DFT functional  $\omega$ B97X-D, which is specifically designed for dispersion interactions. Potential energy surfaces were then calculated for a training set of six molecules containing two nitramines (CH<sub>2</sub>NNO<sub>2</sub> and CH<sub>3</sub>NHNO<sub>2</sub>), two nitrate esters (CH<sub>3</sub>ONO<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>ONO<sub>2</sub>) and two nitroalkanes (CH<sub>3</sub>NO<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>NO<sub>2</sub>). An analytical pairwise intermolecular potential (modified Buckingham potential termed as exp/6) was parametrized using the ab initio data acquired at MP2/CBS level of theory. By sampling many spherically uniform orientations for the interaction of target molecule with bath gas within the one-dimensional minimization approach, Lennard-Jones parameters were calculated for training set as well as a separate test set containing nine organic energetic molecules. Lennard-Jones collision rates for molecules in test set, calculated using exp/6 potential, are within ~20% of those obtained via MP2/aug-cc-pVDZ calculations. Instead of choosing a preferred bath gas to obtain pure-gas Lennard-Jones parameters, least-square optimization was used to reproduce binary Lennard-Jones parameters for all four bath gases. Three combining rules were considered, and the sixth-power mean rules proposed by Waldman and Hagler are recommended for obtaining pure-gas Lennard-Jones parameters from calculated binary Lennard-Jones parameters. Calculated gas-phase viscosity of nitromethane was found to be in excellent agreement with experimental results with mean unsigned error of less than 1%. Thermal conductivities and binary diffusion coefficients of nitromethane were also calculated and found to be in reasonable agreement with the experimental data.

The usefulness of the analytical potential parametrized here is demonstrated by developing CHEMKIN compatible transport properties database for combustion modeling of nitramines. A comparative sensitivity analysis was also performed and the temperature gradient controlling the burn-rate of RDX was found to be more sensitive to the transport parameters than to the reaction rate parameters. Hence, it is recommended to consider transport parameters in conjunction with chemical kinetics while developing or validating reaction mechanisms. Failure to consider sensitivity to transport parameters could result in errors being compensated for by adjusting chemical rate parameters. The sensitivity to transport properties will become even more influential when combustion is not premixed. The methodology presented here can be used to develop transport parameters for large number of species present in the combustion mechanisms. The parameters for the most sensitive species can then be updated via accurate ab initio methods.

## CHAPTER 5

### MULTI-PHASE COMBUSTION MODELING OF HMX

#### 5.1 Introduction

Quantifying the burn-rate of a solid propellant under various operating conditions is of fundamental importance for the safe and reliable design of propulsion systems which use solid propellants. Hence, this macroscopic parameter of solid propellant combustion has been extensively measured by various investigators. Atwood et al. [103,104] measured the burn-rate of solid propellant as a function of pressure and initial temperature and determined the temperature sensitivity of burn-rate. Zenin and co-workers [105] have extensively utilized the microthermocouple technique over the years and measured various aspects of burning wave structures of HMX and RDX, such as burn rate, burning-surface temperature, heat release in solid, heat feedback from gas to solid, sensitivities of the burning rate etc.

A review of very early models that do not account for chemical kinetics and solve only the mass and energy equation is given by Beckstead et al. [106]. Combustion models based on global kinetics were also reviewed and are not repeated here. Detailed chemical kinetics mechanism in the gas phase for RDX was first reported by Ermolin [107] based on species concentration measurements at the propellant surface. Based on a quantum mechanical approach [108], Melius developed a detailed chemical kinetics mechanism for RDX ignition and combustion, consisting of 38 species and 158 reactions [109]. Thermal decomposition steps of RDX were added to the hydrocarbon/air flame model of Miller and Bowman [110], however, the condensed phase was represented by a single decomposition reaction. Burn-rate and surface temperature predictions were reasonable at 1 and 20 atm.

The secondary reactions in the model were further modified by Yetter et al. [55], where a hierarchical approach was employed for specific sub-models of increasing complexity using data from kinetics experiments. The mechanism consists of 38 species and 178 reactions, which was later expanded to 48 species and 228 reactions by Prasad et al. [72,73]. Chakraborty et al. performed quantum mechanics calculations on larger molecular and radical intermediates of RDX and HMX decomposition and updated the nitramine kinetics mechanism to 89 species and 462 reactions [33,68,111]. The gas-phase mechanism for combustion of nitramines was further updated based on quantum mechanics calculations.

The combustion model utilizing these detailed chemical kinetics mechanisms in the gas phase can be classified into three categories – 1) two-layer semi-empirical model (2) three-layer model with homogeneous liquid phase, and (3) three-layer model with two-phase foam region. The models are summarized in Table 5-1.

Table 5-1. Different types of monopropellant combustion models

| Model                                     | Researchers                      | Chemical kinetics mechanism |           |
|-------------------------------------------|----------------------------------|-----------------------------|-----------|
|                                           |                                  | Condensed phase             | Gas phase |
| Two-layer semi-empirical                  | Miller and Anderson [74]         | None                        | Detailed  |
| Three-layer with homogeneous liquid phase | Prasad et al. [72,73]            | Global                      | Detailed  |
| Three-layer with two-phase foam region    | Liau and Yang [69]               | Global                      | Detailed  |
|                                           | Davidson and Beckstead [112,113] |                             |           |
| Three-layer with homogeneous liquid phase | Present work                     | Detailed                    | Detailed  |

In the two-layer semi-empirical model, RDX is assumed to completely sublime from solid layer into the gas phase at the surface of the burning propellant and the liquid layer is not modeled. A detailed kinetic mechanism is used in the gas phase. Miller and Ander [74] used the this semi-empirical model to compute the burn-rate of RDX monopropellant by employing a pyrolysis law derived from the experimental data of Zenin [114]. Using the same model, Anderson and Conner [75] compared the two gas-phase combustion mechanisms of RDX. Prasad et al. developed the three-layer model with homogeneous liquid phase and presented the results for laser-assisted and self-deflagration of RDX and HMX monopropellants [72,73]. Evaporation and condensation rate laws were not used and the experimentally measured value of

the surface temperature was used for closure of the problem. A more complicated model for the condensed phase to account for the evaporation, bubble formation, gas-phase reactions in bubbles was adopted by Liao and Yang [69] and Davidson and Beckstead [112,113]. A two-phase foam layer model was used based on a spatial averaging technique.

These models are able to predict burning characteristics of nitramine monopropellants reasonably well. However, the decomposition of RDX and HMX in the homogeneous liquid phase or the two-phase foam layer is still represented by three-step global reaction of Brill [115] and Thynell et al. [36]. Species evolving from condensed phase determine near-surface gas-phase reactions, which in turn dictate gas-phase heat feedback and hence the burn rate. Therefore, it is important to describe condensed-phase chemistry in more detail.

The objectives of this chapter are to 1) describe the multiphase combustion model in detail which can incorporate detailed chemical kinetics mechanism in the condensed phase, 2) discuss the model inputs and relevant calculations, and 3) demonstrate that the model performs reasonably well in predicting and explaining the experimental data. The combustion model and kinetic mechanisms developed for this monopropellant can then be extended to other propellant formulations or burn-rate modifiers for predictive calculations.

## 5.2 Model description and input parameters

The detailed governing equations, kinetic mechanisms in the liquid and the gas phase along with all the input parameters is given in [116].

## 5.3 Results and Discussions

Using the computational model in conjunction with the inputs described above, the burn rate,  $\delta$ -HMX region and melt layer thickness, species and temperature profiles in liquid-phase as well as gas phase regions are obtained. Results are presented and discussed in this section with the emphasis on the effect of including detailed reaction mechanism in liquid phase.

The burn rate of 0.035 cm/s, obtained from the model at 1 atm, is in excellent agreement with the experimental value of 0.035 cm/s [114]. The computed values for the thickness of the  $\delta$ -HMX region and the melt layer are 178  $\mu\text{m}$  and 69  $\mu\text{m}$ , respectively. The experimental value for melt layer thickness at 1 atm is 70  $\mu\text{m}$  [114]. The sensitivity of the burn rate  $\sigma_p$  to the initial temperature  $T_i$  at a given pressure, defined by Eq. (5-1), was found to be  $6.5 \times 10^{-4} \text{ K}^{-1}$ . Similar value ( $6.1 \times 10^{-4} \text{ K}^{-1}$ ) was obtained in a computational study by Prasad et al. [73].

$$\sigma_p = \left[ \frac{\partial \ln(r_b)}{\partial T_i} \right]_p \quad (5-1)$$

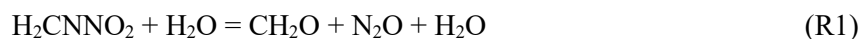
The decomposition of HMX in the liquid melt layer is described by the detailed reaction mechanism. At a pressure of 1 atm, the mass fraction of HMX at the liquid-gas interface is 75% which means that 25% of HMX decomposes in the liquid phase. To understand the effect of the liquid-phase decomposition on combustion wave parameters of HMX monopropellant, the calculations were also performed by suppressing the liquid-phase decomposition. For 100% HMX evaporating at the liquid-gas interface, the predicted value for the burn-rate is 0.028 cm/s. Hence, the liquid-phase decomposition affects the burn rate by dictating heat release in the liquid melt layer as well the species evolving into the gas phase which in turn affects the heat feedback from the gas to the liquid. Table 5-2 summarizes the main combustion wave parameters for self-deflagrating HMX monopropellant at 1 atm pressure with and without liquid-phase decomposition.

The variation of the burn-rate with pressure is shown in Figure 5-1. The gas phase combustion mechanism developed by Yetter et al. [55] and further refined by Prasad et al. [73] overpredicts the burn-rate at higher pressures when used in conjunction with our combustion model and the thermophysical properties in the liquid and the solid phase. The pressure dependent burn-rate values obtained using our combustion model and the gas-phase mechanism updated by Chakraborty et al. at Caltech are also shown in Figure 5-1. This mechanism also overpredicts the burn-rate at higher pressures. Upon closer examination of these two mechanisms, it was revealed that the bimolecular reaction (R1) leads to higher heat release at

higher pressures. However, this reaction does not occur in a single step with the rate parameters used in previous gas-phase combustion mechanism. Based on quantum mechanics calculations two elementary reaction steps were added for this reaction in the updated gas phase mechanism.

Table 5-2. Combustion wave parameters for self-deflagrating HMX monopropellant at 1 atm with and without liquid-phase decomposition effects

| Parameter                                              | Liquid-phase decomposition | Present study        | Literature values [Ref.]  |
|--------------------------------------------------------|----------------------------|----------------------|---------------------------|
| Burn-rate<br>(cm/s)                                    | Included                   | 0.035                | 0.035 [114]               |
|                                                        | Suppressed                 | 0.028                |                           |
| Thickness of $\delta$ -HMX region<br>( $\mu\text{m}$ ) | Included                   | 178                  | 195 [73]                  |
|                                                        | Suppressed                 | 220                  |                           |
| Thickness of melt layer<br>( $\mu\text{m}$ )           | Included                   | 69                   | 70 [114]                  |
|                                                        | Suppressed                 | 73                   |                           |
| Temperature sensitivity<br>(1/K)                       | Included                   | $6.5 \times 10^{-4}$ | $6.1 \times 10^{-4}$ [73] |
|                                                        | Suppressed                 | $2.1 \times 10^{-4}$ |                           |
| Heat conduction from gas phase<br>(K/cm)               | Included                   | $1.10 \times 10^5$   | $1.51 \times 10^5$ [73]   |
|                                                        | Suppressed                 | $1.67 \times 10^5$   |                           |



Moreover, the Caltech mechanism used B3LYP/6-31G(d) level of theory for the calculation of rate constants for gas phase decomposition reactions of HMX, which severely underpredicts the reaction barrier heights and hence overpredicts the rate constants. All the pathways in the Caltech mechanism were re-calculated using the M06-2X/6-311++G(d,p) level of theory. Additional pathways were also discovered and added to the gas phase decomposition and combustion mechanism of HMX. The computational results obtained using the updated gas-phase mechanism in conjunction with the liquid-phase mechanism are in reasonable agreement with the experimental data [103,114]. The model predictions for the initial temperature of 223 K and 373 K are also in reasonable agreement with the experimental data as shown in Figure 5-2 and Figure 5-3 respectively.

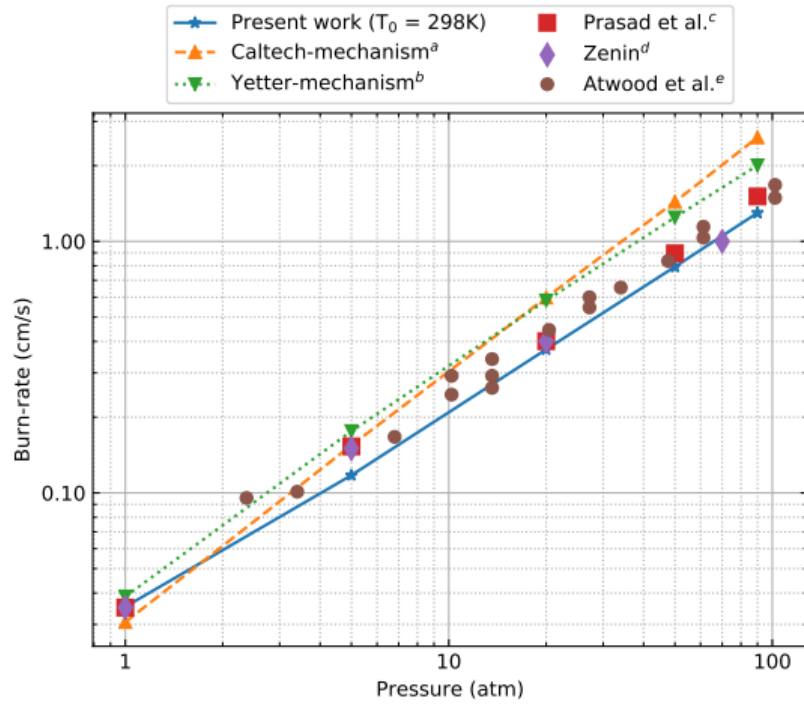


Figure 5-1. Variation of the burn-rate with pressure for self-deflagrating HMX. The initial temperature of the unburnt propellant is 298 K. <sup>a</sup>:Ref. [68], <sup>b</sup>:Ref. [73], <sup>c</sup>:Ref. [73], <sup>d</sup>:Ref. [114], <sup>e</sup>:Ref. [103].

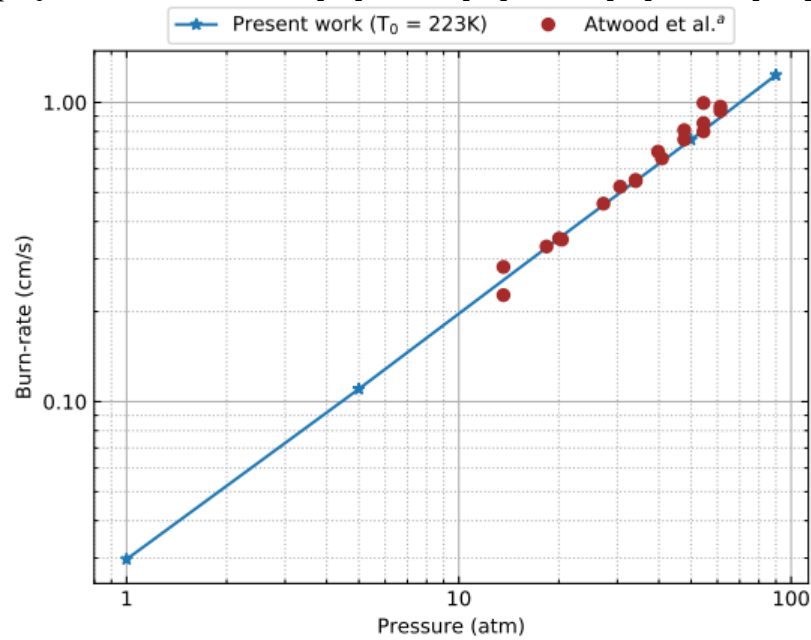


Figure 5-2. Variation of the burn-rate with pressure for self-deflagrating HMX. The initial temperature of the unburnt propellant is 223 K. <sup>a</sup>:Ref. [103].

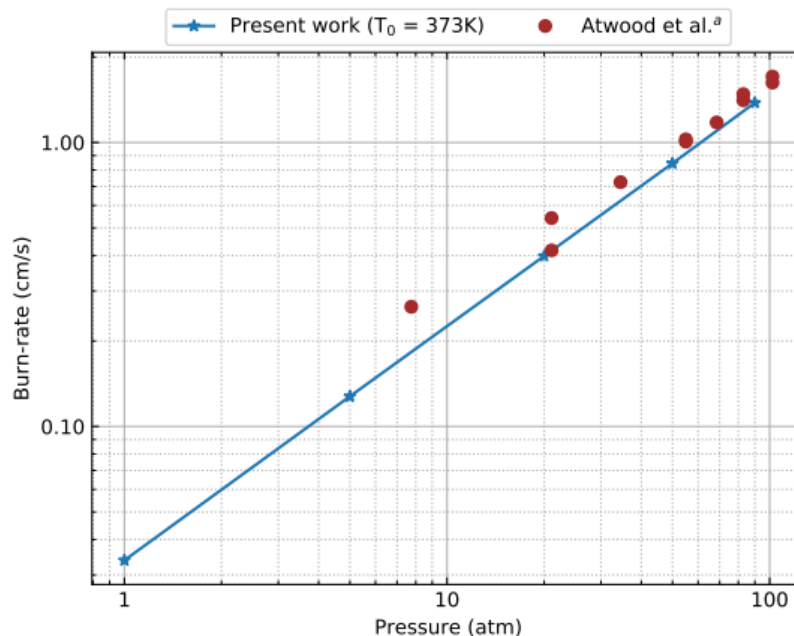


Figure 5-3. Variation of the burn-rate with pressure for self-deflagrating HMX. The initial temperature of the unburnt propellant is 373 K. <sup>a</sup>:Ref. [103].

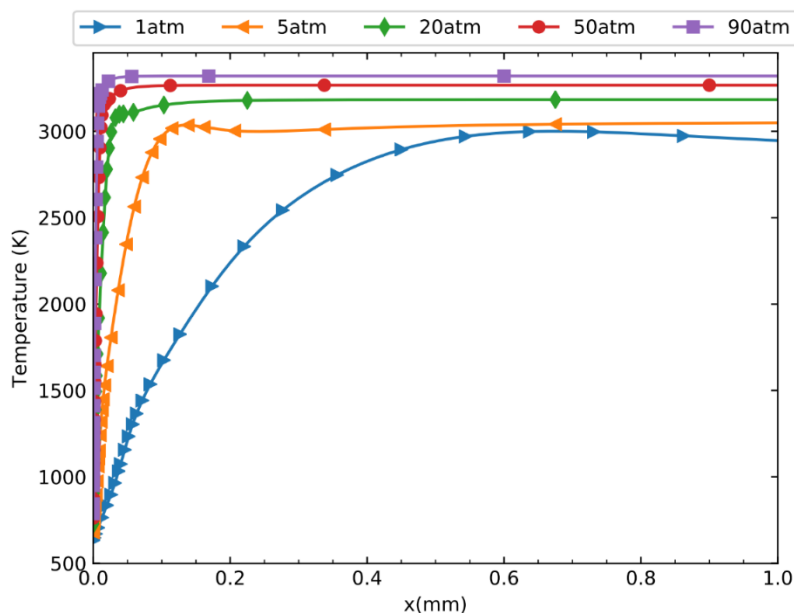


Figure 5-4. Temperature profiles in the gas phase during self-deflagration of HMX monopropellant at various pressures.

During self-deflagration of HMX monopropellant, the primary and the secondary flames superimpose on each other and a single flame is produced. The temperature profiles in the gas phase, shown in Figure 5-4, indicate that the two-zone flame structure observed in various experimental studies during laser-assisted deflagration is not present. As the pressure is increased, temperature profiles become steeper near the surface. This increases the heat feedback from the gas phase to the liquid phase and thus explains the higher burning rate at higher pressures. The maximum flame temperature also increases with the pressure.

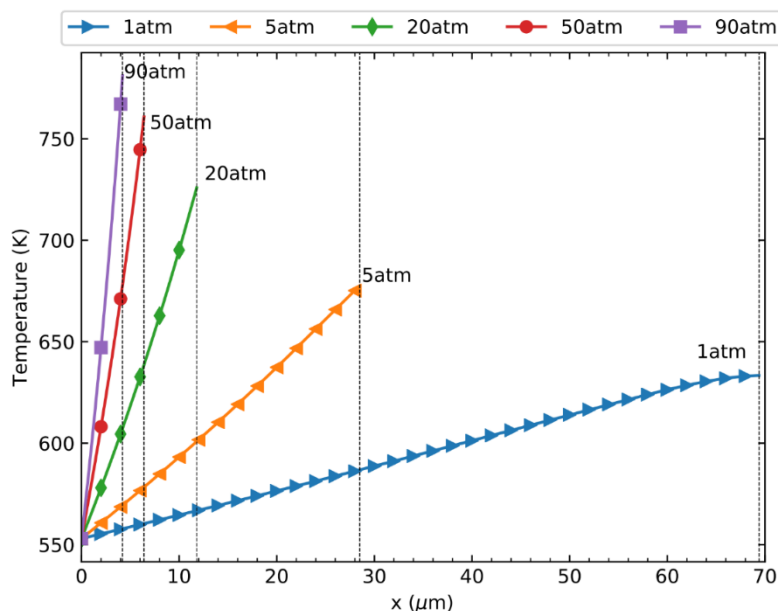


Figure 5-5. Temperature profiles in the liquid melt layer during self-deflagration of HMX monopropellant at various pressures.

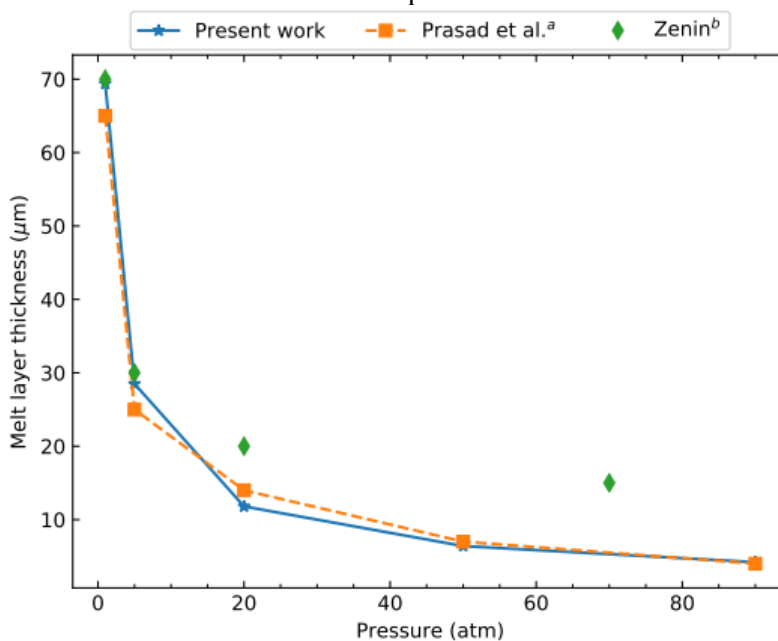


Figure 5-6. Thickness of the melt layer with pressure during self-deflagration of HMX. <sup>a</sup>:Ref. [73], <sup>b</sup>:Ref. [114]

The temperature profiles in the liquid melt layer are illustrated in Figure 5-5 at different pressures considered in this study. Since the thickness of the melt layer is very small, a linear temperature profile is obtained. On increasing the pressure, the thickness of the melt layer decreases as shown in Figure 5-6 but the liquid-gas interface temperature increases due to higher heat feedback from the gas phase. In addition to burn-rate predictions, a more rigorous test of the combustion model should include the gas phase flame structures. Figure 5-7 illustrates the decomposition chemistry of HMX in the gas phase near the surface at 1 atm obtained using the multiphase combustion model. Near the propellant burning surface, HMX decomposes and forms HCN and NO among other products. The concentration of HMX,  $\text{H}_2\text{CNNO}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  decreases whereas the concentration of HCN, NO, CO,  $\text{CO}_2$ , and  $\text{N}_2$  increases. The product

species from the decomposition of HMX in the gas phase as well as the liquid phase then react to form the final products such as  $N_2$ , CO,  $CO_2$  and  $H_2O$  as shown in Figure 5-8. Although the temperature profile in the gas phase does not show the two-stage combustion due to overlap of primary and secondary flames, the species profiles do reveal the characteristic two-stage combustion process.

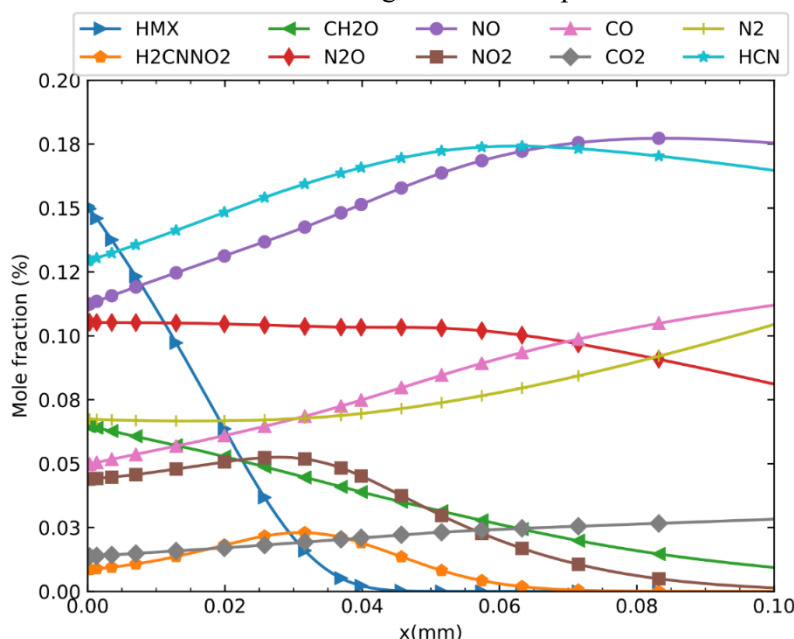


Figure 5-7. HMX decomposition in the gas phase near the surface at a pressure of 1 atm.

Species mass fraction profiles in the melt layer, shown in Figure 5-9, were obtained using the detailed liquid-phase decomposition mechanism. The species mole fractions at the liquid-gas interface determines the input conditions for the gas-phase premixed flame calculations. At 1 atm pressure, 25% HMX decomposes in the liquid phase and forms various species including, among others,  $N_2O$ ,  $CH_2O$ ,  $N_2$ , HCN,  $NO_2$ , NO,  $H_2O$ ,  $ONNO_2$ , CO, and  $CO_2$ . Larger molecular weight species produced from the liquid-phase decomposition of HMX include mono-nitroso analogue ONTNTA, as well as  $CH_2NNO_2$ ,  $CH_2NH$ , and  $HCOOH$ .  $N_2$  has been detected as a product from condensed-phase decomposition of HMX in various experimental studies [6,117]. The global three-step reaction mechanism used in previous combustion models was not able to explain the formation of these species evolving from the melt layer into the gas phase near the burning surface. The detailed reaction mechanism predicts the formation of  $N_2$  and other species in the melt layer.

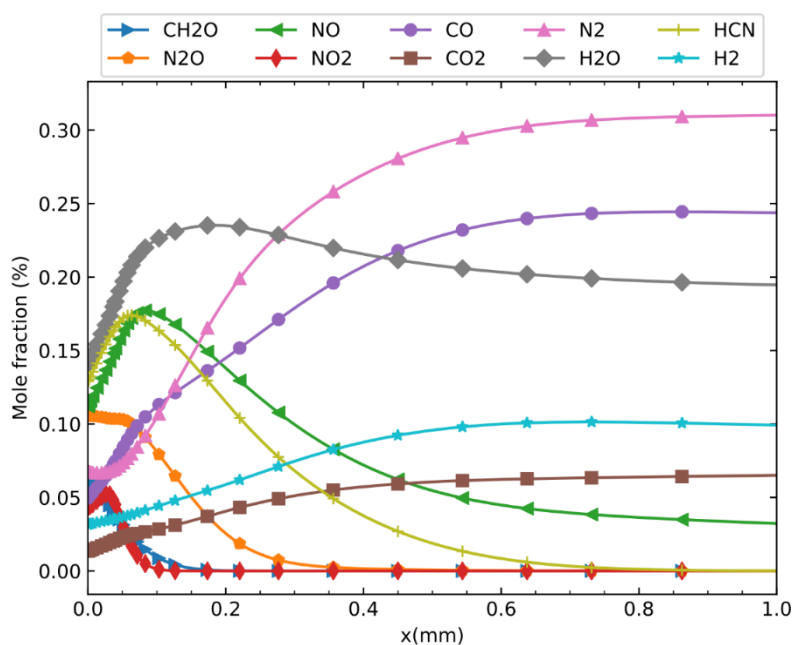


Figure 5-8. HMX flame structure in the gas phase at a pressure of 1 atm.

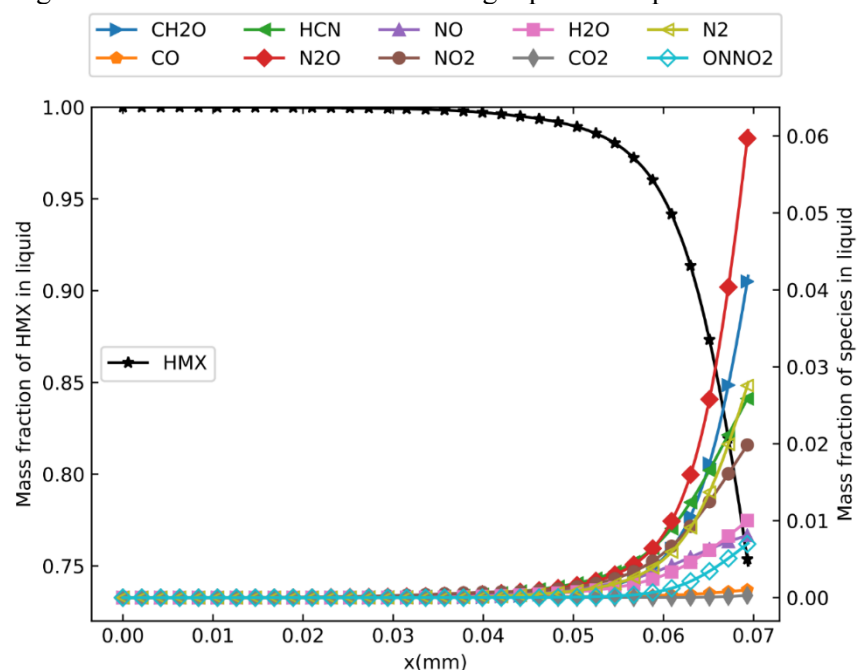


Figure 5-9. Species mass fraction profiles in the melt layer for self-deflagration of HMX monopropellant at 1 atm.  $x = 0$  represents the solid-liquid interface.

## 5.4 Conclusions

Self-deflagration of HMX monopropellant was investigated using a one-dimensional steady-state multiphase combustion model. A detailed reaction mechanism in the liquid phase, developed using quantum mechanics calculations, was used as opposed to a global three-step mechanism used till date in previous combustion models.  $\beta$ -HMX to  $\delta$ -HMX phase transformation was also modeled and the thickness of the  $\delta$ -HMX region was calculated in addition to the thickness of the melt layer. Thermophysical properties required as inputs to the model were obtained using quantum mechanics calculations and molecular dynamics simulations. The predicted burn-rate and the melt-layer thickness are in excellent agreement with

the experimental values. The importance of including the liquid phase decomposition in combustion modeling is also emphasized.

## CHAPTER 6

### A MULTI-PHASE COMBUSTION MODEL FOR RDX WITH BUBBLE FORMATION AND DETAILED CHEMICAL KINETICS

#### 6.1 Introduction

In this work, the combustion model developed by Khichar et al. [118] for self-deflagration of RDX was further improved by modeling the experimentally observed bubble formation phenomenon in the melt layer. In a previous combustion model by Liao and Yang [69], the bubble formation phenomenon was considered but the interfacial mass transfer was excessively simplified by assuming that all decomposition products of RDX in the melt layer were instantly collected in bubbles. In the current model, the bubble growth due to interfacial mass transfer was modeled by considering the species vapor pressure, species size, temperature, solution viscosity, super-saturation ratio, bubble size, surface tension, and pressure. Similar to Khichar et al. [118], detailed reactions mechanisms were used in both liquid and gas phases. The reaction mechanisms provided by Khichar et al. [34] and Chakraborty et al. [50,68] were used in the liquid and gas phase, respectively. Efforts were also made to update the gas-phase mechanism of RDX. All the liquid-phase decomposition pathways of RDX were reinvestigated in the gas phase and added to the gas-phase mechanism. Also, reactions that convert the liquid-phase intermediate decomposition products of RDX to the gas-phase species were investigated. The model is used to investigate the importance of liquid-phase decomposition at high pressures relevant to rocket motors. The developed model was used for calculation of burn rate, melt layer thickness, temperature profile, heat feedback from gas-to-liquid phase, overall heat release in the melt layer, and species evolution profiles in the gas and liquid-phase region for a pressure range of 1–90 atm. Comparison of obtained results with experimental data and earlier combustion model results showed good agreement.

#### 6.2 Model description

After the initial ignition process, self-deflagration of a monopropellant under constant pressure condition can be modeled as a one-dimensional, steady-state process in the frame of reference of regressing propellant surface. The entire combustion-wave structure can be segmented into three distinguishable regions: 1) solid phase, 2) melt layer, and 3) gas phase. All the three regions are independently modeled with suitable assumptions as described below.

##### 6.2.1 Solid-phase region

For RDX, it is widely accepted that its decomposition rate below the melting point is very low. Hence, no chemical reactions were assumed to occur in the solid-phase region.

##### 6.2.2 Liquid-phase region

During RDX combustion, a thin melt layer is observed experimentally. In this layer, multiple complex physicochemical processes occur simultaneously, such as liquid-phase decomposition, bubble formation and growth, gas-phase decomposition inside bubbles, and energy diffusion. To account for the decomposition, the reaction mechanisms provided by Khichar et al. [34] and Chakraborty et al. [50,68] were used in the liquid and gas phase, respectively. Similar to Khichar et al. [118], HNCO production reactions in the liquid phase were added. New reactions were added to the gas-phase mechanism and are described in section 6.2.3. Similar to the combustion model by Liao and Yang [69], uniform bubble nucleation was assumed across the propellant surface with a fractional area  $\phi$ . For bubble growth, both kinetic and diffusive rates of interfacial species transport across the bubble surface were considered. The kinetic rate was calculated using the gas-kinetics theory. The derivation for the net species evaporation rate for RDX is provided by Liao and Yang [69] and is not repeated here. Their model was extended for all the species which evaporates from the liquid phase to enter bubbles. The required vapor pressure data were obtained using Henry's law constant data by Sander [119]. The diffusive rate of species transport was derived using the steady-state diffusive bubble growth theory by Kuchma et al. [120] for super-saturated solutions. Under the ideal-gas assumption for bubbles, interfacial diffusive mass flow rate per unit volume for species  $i$  ( $\dot{m}_{\text{diff},i}$ ) is given by

$$\dot{m}_{\text{diff},i} = \rho_g \left( \frac{[k_B T D_{\text{bubble}}]^2}{6\eta R_i} \right) \left[ n_0 - n_\infty - \frac{4 \sigma n_\infty}{P_0 D_{\text{bubble}}} \right] \left[ \frac{3}{1.5 P_0 D_{\text{bubble}} + 4\sigma} \right] n_{\text{bub}} \quad (6-1)$$

Here,  $\rho_g$  is the gas density inside bubbles,  $k_B$  is the Boltzmann constant,  $D_{\text{bubble}}$  is the bubble diameter,  $\eta$  is the solution viscosity,  $R_i$  is the radius of species  $i$ ,  $n_0$  is the number density of species  $i$ ,  $n_\infty$  is the number density of species  $i$  for the saturated solution,  $P_0$  is the solution pressure,  $\sigma$  is the bubble surface tension, and  $n_{\text{bub}}$  is the bubble density per unit volume.

Similar to Kumbhakarna et al. [121], we assume that bubble velocity is equal to the bulk velocity in the liquid phase. This assumption is justified because of the high viscosity of the mono-propellant and small melt layer thickness. Under this assumption, the governing equations for species mass fractions in liquid ( $Y_{l,i}$ ) and bubbles ( $Y_{g,i}$ ), bulk velocity ( $u_f$ ), the volume fraction of bubbles ( $\phi$ ), and temperature ( $T$ ) in a normalized coordinate system ( $\bar{x}$ ) are given by,

$$\frac{dY_{l,i}}{d\bar{x}} = \frac{(l_s + l_m)}{(1 - \phi)\rho_l u_f} \left[ \dot{\omega}_{l,i}''' - Y_{l,i} \sum_{j=1}^{N_l} \dot{\omega}_{l,j}''' \right], i = 1, \dots, N_l \quad (6-2)$$

$$\frac{dY_{g,i}}{d\bar{x}} = \frac{(l_s + l_m)}{\phi \rho_g u_f} \left[ \dot{\omega}_{g,i}''' - Y_{g,i} \sum_{j=1}^{N_g} \dot{\omega}_{g,j}''' \right], i = 1, \dots, N_g \quad (6-3)$$

$$\frac{du_f}{d\bar{x}} = (l_s + l_m) \left[ \sum_{j=1}^{N_l} \frac{\dot{\omega}_{l,j}'''}{\rho_{l,j}} + \frac{\bar{W}_g}{\rho_g} \sum_{j=1}^{N_g} \frac{\dot{\omega}_{g,j}'''}{W_j} \right] + \frac{\phi}{T} u_f \frac{dT}{d\bar{x}} \quad (6-4)$$

$$\frac{d\phi}{d\bar{x}} = \frac{(1 - \phi)}{u_f} \frac{du_f}{d\bar{x}} - \frac{(l_s + l_m)}{u_f} \sum_{j=1}^{N_l} \frac{\dot{\omega}_{l,j}'''}{\rho_{l,j}} \quad (6-5)$$

$$\begin{aligned} & \left( \sum_{i=1}^{N_l} \rho_l (1 - \phi) u_f Y_{l,i} C_{p,l,i} + \sum_{i=1}^{N_g} \rho_g \phi u_f Y_{g,i} C_{p,g,i} \right) (l_s + l_m) \frac{dT}{d\bar{x}} \\ &= \frac{d}{d\bar{x}} \left( \lambda_f \frac{dT}{d\bar{x}} \right) - (l_s + l_m)^2 \left[ \sum_{i=1}^{N_l} \dot{\omega}_{l,i}''' h_{l,i} + \sum_{i=1}^{N_g} \dot{\omega}_{g,i}''' h_{g,i} \right] \end{aligned} \quad (6-6)$$

Here,  $l_s$  and  $l_m$  are the domain size of solid region and melt layer thickness, respectively. A large  $l_s$  is essential to accurately solve the system of governing equations. The solution can be checked by confirming the zero-temperature gradient at the far boundary of the solid phase. Melt layer thickness is defined using the temperature profile and melting point of RDX.  $\rho_l$  and  $\rho_g$  are weighted average densities of liquid region and bubbles, respectively.  $N_l$  and  $N_g$  are number of species in liquid region and bubbles, respectively. The weighted average molecular weight of bubbles is represented by  $\bar{W}_g$ .  $C_{p,l,i}$  and  $C_{p,g,i}$  are specific heat of species  $i$  in liquid region and bubbles, respectively. The weighted average thermal conductivity of the melt layer (liquid + bubbles) is represented by  $\lambda_f$ .  $h_{l,i}$  and  $h_{g,i}$  are enthalpy of species  $i$  in liquid region and bubbles, respectively.  $\dot{\omega}_{l,i}'''$  and  $\dot{\omega}_{g,i}'''$  are the net mass-based production rate of species  $i$  per unit volume in liquid region and bubbles, respectively. The net species production rate is governed by the rate of chemical reactions and the evaporation phenomenon. Species production due to chemical reactions is modeled as described by Khichar et al. [34]. Equation (6-1) was used along with the kinetic rate of evaporation provided by Liao and Yang [69]. In a recent study by Khichar et al. [122], the evaporation rate was experimentally determined during the thermal decomposition of RDX. The experimental evaporation rate was used to limit the net evaporation rate in the model.

### 6.2.3 Gas-phase region

The gas-phase region was solved using the open-source chemical kinetics software package CANTERA [102] in the burner-stabilized mode. The gas-phase reaction mechanism by Chakraborty et al. [50,68] was used with some refinement to find the solution of mass and energy conservation equations. The N-NO<sub>2</sub> homolytic cleavage pathway of RDX and H<sub>2</sub>CNNO<sub>2</sub> decomposition reactions were updated using

a recently updated gas-phase reaction mechanism of HMX by Patidar [123]. Four liquid-phase decomposition pathways missing from the gas-phase mechanism were also added – 1) HONO elimination followed by HONO addition in a different orientation and ring-opening pathway, 2) HONO elimination followed by ring-opening pathway, 3) Nitroso pathway and 4) hydrogen abstraction pathway. Note that ONNO<sub>2</sub> addition pathway, which is present in the liquid phase, is not important for the gas phase mechanism because ONNO<sub>2</sub> readily separates to NO and NO<sub>2</sub> in the gas phase. Additionally, decomposition reactions for all the liquid-phase species entering into the gas phase were investigated and added to the mechanism. Quantum chemical calculations were performed at the B3LYP/6-311++G(d,p) level to determine the rate kinetics parameters for all the new gas-phase elementary reactions. The updated gas-phase mechanism for RDX has 125 species and 496 reactions.

#### 6.2.4 Numerical solution of the governing equations

To close the system of governing equations, mass and energy conservation constraints were imposed at both solid-liquid and liquid-gas interfaces. Also, similar to the model by Anderson and Conner [75] and Kumbhakarna et al. [121], pyrolysis law [74] obtained from the experimental data of Zenin [124] was used to correlate mass flux with the propellant surface temperature. Thermodynamic properties for the liquid-phase species, like enthalpy and constant pressure heat capacity, required for the combustion model, were calculated using equilibrium molecular dynamics calculations at various temperatures and fitted to NASA polynomials. Since only a small amount of RDX decompose in the melt layer, the thermal conductivity of the melt layer was approximated by the thermal conductivity of RDX, which was obtained using non-equilibrium molecular dynamics calculations. In gas-phase, the data required for thermodynamic and transport properties calculation was obtained from the work of Chakraborty et al. [50,68].

For numerically solving the system of conservation equations, the burner-flame module of the Cantera software [102] was used for the gas phase, whereas DVODE routines [47] and tridiagonal matrix solver were used for the condensed phase (solid + melt layer), respectively. An iterative solution technique similar to Kumbhakarna et al. [121] and Liao and Yang [69] was used. Both solid- and liquid-phase regions (condensed phase) were solved simultaneously based on assumed heat feedback from the gas phase. In the condensed phase, the species conservation equations were solved first using an assumed temperature profile. The obtained species profile in the condensed phase was used to update the temperature profile and melt layer thickness. The updated temperature profile was then used to again solve the species equations. This process was repeated until a converged solution was obtained. The condensed-phase solution provides input fuel composition, mass-flow rate, and temperature to the gas-phase solver (Cantera). The updated heat feedback from the gas-phase solver is then used in the condensed-phase solver. This process is repeated until convergence is achieved.

### 6.3 Results and discussion

The multi-phase combustion model was used to evaluate the combustion wave-structure of RDX in the pressure range of 1–90 atm. Burn rate, melt layer thickness, temperature profile, heat feedback from gas-to-liquid phase, overall heat release in the melt layer, and species evolution profiles in the gas and liquid-phase region were calculated. Results are presented and discussed in this section with the emphasis on the effect of bubble formation and including detailed liquid- and gas-phase mechanisms in the melt layer. In particular, the model is used to investigate the importance of liquid-phase decomposition at high pressures relevant to rocket motors.

The burn-rate variation with pressure for an initial (unburnt) propellant temperature of 293 K is shown in Figure 6-1. The burn-rate increases with an increase in pressure due to the fast gas-phase exothermic reactions pressed near the propellant burn surface which increases the heat feedback to the condensed phase. The early increase in temperature in the gas-phase at higher pressures can be observed in Figure 6-2. The model predictions for burn-rate are in reasonable agreement with the experimental data of Zenin [124], Glaskova [125], Atwood et al. [126], Zimmer-Galler [127], Homan et al. [128], Ulas et al. [129] and combustion model data of Kumbhakarna et al. [121], Miller and Anderson [74], Prasad et al. [72], and Liao and Yang [69]. The calculated burn-rate values are slightly higher. This is partially due to the level of theory (B3LYP/6-311++G(d,p)) we used to update the gas-phase mechanism or the level of

theory (B3LYP/6-31G(d)) used by Chakraborty et al. [50,68] to develop their gas-phase mechanism. These theories under-predict the reaction barrier heights and hence overpredict the reaction rates in the gas phase which leads to higher calculated burn rates. In addition to this, the reaction rates calculated using the quantum chemical calculations are only valid for high-pressure limits. Correction for low pressures was not applied in the current work.

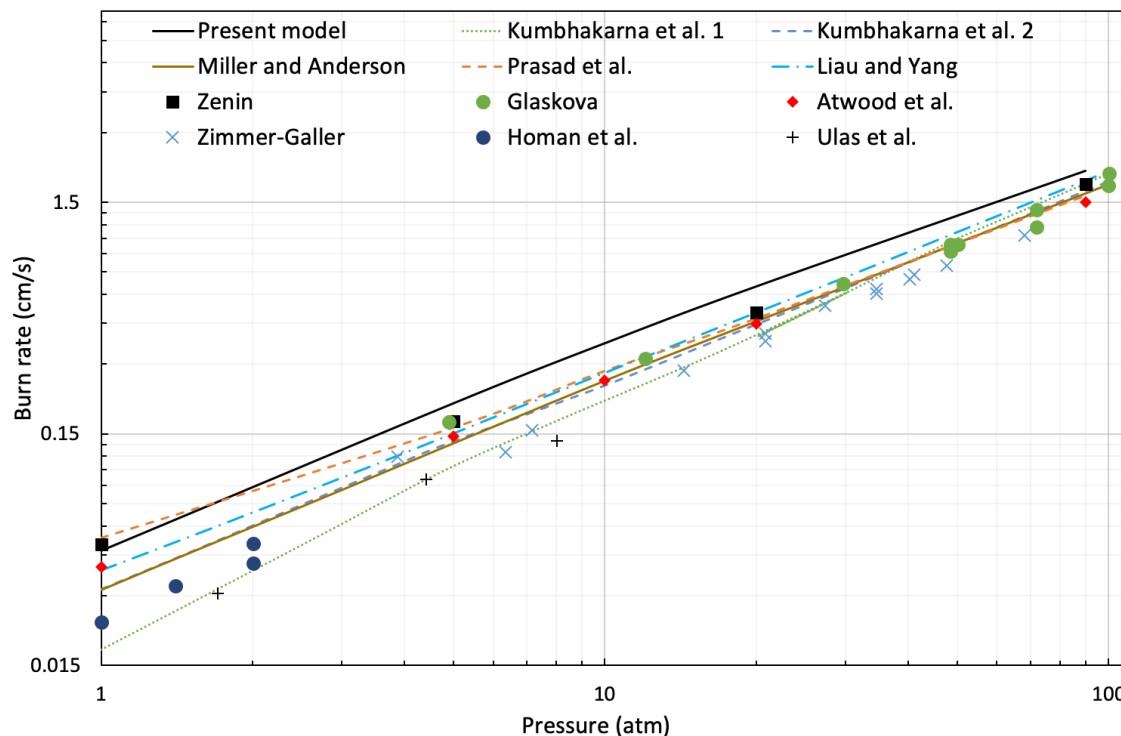


Figure 6-1. Variation of burn-rate with pressure for self-deflagration of RDX mono-propellant. The initial temperature of the unburnt propellant was 293 K. References are provided in text.

The burn rate is often expressed in the form,  $r_b = aP^n$ , where  $r_b$  is the burn-rate,  $a$  is the pre-exponential factor,  $P$  is the pressure and  $n$  is the pressure exponent. Using the current model, the pressure exponent was found to be 0.78, and matches very well with the theoretical values of 0.76 by Prasad et al. [72] and 0.83 by Liau and Yang [69], and the experimental values of 0.81 by Atwood et al. [126] and 0.80 by Mason et al. [130]. Other than pressure, burn-rate also varies with the initial temperature of the unburnt propellant ( $T_i$ ). The burn-rate temperature sensitivity is defined as  $\sigma_p = \partial(\ln r_b)/\partial T_i$ . Using the current model, the burn-rate temperature sensitivity was found to vary in the range  $1 \times 10^{-3}$  to  $2 \times 10^{-3} \text{ K}^{-1}$ , and matches very well with the theoretical values obtained by Prasad et al. [72] and Liau and Yang [69]. Positive temperature sensitivity values indicate an increase in burn-rate with initial temperature. A higher initial temperature leads to enhanced liquid-phase decomposition and hence increases the burn-rate. With an increase in pressure, the burn-rate temperature sensitivity decreases for RDX.

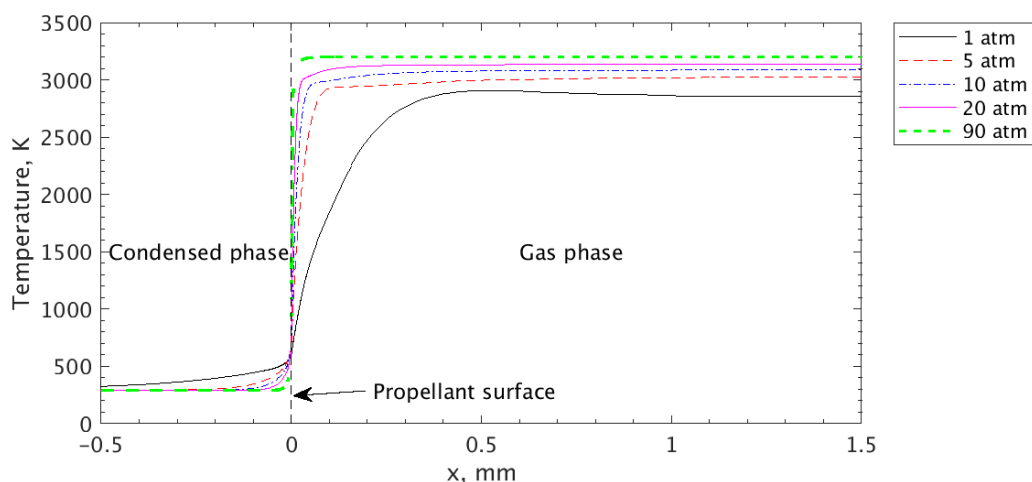


Figure 6-2. Temperature profiles for self-deflagration of RDX mono-propellant. The initial temperature of the unburnt propellant was 293 K.

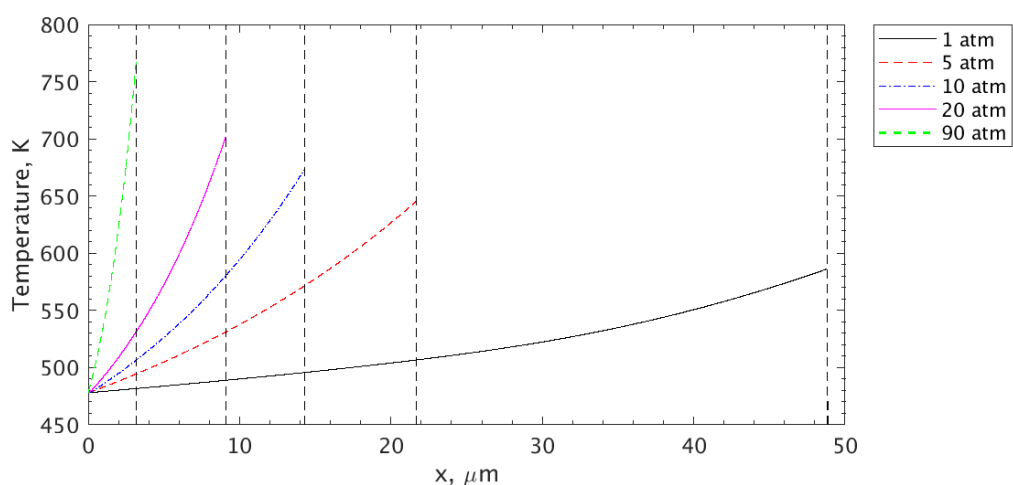


Figure 6-3. Melt layer temperature profiles during self-deflagration of RDX. The initial temperature of the unburnt propellant was 293 K.

Figure 6-2 shows the temperature distribution during RDX combustion at constant pressure in 1–90 atm range. The obtained temperature profiles are in good agreement with results from Liao and Yang [69]. With an increase in pressure, the temperature profile becomes steeper in both gas and condensed phases. In the solid phase, exponentially increasing profiles are obtained due to the presence of conductive energy transfer and the absence of chemical reactions. The melt layer temperature profile is not properly visible here and is provided in Figure 6-3. Monotonous increasing profiles are obtained in the gas phase. Similar to the experimental observation for RDX self-deflagration by Zenin [124] and Hanson-Parr and Parr [131], a temperature plateau corresponding to a dark zone was not observed. A two-stage flame structure in the temperature profile, which is present during the laser-assisted deflagration of RDX, is absent during the self-deflagration of RDX. Steep temperature profiles at higher pressures explain the high burn-rates due to the increased conductive heat feedback from the gas phase to the melt layer.

Figure 6-3 illustrates the temperature variation inside the melt layer. With an increase in pressure the melt-layer thick decreases whereas the propellant surface temperature increases. The increase in surface temperature is due to the increase in heat feedback from the gas phase. The liquid-phase temperature profiles are slightly exponential in nature and approach linear behavior for higher pressures. Most of the liquid-phase decomposition occur very close to the propellant surface. The extent of RDX decomposition in the melt layer can be represented by the RDX mass fraction at the propellant surface. In the presence of

bubbles at the propellant surface, a weighted mass fraction of RDX was calculated and is provided in Figure 6-4. The results show that with an increase in pressure the extent of decomposition slightly increases in the melt layer. This behavior is the combined effect of an increase in propellant surface temperature and a decrease in melt layer thickness with an increase in pressure. Moreover, at higher pressures the liquid-phase decomposition products of RDX, such as HONO and  $\text{NO}_2$  remain dissolved and participate in the secondary reactions. For a pressure variation of 1-90 atm, the RDX mass fraction at the propellant surface varies from 0.997 to 0.987. The corresponding RDX mole fraction values are 0.992 to 0.969. Our results differ significantly from the earlier combustion models based on global reaction kinetics in the liquid phase. Prasad et al. [72] and Liao and Yang [69] obtained RDX mole fraction values of 0.6 and 0.5, respectively, at the propellant surface for 1 atm pressure. Liao and Yang [69] obtained approximately the same value (0.5) for 90 atm, whereas Prasad et al. [72] obtained a value approaching one.

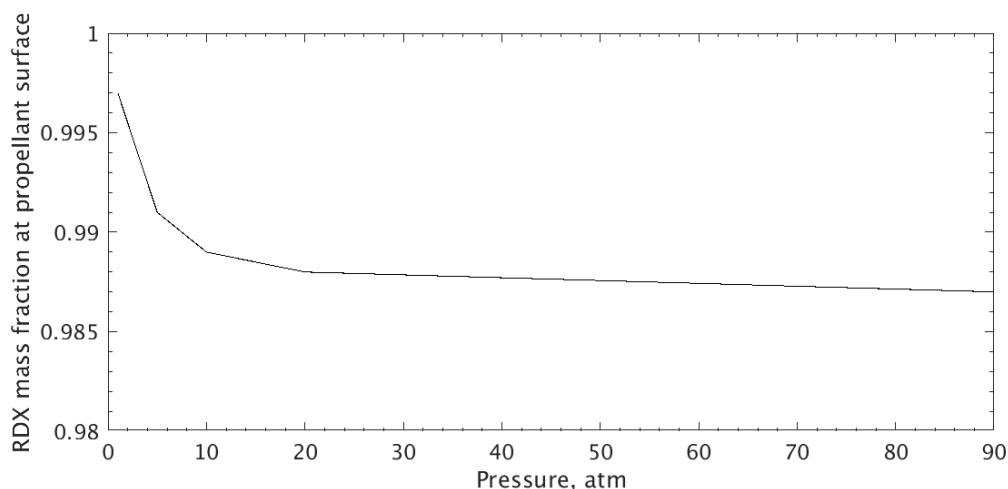


Figure 6-4. Extent of RDX decomposition in the melt layer during its self-deflagration. The initial temperature of the unburnt propellant was 293 K.

Figure 6-5 shows the comparison between the propellant surface temperature values calculated from our model with the experimental data from Zenin [124] and theoretical data from Prasad et al. [72] and Liao and Yang [69]. The calculated surface temperature values lie well within the experimental data scatter at all pressures. A reasonable match with the earlier combustion models is also present.

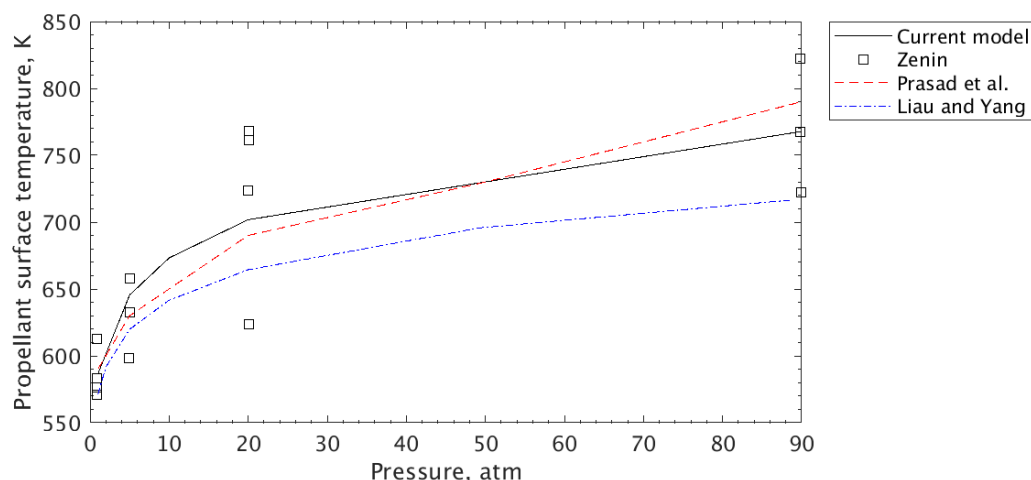


Figure 6-5. Variation of propellant surface temperature with pressure for self-deflagration of RDX monopropellant. The initial temperature of the unburnt propellant was 293 K. References are provided in the text.

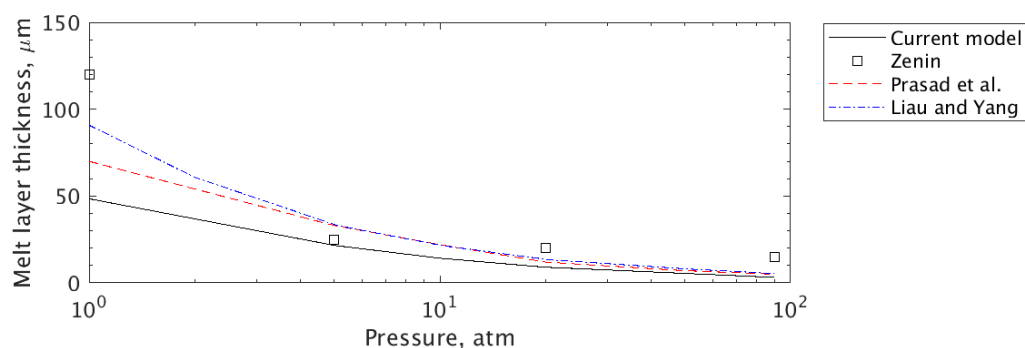


Figure 6-6. Melt layer thickness variation pressure during self-deflagration of RDX. The initial temperature of the unburnt propellant was 293 K. References are provided in the text.

Figure 6-6 shows the comparison between the melt layer thickness values calculated from our model with the experimental data from Zenin [124] and theoretical data from Prasad et al. [72] and Liao and Yang [69]. At pressures greater than 5 atm, a very good match is achieved among our calculated values and other experimental and theoretical values. At atmospheric pressure our model under-predicts the melt layer thickness.

Figure 6-8 shows the extent of bubble formation and growth in the melt layer and its dependence on pressure. With an increase in pressure the tendency of dissolved species to evaporate and enter the bubbles decreases. Hence, smaller void fraction values are obtained at higher pressures. For 20 atm and higher pressures, the fractional volume of bubbles remains lower than 1%. On the other hand, bubbles formation becomes dominant for pressures below 5 atm. For 1 atm pressure, the fractional volume of bubbles at the propellant surface was found to be 55.65%. This value compares well with the 45% surface void fraction value obtained by Liao and Yang [69]. Volkov et al. and Zenin also reported the presence of bubbles during the experimental studies of RDX combustion under atmospheric pressure [124,132]. At lower pressures, even though the temperature in the melt layer is low, more time is available for evaporation to the slower burn rate.

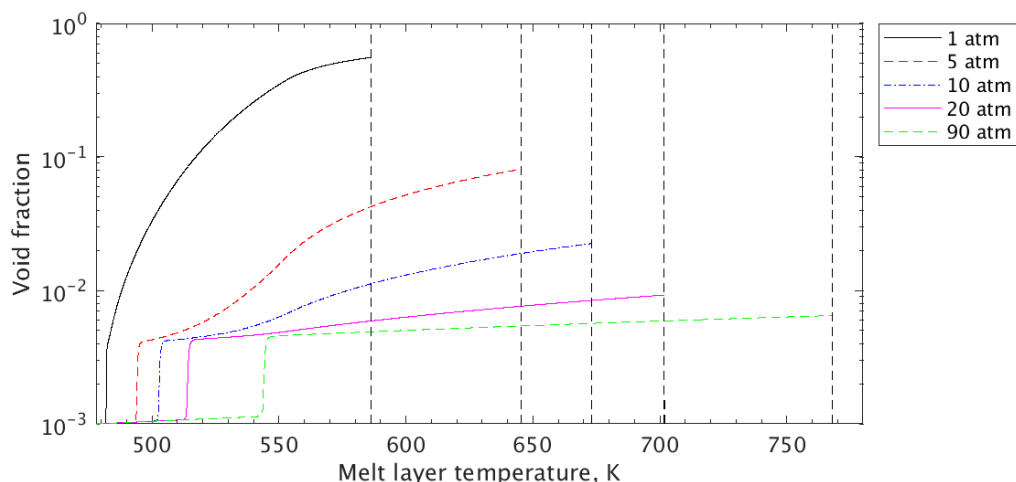


Figure 6-8. Variation of void fraction in the melt layer during self-deflagration of RDX. The initial temperature of the unburnt propellant was 293 K.

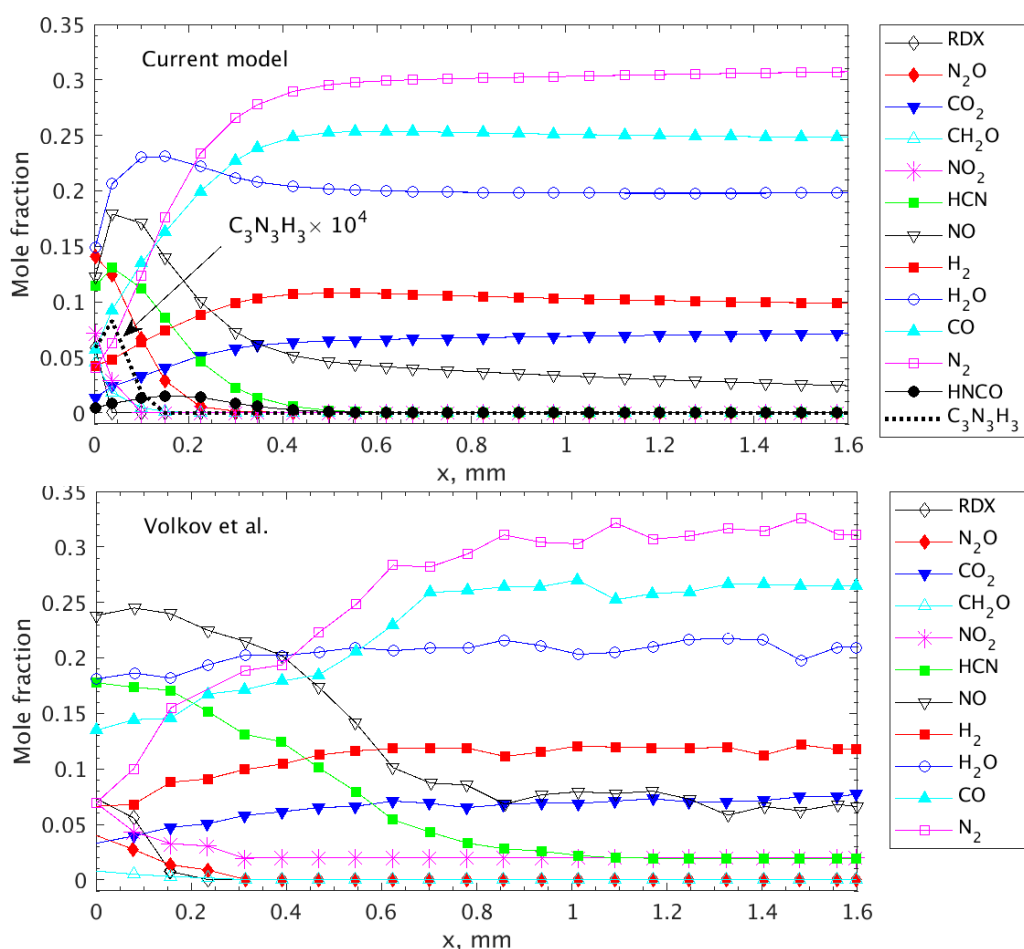


Figure 6-7. RDX flame structure in the gas phase at 1 atm.

Figure 6-7 shows the comparison between the computed and experimental mole fraction profiles of the major species in the gas-phase region for RDX self-deflagration at 1 atm. The experimental results shown here were acquired from Volkov et al. [132]. The computed mole fraction profiles from the current combustion model matches closely with our previous model [118] for species in higher concentrations. The

effect of considering bubble formation in the melt layer and updating gas-phase mechanism is observed mainly on the trace species profiles, such as HNCO and  $C_3N_3H_3$ . A two-stage flame structure is obtained in the species profiles, and matches with earlier combustion models and experimental studies [69,72,75,132]. Excellent agreement between the experimental and computed profiles has been obtained for CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and N<sub>2</sub>. Since the relative concentration of these species govern the final flame temperature, the temperature value calculated from the combustion model (2867 K) is close to the measured value of Volkov et al. [132] (2800 K). Compared to our previous model [118], a better agreement in flame temperature is achieved by considering bubble formation and updating the gas-phase decomposition mechanism. The predicted flame temperature is slightly higher because of the adiabatic flame assumption. Other gas phase species profile also match with reasonable accuracy. In particular, the current model eliminates the inaccuracy in estimation of  $C_3N_3H_3$  evolution. Previously, it was realized by Anderson and Conner [75] that  $C_3N_3H_3$  concentration in the gas-phase was highly over-predicted by their model while using the gas-phase mechanism by Chakraborty et al. [50,68]. They obtained a maximum mole fraction of 0.145 for  $C_3N_3H_3$  near the propellant surface. In our previous model [118] where we used the detailed liquid-phase mechanism by Khichar et al. [34],  $C_3N_3H_3$  was found to be present in small concentrations in the gas phase. A maximum mole fraction of 0.01 was obtained for  $C_3N_3H_3$  near the propellant surface. Using the current model with detailed liquid-phase mechanism and updated gas-phase mechanism,  $C_3N_3H_3$  was found to be present in very small concentrations with a maximum mole fraction of  $8 \times 10^{-6}$ . This justifies why  $C_3N_3H_3$  has not been detected in experimental studies of RDX flame structure.  $C_3N_3H_3$  is the formed from the successive HONO elimination pathway in the gas phase. In our updated gas-phase mechanism, additional RDX decomposition pathways are added which favor HONO re-attachment in a different orientation and ring-opening after the first HONO elimination step. Another species pointed by Anderson and Conner [75] which is present in trace amount and is difficult to estimate by earlier combustion models is HNCO. Similar to the experimental observations [133], HNCO concentration peak was found to be near the propellant surface. A part of the HNCO concentration just next to the propellant surface in the gas-phase comes from the melt layer. HNCO is produced from both liquid- and gas-phase decomposition of RDX inside the melt layer (liquid + bubbles). Earlier combustion models could not capture this trend because of the absence of a detailed liquid-phase decomposition mechanism.

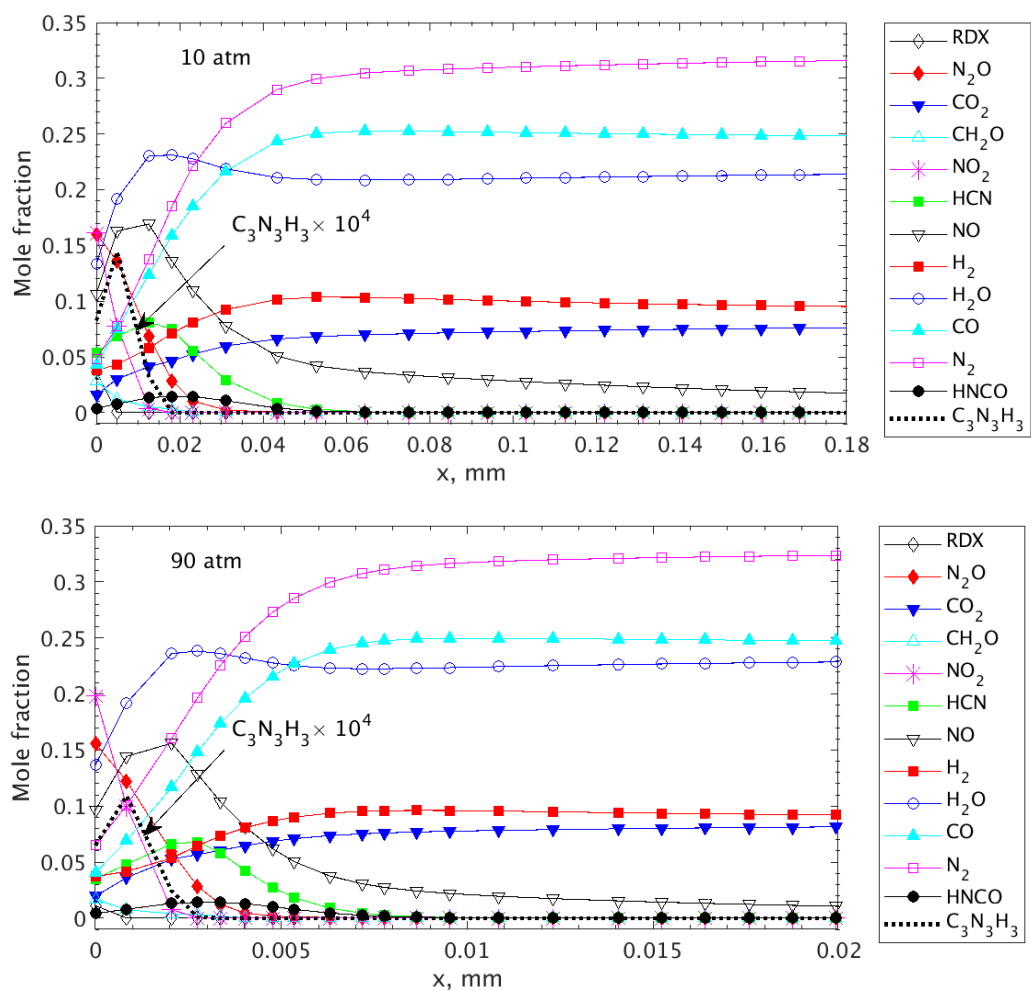


Figure 6-9. RDX flame structure in the gas phase at high pressures.

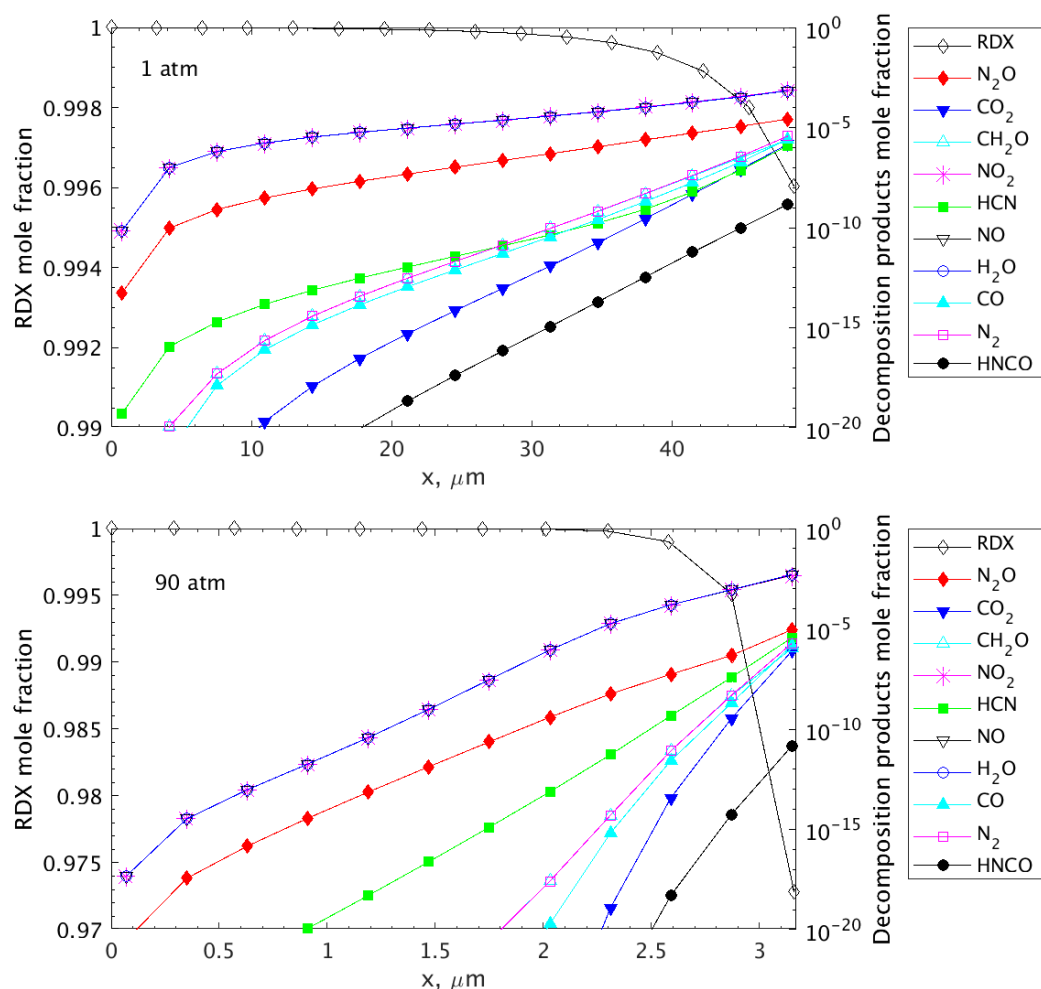


Figure 6-10. Species profiles in the liquid-phase volume fraction of the melt layer during RDX deflagration.

Figure 6-9 shows the computed mole fraction profiles of the major species in the gas-phase region for RDX self-deflagration at 10 and 90 atm pressures. Figure 6-7 and Figure 6-9 collectively indicate that as the pressure increases, the shape of gas-phase species profiles remains almost the same but are compressed in the spatial dimension. At higher pressures, the exothermic gas-phase reactions occur very close to the propellant surface which increases the heat feedback and hence the burn rate. On closer inspection of the RDX flame structure, it can be noted that the relative ratio of  $\text{NO}_2:\text{N}_2\text{O}$  at the propellant surface increases with pressure. A similar trend is also present in the experimental studies of RDX thermal decomposition and combustion [34,45,117,132,133]. Much of this increase in  $\text{NO}_2:\text{N}_2\text{O}$  ratio is because of the decomposition reactions inside the melt layer. A higher  $\text{NO}_2:\text{N}_2\text{O}$  ratio is obtained at higher pressures for the propellant mixture which enters the gas phase at the propellant surface (refer Figure 6-10).

Table 6-1. Heat feedback from gas-to-liquid phase and overall heat release in the melt layer during self-deflagration of RDX.

| Pressure:<br>(atm) | Heat feedback from gas-to-liquid phase, $\dot{q}_g$<br>(cal cm <sup>-2</sup> s <sup>-1</sup> ) |       |       |       |        | Overall heat release in the melt layer, $\dot{Q}_c$ (cal<br>cm <sup>-2</sup> s <sup>-1</sup> ) |     |     |      |     |
|--------------------|------------------------------------------------------------------------------------------------|-------|-------|-------|--------|------------------------------------------------------------------------------------------------|-----|-----|------|-----|
|                    | 1                                                                                              | 5     | 10    | 20    | 90     | 1                                                                                              | 5   | 10  | 20   | 90  |
| Model              | 21.6                                                                                           | 103.1 | 192.9 | 353.6 | 1251.6 | 0.01                                                                                           | 0.1 | 0.3 | 0.5  | 2.2 |
| Zenin              | 16.9                                                                                           | 53.5  | —     | 74.7  | 87     | -7                                                                                             | -17 | —   | 48.1 | 420 |

Table 6-1 shows the comparison between the computed and experimental values of heat feedback from gas-to-liquid phase ( $\dot{q}_g$ ) and overall heat release in the melt layer ( $\dot{Q}_c$ ). Zenin [124] used gas-phase temperature measurement data with the values of thermal conductivity, specific heat capacity, and enthalpy of vaporization of RDX from the literature to estimate  $\dot{q}_g$  and  $\dot{Q}_c$ . Both experimental and computed values indicate an increase in the heat feedback from the gas phase and heat release in the melt layer with an increase in pressure. But there is mismatch in the values, and the error increases with pressure. This error is mainly attributed to the inability of experimental techniques to measure temperature accurately in the close vicinity of the propellant surface. Since the RDX flame structure is compressed near the propellant surface at high pressures, it becomes extremely difficult to experimentally obtain the temperature gradient at the propellant surface. Additionally, errors in the calculated thermal properties of all the liquid- and gas-phase decomposition products of RDX may also lead to some error in the combustion model predictions.

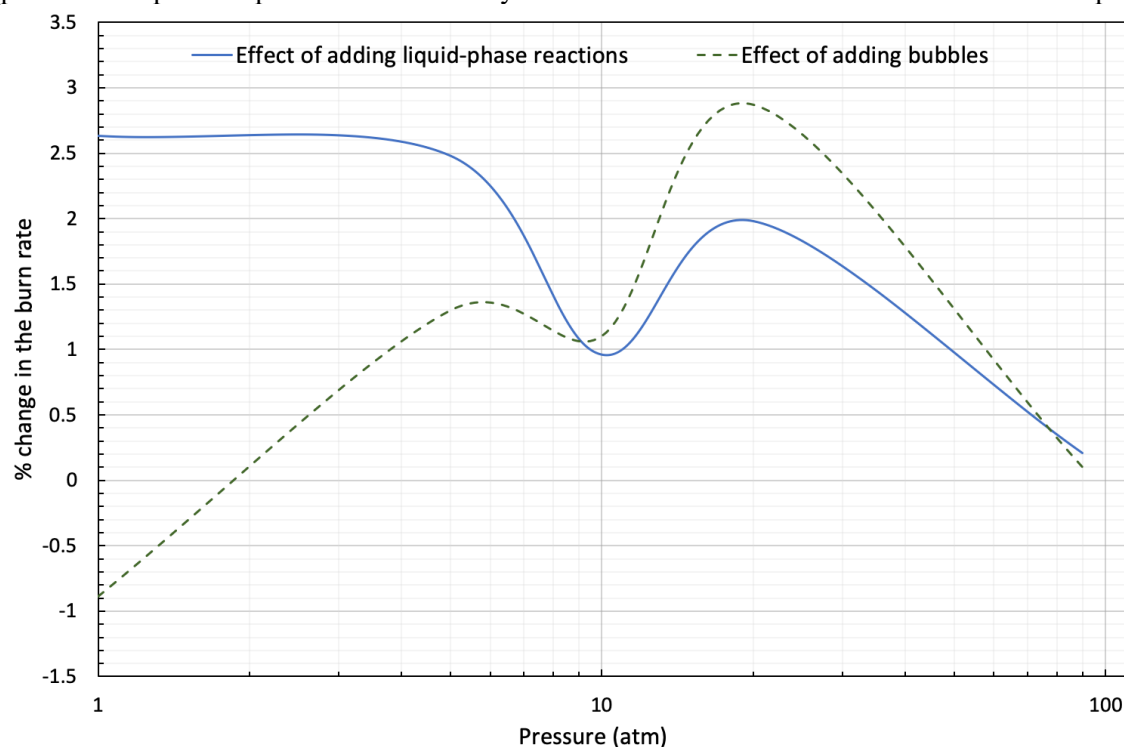


Figure 6-11. Effect of adding liquid-phase decomposition reactions and bubble formation in the melt layer on the propellant burn-rate.

Figure 6-11 shows the effect of including the detailed liquid-phase reaction mechanism and bubble formation and growth phenomenon in our combustion model on the prediction of propellant burn-rate. Results show that even though the extent of RDX decomposition in the melt layer increases with pressure (refer Figure 6-4), the effect of considering liquid-phase decomposition, specifically, on the burn-rate decreases with an increase in pressure. This implies that the increase in heat feedback with pressure is much more than the corresponding increase in heat release in the melt layer due to the decomposition reactions.

Results shown in Table 6-1 agree with it. The effect of considering bubbles in the melt layer on the predicted values of burn-rate is rather convoluted. A maximum percentage change in the burn-rate is observed at 20 atm pressure. This overall effect is because of two opposing factors. The volume fraction of bubbles decreases with pressure whereas the extent of exothermic gas-phase reactions inside the bubbles increases with pressure due to the elevated melt-layer temperatures.

#### 6.4 Conclusions

A new multi-phase combustion model for constant pressure self-deflagration of RDX has been developed. The three characteristic features which separate it from the previous models are 1) consideration of a detailed liquid-phase mechanism to model decomposition in the melt layer, 2) detailed modeling of the experimentally observed bubble formation phenomenon in the melt layer, and 3) usage of an updated detailed gas-phase mechanism in both gas-phase region above the propellant surface and bubbles in the melt layer. The model uses an experimentally obtained pyrolysis law, and hence is not completely predictive in nature. The model was used to estimate the RDX flame structure in a pressure range of 1–90 atm. A reasonably good agreement was achieved with the experimental data for various combustion characteristics. A shortcoming of the previous combustion models to accurately predict the concentration profiles of trace species in the gas phase was corrected by the current model. The results indicate that approximately 0.3% of RDX by mass decomposes in the melt layer at 1 atm, and increases to about 1.3% at 90 atm. Even though only a small fraction of RDX decomposes in the melt layer it changes the chemical structure of the flame in the gas-phase region. Hence, it is important to include detailed liquid-phase chemical kinetics in the combustion models. The results show that the products of liquid-phase decomposition of RDX have a high tendency to collect inside bubbles at pressures close to the atmospheric pressure. Approximately 50% of the propellant surface is covered with bubbles at 1 atm pressure. Hence, it is important to model bubble formation and growth at lower pressures. The effect of updating the detailed gas-phase mechanism was observed on  $C_3H_3N_3$  profile in the gas phase. The new RDX decomposition pathways added to the mechanism competes with the successive HONO elimination pathway responsible for the excessive formation of  $C_3H_3N$ .

## CHAPTER 7

### A REDUCED REACTION MECHANISM FOR LIQUID-PHASE DECOMPOSITION OF TAGZT WITH OPTIMIZED PARAMETERS

#### 7.1 Introduction

In a recent study by Kumbhakarna et al., decomposition pathways for the production of all the major liquid-phase decomposition products of TAGzT ( $\text{N}_2$ , HCN,  $\text{N}_2\text{H}_4$ ,  $\text{NH}_3$ , triaminoguanidine, and 3-azido-1,2,4-triazol-4-ide anion) were provided [134]. The study was focused mainly on initiation pathways. In this study, we investigated a detailed reaction mechanism for liquid-phase decomposition of TAGzT. The reaction mechanism was developed using the initiation pathways provided by Kumbhakarna et al. [134]. Several new decomposition pathways were identified using quantum chemical calculations and added to the reaction mechanism with their kinetics parameters. The autocatalytic effects of different decomposition products on the overall decomposition process were studied. Secondary reactions among numerous smaller molecular weight intermediate species were added to the mechanism. Efforts were also made to identify and explain the formation of residual products. We validated the developed mechanism using results obtained from simultaneous thermal analysis (STA) experiments and a detailed kinetic model. The reaction kinetics parameters obtained using the quantum chemical calculations were optimized within their range of uncertainty using the experimental mass loss and species evolution profiles obtained at three different heating rates – 5, 10, and 15°C/min. A reduced reaction mechanism was also obtained which can be used in combustion models to enhance their predictive capabilities without much loss of computational efficiency.

#### 7.2 Quantum chemical calculations

Quantum chemical calculations were used to identify the elementary reactions that occur during the liquid-phase decomposition of TAGzT. The Gaussian 09 software package was utilized for performing these calculations [13]. An approach similar to the work by Kumbhakarna et al. was followed [134]. A brief summary is provided here. An extensive search for identifying the numerous intermediate species and transition states involved in the decomposition process was performed using less computationally expensive hybrid density functional methods. In most cases, the calculations were performed at B3LYP/6–31G(d), B3LYP/6–311++G(d,p), or  $\omega$ B97X-D/6–311++G(d,p) level of theory [89,98,135,136]. All the obtained intermediates and transition state structures were reoptimized using the complete basis set CBS-QB3 compound method [137]. Thermodynamic parameters obtained from the CBS-QB3 level calculations were used to evaluate the reaction barriers in the developed mechanism. The integral equation formalism variant of the polarizable continuum model (IEFPCM) was used to account for the continuum solvation effects [138]. Typical polar solvent, acetonitrile ( $\text{CH}_3\text{CN}$ ) with a dielectric constant of 35.688, was used. Discussion on solvent selection is provided by Kumbhakarna et al. [134].

#### 7.3 Thermolysis experiments

To study the thermal decomposition of TAGzT in the liquid phase, we employ results from simultaneous thermal analysis experiments. TAGzT obtained from the Los Alamos National Laboratory was used without further purification. The coupled TGA/DSC-FTIR experimental setup described by Khichar et al. was used [139]. After calibration, two sets of experiments were performed – 1) open crucible and 2) crucible covered with aluminum mesh. In both sets of experiments, the evolved product gases freely escape the heated sample and mix with inert nitrogen gas in a relatively cooler environment. Hence, the experimental technique is suitable to study the liquid-phase decomposition [18,139]. Experiments with a closed crucible or a crucible with pinhole lid were not performed to minimize gas-phase reactions.

In all experiments, TAGzT was subjected to temperatures ranging from 40 to 300°C under atmospheric pressure, and a purge gas ( $\text{N}_2$ ) flow rate of 70 ml/min was maintained. A 0.5–2 mg sample was used in each experiment. Samples were heated at three different heating rates – 5, 10, and 15°C/min. For repeatability, three or more experiments were conducted for each of the three heating rates. The evolved gases were transferred to an FTIR cell maintained at 150°C where spectral transmittance was recorded in

600–3750  $\text{cm}^{-1}$  range. A 2  $\text{cm}^{-1}$  spectral resolution was achieved with a time resolution of 1.5 spectra per degree change in sample temperature for the highest selected heating rate (15°C/min).

### 7.3.1 Conversion of FTIR data to species evolution profiles

To analyze the spectral transmittance data obtained from STA experiments, an approach similar to Khichar et al. was followed [34]. Assuming the validity of Beer's law, the data-reduction model described by Mallery and Thynell was selected [40]. A numerical solver based on the Levenberg-Marquardt algorithm was used [140]. The required radiative properties of the IR active species were obtained from the HITRAN database [41]. The model provided temporal evolution data for two of the major IR active decomposition products of TAGzT – HCN and  $\text{NH}_3$ . The model could not be used for other major IR active decomposition products due to the unavailability of their radiative properties.

## 7.4 Kinetic modeling

Thermolysis experiments were simulated using a chemical kinetics model based on conservation laws. The experimental setup was modeled as two connected sub-systems at constant pressure – 1) liquid-phase region and 2) gas-phase region. Uniform mixing was assumed in both regions. The liquid-phase TAGzT sample was assumed to have a constant density ( $\rho_l = 1.6 \text{ g cm}^{-3}$  [141]) during the entire thermolysis process. Further details are provided in [142].

## 7.5 Results and discussion

### 7.5.1 Experimental mass loss and heat release

Using the coupled TGA/DSC-FTIR setup described by Khichar et al. [139], liquid-phase decomposition of TAGzT was studied at three heating rates. The experimentally measured mass-loss data as a function of temperature are shown in Figure 7-1. Results show that significant mass loss only starts to occur near the melting point of TAGzT (195°C). For higher heating rates, the initiation of mass loss is delayed since less time is available for decomposition. Figure 7-1 shows that the first mass-loss step is very steep. Also, no corresponding FTIR spectra of IR-active species were observed. This indicates that the first mass-loss step corresponds to a sudden release of an IR inactive gas from the sample, most likely  $\text{N}_2$ . The anionic part of TAGzT ( $\text{AzT}^{2-}$ ) starts to decompose in the solid phase at temperatures below the melting point. Since molecules are tightly packed in the solid phase, the decomposition pathway is likely unimolecular. The  $\text{N}_2$  gas produced from the unimolecular dissociation of tetrazole rings remains trapped inside the TAGzT crystals. When the  $\text{N}_2$  gas concentration increases and the sample temperature reaches the melting point, a sudden release of  $\text{N}_2$  gas occurs. This abrupt gas release often throws away the needle-like crystals of TAGzT outside the open crucible. Hence, a large variation in the mass-loss step size was obtained in the open crucible experiments, shown in Figure 7-1-a. Undecomposed TAGzT crystals were also found on the sample holder inside the TGA setup after the completion of the heating cycle. The amount of TAGzT ejected from the crucible also increased variation in the successive mass loss steps and the residual mass. For higher sample heating rates,  $\text{N}_2$  releases more vigorously and hence larger variations in the experimental mass-loss profiles were observed, shown in Figure 7-1-a.

To mitigate the issues caused by TAGzT crystals being expelled from the crucible, a different set of thermolysis experiments were performed. In these experiments, the sample crucible was covered with a thin aluminum mesh. Since the TAGzT crystals are long, they remained trapped by the Al mesh inside the crucible during the abrupt  $\text{N}_2$  release. Almost no undecomposed TAGzT crystals were found on the sample holder in these experiments after the completion of the heating cycle. Figure 7-1-b shows the mass-loss profiles obtained from these experiments at three different heating rates. Compared to open crucible experiments, much less variation in the mass-loss profiles was obtained. As the heating rate increases, the size of the first mass-loss step decreases. It suggests that liquid-phase decomposition dominates over the solid-phase decomposition of TAGzT at high heating rates. After the first mass-loss step, two additional liquid-phase decomposition steps are observed. Step 2 is due to the complete decomposition of the  $\text{AzT}^{2-}$  dianion and partial decomposition of  $\text{TAG}^+$  cation.  $\text{AzT}^{2-}$  produces  $\text{N}_2$ , HCN, and  $\text{CN}^-$  as the major products. For all heating rates, step 2 ends at around 40 % residual mass. Step 3 mass loss is relatively slower compared to step 2, which indicates the decomposition of relatively stable species.  $\text{TAG}^+$  and other stable

intermediates decompose to form  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  as the major final products observed in the gas phase. Approximately 15 % of the residual mass was observed at all three heating rates.

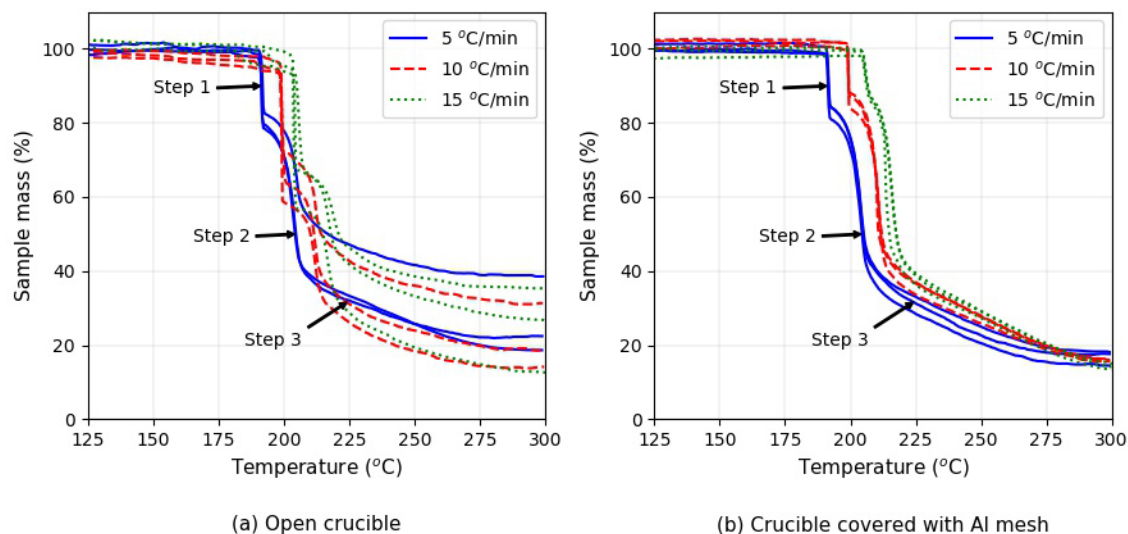


Figure 7-1. Mass loss profiles for TAGzT samples heated at three different heating rates under atmospheric pressure.

Figure 7-2 shows the rate of heat release per unit mass of the sample as a function of temperature. The differential scanning calorimetry (DSC) data were acquired simultaneously with the thermogravimetry data. Data presented in Figure 7-1 and Figure 7-2 correspond to the same set of experiments. No endothermic or exothermic peak was observed in the range 40–125°C. A small exothermic peak was observed near the melting point of TAGzT because of simultaneous decomposition. This confirms our assertion that TAGzT starts to decompose in the solid phase near the melting point. The solid-phase decomposition is exothermic and compensates for the energy requirement for melting. Quantum chemical calculations for the liquid phase show that the first  $\text{N}_2$  release from the tetrazole ring in  $\text{AzT}^{2-}$  dianion is endothermic ( $\Delta H_{rxn} = +113.5$  kJ/mol) but the second  $\text{N}_2$  release is highly exothermic ( $\Delta H_{rxn} = -187.9$  kJ/mol). A similar trend can also be expected in the solid phase.

After the solid-to-liquid phase change of TAGzT, a highly exothermic peak was observed in the DSC plots, as shown in Figure 7-2. This peak corresponds to the rapid mass-loss step marked as step 2 in Figure 7-1. No peak-height correlation with the heating rate could be established for the open crucible experiments, as shown in Figure 7-2-a. This was due to the abrupt release of  $\text{N}_2$  gas and the uncertainty it caused in the actual mass of the decomposed sample. Figure 7-2-b shows results for experiments in which crucible were covered with Al mesh. As the heating rate increases, the exothermicity of step 2 of the mass loss increases. The exothermic nature of the decomposition reactions makes the sample temperature higher relative to the crucible temperature, which further increases the decomposition rate. Since the crucible temperature was measured in the experiments, the slope of mass-loss step 2, shown in Figure 7-1, is higher than the real value. This error in the slope increases with an increase in the heating rate. No exothermic or endothermic peak was observed during step 3 of the mass-loss profile at all heating rates.

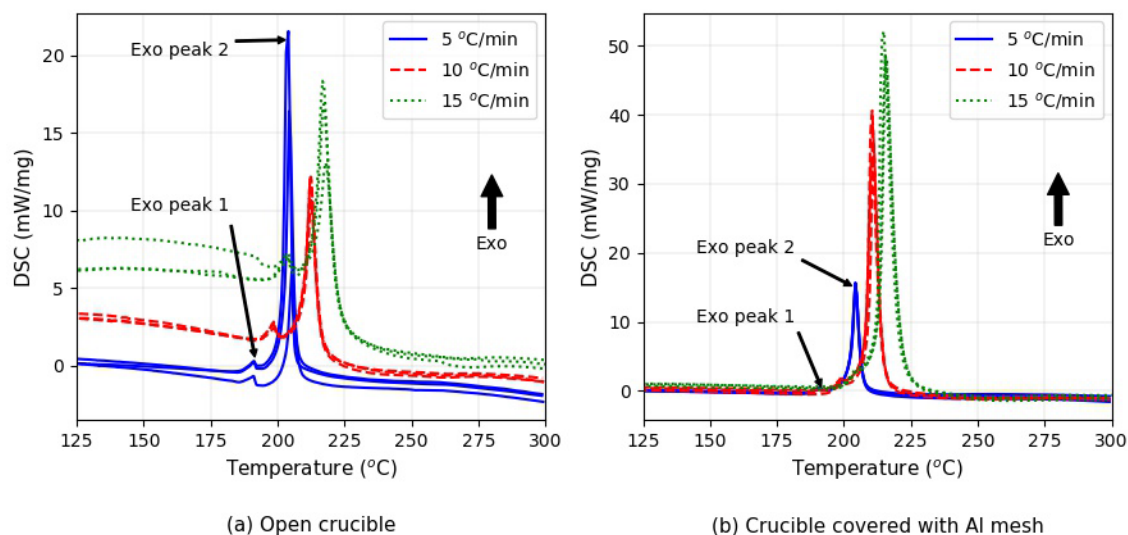


Figure 7-2. DSC profiles for TAGzT samples heated at three different heating rates under atmospheric pressure.

### 7.5.2 The liquid-phase reaction mechanism

The extensive search for the decomposition reactions of TAGzT in the liquid phase provided a detailed reaction mechanism. The obtained mechanism has 495 elementary reactions and 355 species. Considering the high computational cost and complexity associated with including a detailed reaction mechanism in a combustion model, a reduced reaction mechanism was developed. The detailed mechanism was reduced by performing a global sensitivity analysis. The sensitivity analysis was based on the identification and removal of elementary reactions whose rate-of-progress remains low throughout the decomposition process. The reduced mechanism has 90 elementary reactions and 70 species. This indicates that out of the 495 reactions in the detailed mechanism, only 90 reactions play a major role in governing the liquid-phase decomposition process and deciding the temporal evolution of product species. For each reaction, data required for estimating its reaction rate, including the imaginary frequency of the transition state for computing the tunneling factor using the Wigner approach [143], as well as the forward and reverse free energy and enthalpy are provided. All these parameters have inherent error ranges associated with them. The error ranges depend upon the level of theory and the solvation model used in the quantum chemical calculations. An uncertainty of about 21–30 kJ/mol in reaction barriers is expected for the CBS-QB3 compound method used with the IEFPCM solvation model for reactions with ionic species. Using the chemical kinetics model and the experimental results, the forward and reverse Gibbs free energy barriers were altered within their range of uncertainty. A maximum change of 20.9 kJ/mol was made to the reaction barriers.

The analysis of the reduced reaction mechanism reveals the important pathways for the liquid-phase decomposition of TAGzT. TAGzT stays as separated  $\text{TAG}^+$  and  $\text{AzT}^{2-}$  ions in the liquid phase due to the solvation effect [134]. The decomposition process starts with  $\text{AzT}^{2-}$  (INTM 164A in the mechanism, where 164 is the molecular weight) due to its relatively lower unimolecular decomposition barrier (161.1 kJ/mol). Figure 7-3 shows the different decomposition pathways and the Gibbs free energy barriers for each step of  $\text{AzT}^{2-}$  decomposition. The decomposition process starts with the primary pathway (PP), as shown in Figure 7-3. One of the tetrazole rings of  $\text{AzT}^{2-}$  opens up to release  $\text{N}_2$ . The resultant intermediate (INTM 136A) readily accepts a proton from  $\text{TAG}^+$  and then releases the second  $\text{N}_2$  to form INTM 109A. After two unimolecular rearrangement steps, two more  $\text{N}_2$  molecules are released successively. The resultant intermediate undergoes unimolecular decomposition to form HCN and  $\text{CN}^-$ . In solid-phase, where bimolecular reactions are not favored, INTM 136A undergoes two unimolecular dissociation steps to release 3  $\text{N}_2$  and 2  $\text{CN}^-$ .

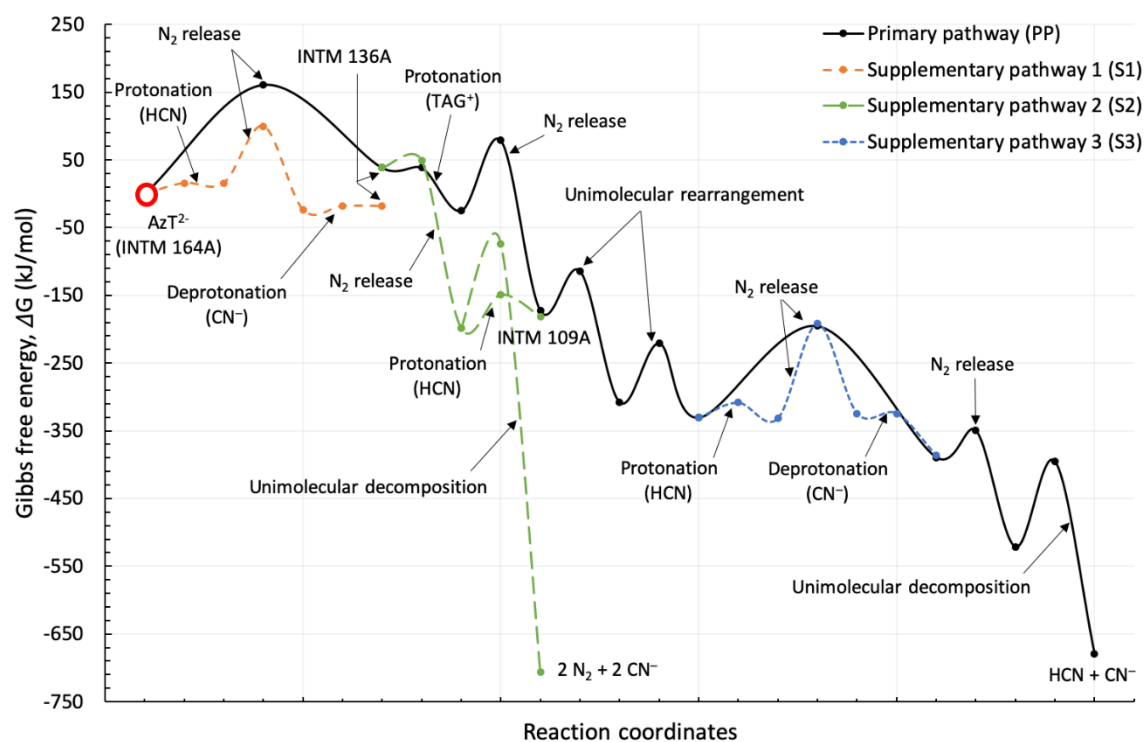


Figure 7-3. Reaction pathways for the liquid-phase decomposition of azotetrazolate dianion ( $\text{AzT}^{2-}$ ).

HCN and  $\text{CN}^-$  show autocatalytic behavior which is responsible for the experimentally observed steep slope of mass-loss step 2, as shown in Figure 7-1. The supplementary pathways (S1, S2, and S3), as shown in Figure 7-3, enhance the decomposition rate of  $\text{AzT}^{2-}$ . These pathways have protonation and deprotonation steps with small barriers. These steps promote the  $\text{N}_2$  release by reducing the free energy barriers and hence increase the overall decomposition rate. The small reaction barriers along the  $\text{AzT}^{2-}$  decomposition pathways and the release of a large amount of  $\text{N}_2$  gas are responsible for the highly exothermic and sharp peak observed in the experimentally obtained DSC plot (shown in Figure 7-2).

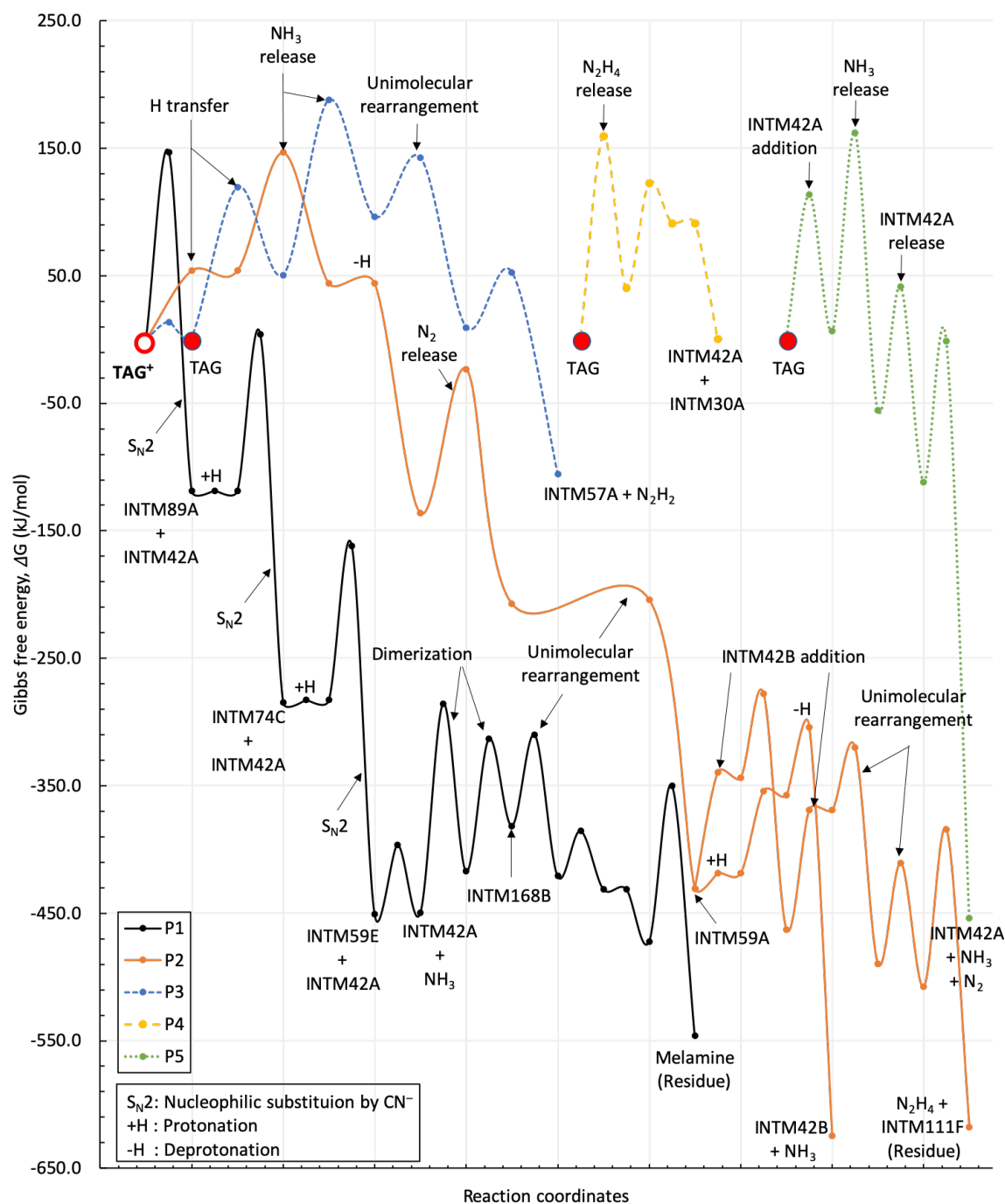


Figure 7-4. Reaction pathways for the liquid-phase decomposition of triaminoguanidinium cation ( $\text{TAG}^+$ ).

Figure 7-4 shows the different decomposition pathways and the Gibbs free energy barriers for each step of  $\text{TAG}^+$  decomposition.  $\text{TAG}^+$  decomposes via five competitive pathways (P1–P5). Except for pathway P2, all other  $\text{TAG}^+$  decomposition pathways require the presence of an  $\text{AzT}^{2-}$  decomposition product ( $\text{CN}^-$  anion) to initiate decomposition.  $\text{CN}^-$  anion can participate in either deprotonation or nucleophilic substitution ( $\text{S}_{\text{N}}2$ ) reactions. Hence,  $\text{TAG}^+$  decomposition is slightly delayed compared to  $\text{AzT}^{2-}$  decomposition.

Pathway P1 is the successive nucleophilic substitution pathway.  $\text{TAG}^+$  is successively attacked by  $\text{CN}^-$  to form diaminoguanidine (INTM 89A), monoaminoguanidine (INTM 74C), and then guanidine (INTM 59E). Cyanamide (INTM 42A) is released at each step. Guanidine forms cyanamide and  $\text{NH}_3$  in the

presence of another  $\text{NH}_3$ . Yang et al. studied pathways for melamine formation from cyanamide in the gas phase [144]. A similar pathway was obtained for the liquid phase. Four molecules of cyanamide combine via two dimerization steps to form an intermediate INTM 168B. INTM 168B intramolecularly rearranges and releases INTM 126A and carbodiimide (INTM 42B). INTM 126A undergoes intramolecular H transfer to form a more stable structure, melamine. Carbodiimide can readily convert to cyanamide in the liquid phase and participate in the dimerization step again. This autocatalytic behavior of cyanamide enhances melamine formation.

$\text{TAG}^+$  decomposition can also initiate via intramolecular H transfer followed by  $\text{NH}_3$  release. This pathway is marked as P2 in Figure 7-4. A deprotonation agent, like  $\text{CN}^-$ , is required to prevent the reverse reaction. The resultant neutral intermediate releases  $\text{N}_2$  and forms an important intermediate  $\text{NH}_2\text{NHCHNH}$  (INTM 59A). INTM 59A can take two pathways to either form carbodiimide and  $\text{NH}_3$ , or formoguanamine (INTM 11F) and  $\text{N}_2\text{H}_4$ , shown in Figure 7-4. Formation of carbodiimide from the first pathway further increases formoguanamine formation. Formoguanamine and melamine (formed from pathway P1) are the two major residue molecules.

Pathways P3–P5 provide decomposition reactions for triaminoguanidine (TAG) which forms from deprotonation of  $\text{TAG}^+$ . Note that the reaction barrier for  $\text{TAG}^+$  deprotonation is very small, as shown in Figure 7-4, and hence this step is diffusion-limited. In pathway P3, an H atom is shifted in a TAG molecule with the help of another TAG molecule. The resultant intermediate undergoes three unimolecular steps to release  $\text{NH}_3$ ,  $\text{N}_2\text{H}_2$ , and  $\text{NH}_2\text{NHCN}$  (INTM 57A). Similar pathways starting with diaminoguanidine, monoaminoguanidine, and guanidine were also investigated. They were found to have comparatively higher barriers. Due to the relatively higher barriers, pathway P3 and other similar pathways become less important compared to pathways P1 and P2.

In Figure 7-4, pathways P4 and P5 are shifted to the right to avoid unwanted overlap with other pathways. In pathway P4, TAG undergoes unimolecular dissociations to form  $\text{N}_2\text{H}_4$ , cyanamide, and INTM 30A. INTM 30A readily converts to  $\text{N}_2\text{H}_2$ . In pathway P5, TAG dissociates to form cyanamide,  $\text{NH}_3$ , and  $\text{N}_2$ . Cyanamide acts as an autocatalytic agent in this pathway and reduces the barrier for TAG decomposition. Similar reactions were also identified for diaminoguanidine and added to the mechanism.

### 7.5.3 Sensitivity analysis of the decomposition pathways

Relative importance of the liquid-phase decomposition pathways of TAGzT was analyzed using sensitivity analysis. Figure 7-5 shows the sensitivity analysis results for both  $\text{AzT}^{2-}$  and  $\text{TAG}^+$  decomposition pathways. The global sensitivity coefficients, representing the cumulative rate-of-progress, are provided for the overall decomposition process. In Figure 7-5-a, the  $\text{N}_2$  release steps of the primary pathway are compared against the three supplementary pathways. Figure 7-5-a shows that after initiation the supplementary pathway S1 becomes much more important than the primary pathway due to its comparatively lower barriers. For 2<sup>nd</sup> and 3<sup>rd</sup>  $\text{N}_2$  release steps, the supplementary pathways S2 and S3 are slightly less important than the primary pathway, nonetheless enhance the overall decomposition rate responsible for the experimentally observed steep mass loss step 2, shown in Figure 7-1. Figure 7-5-b shows that pathway P2 is the most significant decomposition pathway followed by pathways P5, P1, P4, and P3 in that same order. Pathway P2 is responsible for formoguanamine formation making it the principal residue. It should be noted that cyanamide formed from pathways P1 and P4 enhance pathways P2 and P5 by autocatalytic effect.

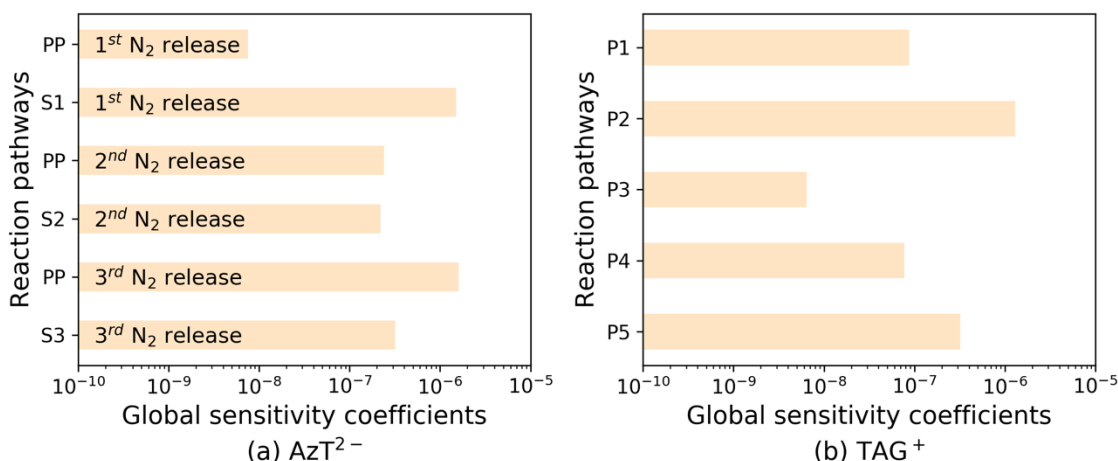


Figure 7-5. Relative significance of the liquid-phase decomposition pathways of TAGzT.

#### 7.5.4 Validation of the reaction mechanism

The chemical kinetics model described in Section 7.4 was solved using the reduced reaction mechanism for TAGzT. The obtained temporal species evolution profiles in the gas phase for HCN, NH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>, and N<sub>2</sub> are shown in Figure 7-6 for 5, 10, and 15°C/min heating rates. Corresponding experimental species evolution profiles in the gas phase for HCN and NH<sub>3</sub> are also shown in Figure 7-6 for comparison. The experimental profiles were obtained by solving the data reduction model described in Section 7.3.1. The experimental evolution profile for N<sub>2</sub>H<sub>4</sub> could not be obtained because of the unavailability of its radiative properties in the HITRAN database [41]. Since the amount of evolved gases depends upon the initial sample mass, both experimental and model species profiles shown in Figure 7-6 are normalized for 1 mg of sample. The experimental results are from the experiments in which the sample crucible was covered with Al mesh.

TAGzT decomposition initiates with AzT<sup>2-</sup> which releases N<sub>2</sub>. The experimental evolution profile for N<sub>2</sub> could not be obtained from our experimental setup because of N<sub>2</sub> being IR inactive. Figure 7-6 shows the predicted profile for N<sub>2</sub>. A large peak is observed which overlaps with step 1 of the mass-loss profile, shown in Figure 7-1-b. N<sub>2</sub> release is entirely responsible for the first mass-loss step. Kumbhakarna et al. [134] used mass spectrometry data to show that N<sub>2</sub>H<sub>4</sub> is released early during TAGzT decomposition. The developed reaction mechanism is able to predict this behavior, as shown in Figure 7-6. N<sub>2</sub>H<sub>4</sub> peaks during mass-loss step 2 and then slowly decreases.

The experimental species evolution profiles shown in Figure 7-6 reveal that HCN is produced early in the liquid-phase decomposition process. The mole fraction of HCN increases rapidly, attains a maximum value, and then decreases rapidly forming a sharp peak. The location of this peak lies within step 2 of experimental mass loss profiles for all heating rates, as shown in Figure 7-1-b. No HCN is produced in the later decomposition stage, represented as step 3 of the mass loss in Figure 7-1-b. The developed reaction mechanism supports the experimental observation. As per the mechanism, HCN is one of the major decomposition products of AzT<sup>2-</sup>. The relatively small reaction barriers along AzT<sup>2-</sup> decomposition pathway indicates its complete decomposition during step 2 of the mass loss. The general evolution trend of HCN predicted by the model is the same as in the experiments. An arguably good match is obtained at all heating rates. A slight delay in the predicted results can be noted which increases with the heating rate. This is possibly due to the highly exothermic nature of the decomposition reactions during step 2 of the mass loss, shown in Figure 7-2, which increases the sample temperature compared to the crucible temperature. The increased sample temperature leads to the early decomposition of TAGzT, and hence species evolution peaks are observed early in the experimental data. Some uncertainty in the experimental peak heights is also present due to the uncertainty in the actual mass of the decomposed sample. Due to the rapid evolution of N<sub>2</sub> during step 1 of the mass loss (shown in Figure 7-6), TAGzT crystals were thrown

out of the crucible. Attempts were made to reduce this effect by using an aluminum mesh in the experiments but could not be completely removed. No catalytic effects were observed due to the presence of the aluminum mesh.

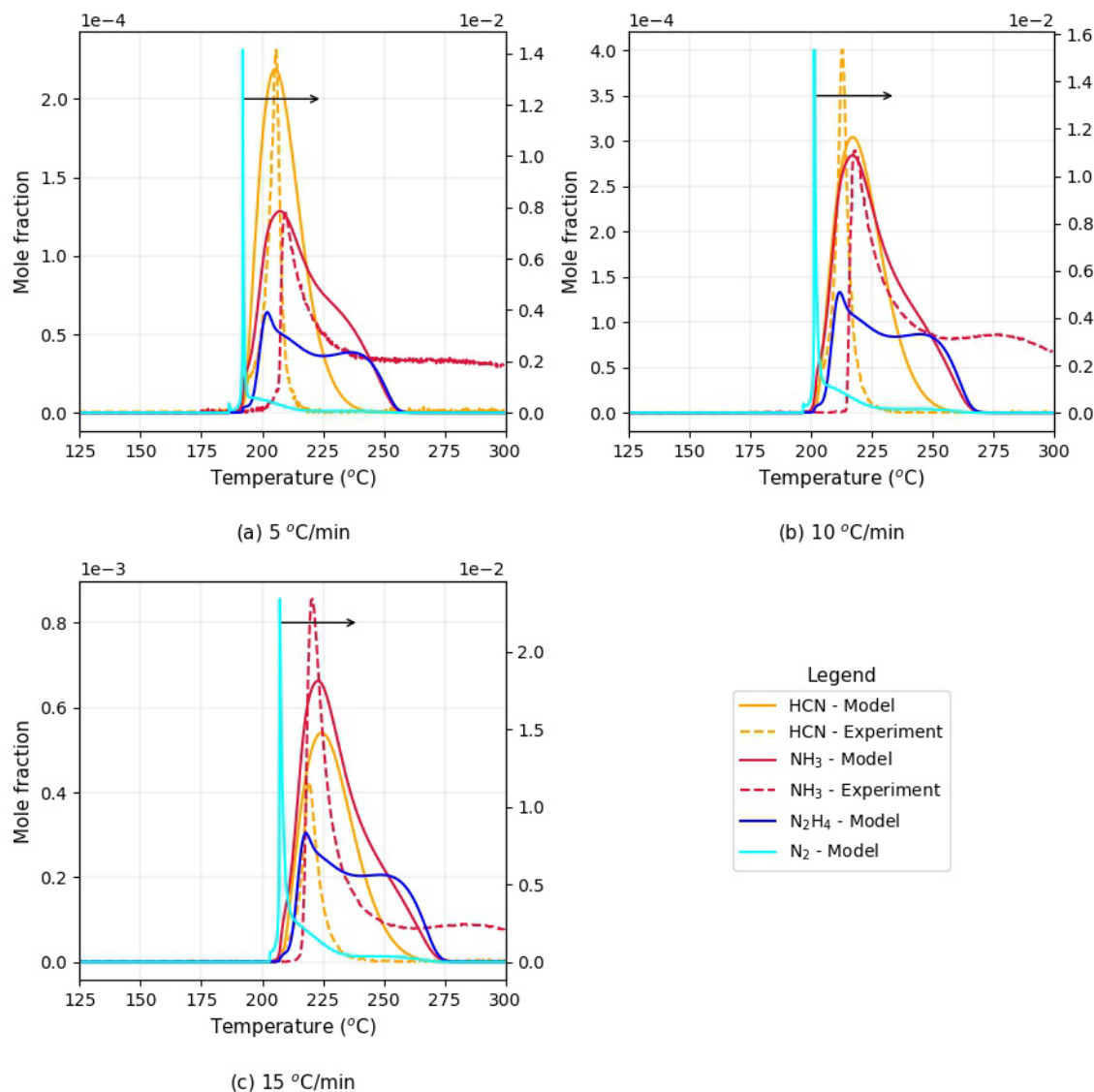


Figure 7-6. Comparison between the experimental and model results for product species evolution from 1 mg of TAGzT sample.

The experimental species evolution profiles shown in Figure 7-6 reveal that HCN production is followed by NH<sub>3</sub>. The developed reaction mechanism suggests the formation of CN<sup>-</sup> along with HCN from AzT<sup>2-</sup> decomposition. As discussed in Section 7.5.2, CN<sup>-</sup> promotes TAG<sup>+</sup> decomposition which leads to the formation of NH<sub>3</sub>. The chemical kinetics model reasonably predicts the NH<sub>3</sub> peak using the reduced reaction mechanism. In experiments, with the increase in heating rate, the height of NH<sub>3</sub> peak increases and even exceeds the HCN peak for 15 °C/min. This trend is also captured by the model. A small amount of NH<sub>3</sub> continues to evolve during step 3 of the mass loss. The model under-predicts NH<sub>3</sub> evolution in this region. This might be caused by reactions among the predicted residual products (formoguanamine and melamine) releasing NH<sub>3</sub> in the process.

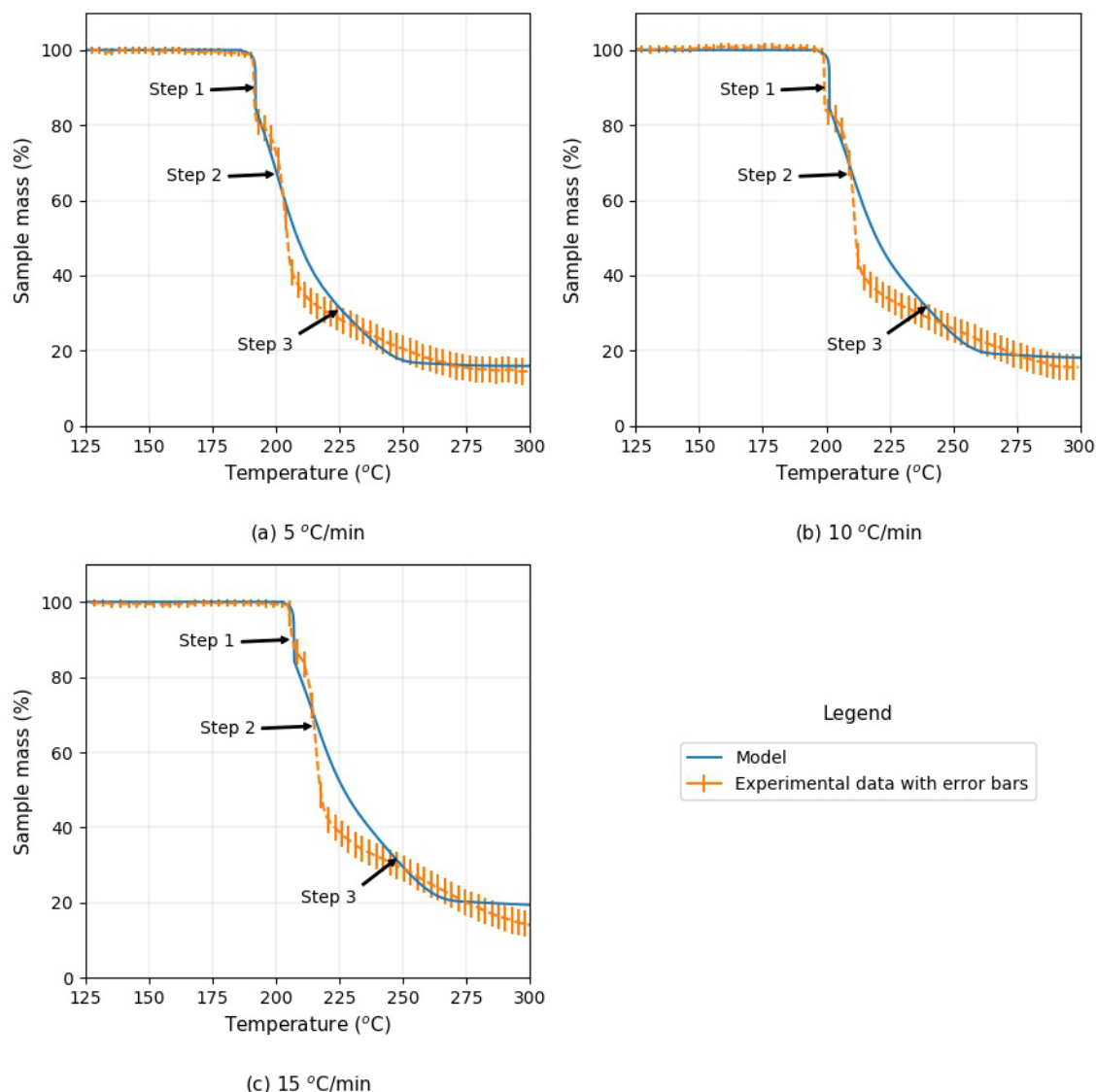


Figure 7-7. Comparison between the experimental and model results for mass loss from TAGzT sample.

Figure 7-7 shows a comparison between the experimental and calculated mass-loss profiles at 5, 10, and 15°C/min heating rates. The three mass-loss steps observed in the experimental results are also predicted by the chemical kinetics model with the help of the reaction mechanism. During step 1, a mass loss of approximately 18, 12, and 10 % occur at 5, 10, and 15°C/min heating rates, respectively. The unimolecular reactions of  $\text{AzT}^{2-}$  which release  $\text{N}_2$  are mainly responsible for step 1 of the mass loss profile. The model accurately reproduces its location and size. For steps 2 and 3 of the mass loss, the chemical kinetics model is successfully able to predict the step sizes but overpredict and under-predict the temperature ranges, respectively. This is possibly due to the highly exothermic decomposition reactions during step 2 (shown in Figure 7-2-b) which increases the decomposition rate, and hence the mass loss. The rapid release of  $\text{N}_2$  during the experiments which throws away the TAGzT sample outside the crucible is also partially responsible for this mismatch. The unavailability of accurate evaporation rates in the literature for different product species of TAGzT also adds to the uncertainty in the model results. Evaporation parameters used in the model are provided Table 7-1. The model is able to predict the residue mass percentage within the range of experimental uncertainty for all heating rates.

Table 7-1. Optimized parameters of the Arrhenius form for calculating liquid-to-gas conversion rates,  
 $k_{lg} = A \exp(-E_v/R_u T)$ .

| Evaporating species           | Pre-exponential, A (s <sup>-1</sup> ) | Activation energy, $E_v$ (kJ/mol) |
|-------------------------------|---------------------------------------|-----------------------------------|
| HCN                           | $9.0 \times 10^0$                     | 26.3                              |
| NH <sub>3</sub>               | $4.0 \times 10^2$                     | 23.1                              |
| N <sub>2</sub>                | $1.0 \times 10^2$                     | 6.0                               |
| N <sub>2</sub> H <sub>4</sub> | $2.0 \times 10^6$                     | 44.5                              |
| TAG                           | $2.0 \times 10^{10}$                  | 117.2                             |
| N <sub>2</sub> H <sub>2</sub> | $2.0 \times 10^6$                     | 44.5                              |
| INTM110F                      | $4.0 \times 10^8$                     | 104.6                             |
| INTM89A                       | $2.0 \times 10^9$                     | 92.0                              |
| INTM74C                       | $2.0 \times 10^9$                     | 92.0                              |
| INTM59E                       | $2.0 \times 10^9$                     | 92.0                              |

Figure 7-8 shows the model predictions for conversion of TAGzT into its decomposition products at 5 °C/min heating rate. Approximately 35.3% of TAGzT by mass converts to N<sub>2</sub>. Most of the N<sub>2</sub> is formed during steps 1 and 2 of the mass loss. It can be noted that step 1 mass loss is entirely due to N<sub>2</sub>. Other major decomposition products of TAGzT are TAG, formoguanamine, HCN, guanidine, NH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>, diaminoguanidine, melamine, 3-azido-1H-1,2,4-triazole, and monoaminoguanidine. FTIR data from the current study and Kumbhakarna et al. [134] suggest that formoguanamine and melamine stay in the liquid phase as residue while all other products evolve in the gas phase. Guanidine, diaminoguanidine, and monoaminoguanidine could not be identified in the study by Kumbhakarna et al. [134] due to their overlapping FTIR bands with TAG. Figure 7-8 shows the production of approximately 1.3% of 3-azido-1H-1,2,4-triazole by mass which is responsible for the prominent FTIR band observed by Kumbhakarna et al. [134] at 2147 cm<sup>-1</sup> wavenumber.

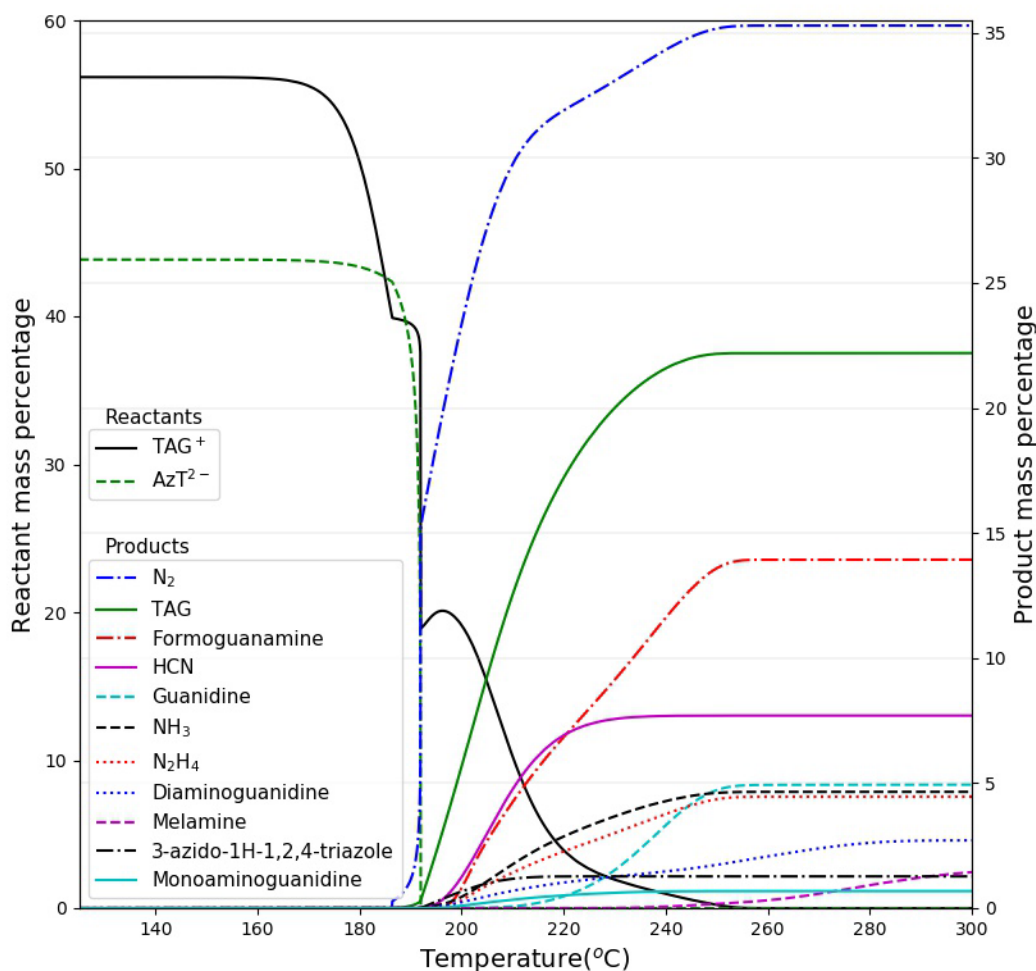


Figure 7-8. Product distribution for TAGzT decomposition at 5 °C/min heating rate.

## 7.6 Summary and conclusions

In this study, the liquid-phase decomposition of TAGzT was investigated and analyzed using quantum chemical calculations, thermolysis experiments, and kinetics modeling. A detailed reaction mechanism with 495 elementary reactions and 355 species was developed. The elementary reactions and intermediate species were identified using hybrid density functional methods. Thermodynamic parameters obtained from the complete basis set CBS-QB3 compound method calculations were used to evaluate the reaction barriers in the developed mechanism. IEFPCM solvation model was used for all quantum chemical calculations. Using the thermolysis experiments and kinetics modeling, the reaction barriers in the detailed mechanism were optimized. Using a sensitivity analysis technique, a reduced reaction mechanism with 90 elementary reactions and 70 species was also generated. The reduced mechanism was validated using the species evolution and mass loss profiles obtained from the thermolysis experiments at three different heating rates. A satisfactory match between experimental and calculated results was achieved. This indicates that the developed mechanism includes most of the key decomposition reactions of TAGzT in the liquid phase. Based on the analysis of the thermolysis experiment and chemical kinetics model results, the following conclusions can be drawn.

1. Somewhat below the melting point, TAGzT decomposes via unimolecular steps in the solid phase to release  $N_2$  gas. It is highly likely that one of the tetrazole rings of  $AzT^{2-}$  dianion opens up to successively release two  $N_2$  molecules.
2. In the liquid phase, the decomposition process initiates with  $AzT^{2-}$  and is followed by  $TAG^+$ .  $AzT^{2-}$  decomposes primarily via a single pathway which is supported by three supplementary pathways whereas  $TAG^+$  decomposes via five competing pathways.
3. HCN and  $CN^-$  are the major decomposition products of  $AzT^{2-}$ . Once enough HCN and  $CN^-$  are formed, the supplementary pathway S1, based on the autocatalytic effect of HCN and  $CN^-$ , becomes much more important.
4. Out of the five decomposition pathways for  $TAG^+$ , the unimolecular decomposition pathway for  $TAG^+$  (P2) plays a relatively more significant role followed by the TAG decomposition pathway in the presence of cyanamide (P5). Cyanamide is formed from the successive nucleophilic substitution pathway (P1).
5. Cyanamide formed from  $TAG^+$  decomposition has an autocatalytic effect on TAG and  $NH_2NHCHNH$  (INTM 59A) decomposition.
6. The major residual products from liquid-phase decomposition of TAGzT are two triazine derivatives – formoguanamine and melamine.
7. The major liquid-phase decomposition products of TAGzT which evolve in the gas phase are  $N_2$ , TAG, HCN, guanidine,  $NH_3$ ,  $N_2H_4$ , diaminoguanidine, 3-azido-1H-1,2,4-triazole, and monoaminoguanidine.

## CHAPTER 8

### A MULTI-PHASE COMBUSTION MODEL FOR RDX-TAGZT PSEUDO-PROPELLANT WITH BUBBLE FORMATION AND DETAILED CHEMICAL KINETICS

#### 8.1 Introduction

Kumbhakarna et al. [121] developed a combustion model for RDX-TAGzT mixtures to analyze the combustion wave structure and burn-rate variation with pressure for different mixture compositions. The obtained burn-rates at low pressures were in good agreement with the experimental data, whereas the model under-predicted burn-rates at higher pressures. The major drawbacks of the model were the uncertainties in the liquid-phase decomposition process and interfacial mass transfer at the bubble surface in the melt-layer. Due to the unavailability of a detailed liquid-phase reaction mechanism, a global reaction mechanism was used in the melt layer. Also, the liquid-phase decomposition products were assumed to instantly collect inside the bubbles.

In this work, the multi-phase combustion model developed for self-deflagration of RDX monopropellant (described in CHAPTER 6) was extended for a multi-component pseudo-propellant. In contrast to the model by Kumbhakarna et al. [121], the bubble growth due to interfacial mass transfer was modeled by taking into account the species vapor pressure, species size, temperature, solution viscosity, super-saturation ratio, bubble size, surface tension, and pressure. Also, detailed reactions mechanisms were used in both gas and liquid phases. An updated gas-phase mechanism was developed in this study. The updated gas-phase mechanism was based on the updated gas-phase reaction mechanism for RDX (discussed in CHAPTER 6) and the gas-phase reaction mechanism for TAGzT by Kumbhakarna et al. [121]. Several other new reactions were also added, and are discussed in this chapter. For the liquid phase, a detailed mechanism was developed using the updated liquid-phase reaction mechanisms for RDX [34] and TAGzT. The liquid-phase interactions among RDX, TAGzT, and their decomposition products were also studied using a combined experimental and theoretical approach. The interaction chemistry explains the experimental observations made in the current study and by Mason et al. [130]. The developed model was used for calculation of burn rate, melt layer thickness, temperature profile, heat feedback from the gas-to-liquid phase, overall heat release in the melt layer, and species evolution profiles in the gas and liquid-phase region for a pressure range of 10–90 atm.

#### 8.2 Model description

Similar to a monopropellant, self-deflagration of a homogeneously mixed pseudo-propellant under constant pressure condition can also be modeled as a one-dimensional, steady-state process in the frame of reference of regressing propellant surface. The entire combustion-wave structure can be segmented into three distinguishable regions: 1) solid phase, 2) melt layer, and 3) gas phase. For both RDX and TAGzT, the decomposition rates below the melting point are very low. Hence, no chemical reactions were assumed to occur in the solid-phase region. The difference in the melting points of pure RDX and pure TAGzT is only about 10°C. Hence, a simplifying assumption was made for the RDX dominated pseudo-propellant mixtures. The melting temperature of the mixture was assumed to be the melting point of RDX (205°C). Also, due to the unavailability of TAGzT properties in the literature thermal conductivity and constant pressure heat capacity of RDX were used for the RDX-TAGzT mixture. The melt layer and gas-phase region were modeled with the same set of governing equations and underlying assumptions as described in CHAPTER 6. To close the system of equations, pyrolysis law for RDX was used. The major difference between the two models is in their liquid- and gas-phase reaction mechanisms. These mechanisms are discussed next.

##### 8.2.1 Liquid-phase decomposition

The liquid-phase decomposition of RDX was accounted for by using the reaction mechanism provided by Khichar et al. [34]. Similar to Khichar et al. [118], HNCO production reactions in the liquid phase were added. The liquid-phase decomposition of TAGzT was accounted for by using the reaction mechanism provided in [142]. The significance of the chemical interactions among RDX, TAGzT, and their

decomposition products was analyzed by performing simultaneous thermal analysis (STA) experiments. Setup details are described in detail by Khichar et al. [139] and are not repeated here. RDX-TAGzT mixture compositions of 90:10 and 80:20 by mass were used. Attempts were made to make the samples homogeneous by properly mixing RDX with TAGzT crystals in a mortar using a pestle. The samples were heated at a constant heating rate of 15 °C/min. The experimentally obtained mass-loss and DSC data for RDX, TAGzT, and RDX-TAGzT mixtures are shown in Figure 8-1. Figure 8-1(a) shows that RDX-TAGzT mixtures decompose at temperatures below the decomposition temperatures for both RDX and TAGzT. A strong exothermic peak is also observed near the melting point of TAGzT (195 °C) for both the mixture samples, shown in Figure 8-1(b). Note that this exothermic peak is absent in the case of pure RDX and pure TAGzT. This clearly indicates that the chemical interactions among RDX, TAGzT, and their decomposition products significantly alter the overall decomposition process and should be accounted for in the combustion model. Similar inference was also made by Behrens et al. [145] and Hayden [146].

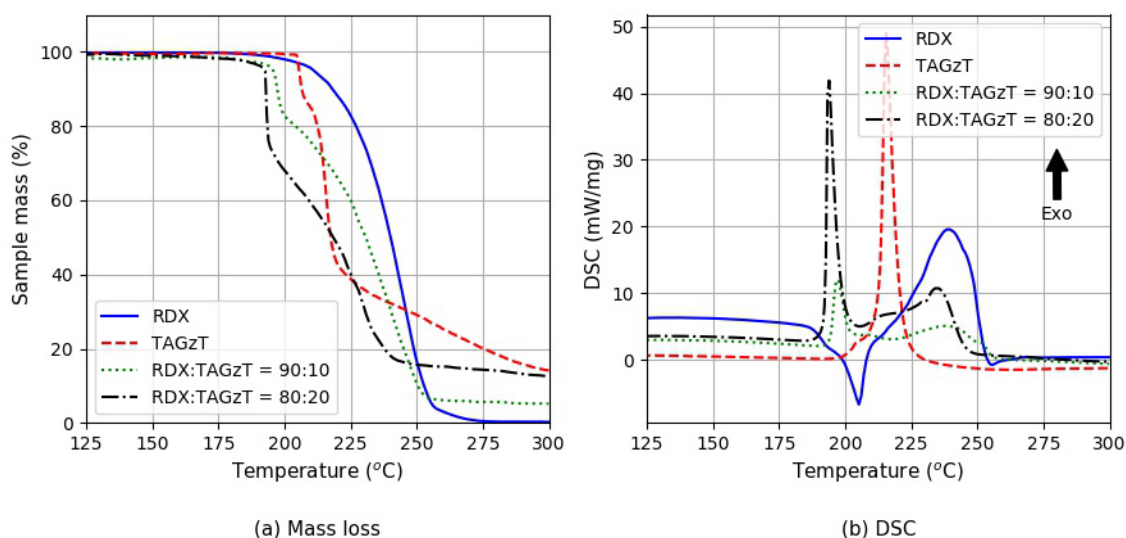


Figure 8-1. The effect of the presence of TAGzT on RDX decomposition. A 15 °C/min heating rate was used for all the samples.

Quantum chemical calculations were used to identify the elementary reactions among RDX, TAGzT, and their decomposition products. The Gaussian 09 software package was utilized for performing these calculations [13]. An approach similar to the earlier work on RDX, HMX, and TAGzT was followed [18,34,134]. An extensive search for identifying the numerous intermediate species and transition states involved in the decomposition process was performed at the B3LYP/6-311++G(d,p) level of theory [98]. The integral equation formalism variant of the polarizable continuum model (IEFPCM) was used to account for the continuum solvation effects [138]. Typical polar solvent, acetonitrile (CH<sub>3</sub>CN) with a dielectric constant of 35.688, was used. The change in the calculated free energy barriers on changing the solvent was found to be less than 1.7 kcal/mol, which is within the uncertainty range of the solvation model. The free energy barriers calculated at B3LYP/6-311++G(d,p) level of theory with IEFPCM solvation model have an uncertainty of approximately 5–7 kcal/mol for ionic species.

The obtained liquid-phase mechanism with the interaction reactions has 36 species and 39 reactions. The reactions can be divided into three groups. The first group of reactions describes a new liquid-phase decomposition pathway for RDX (P1) in the presence of TAGzT. CN<sup>-</sup>, an early decomposition product of TAGzT, reacts with RDX to form INT175a, NO<sub>2</sub><sup>-</sup>, and HCN. The forward free energy barrier for this reaction is 24.4 kcal/mol which is lower than the 39.1 kcal/mol barrier for the dominant initiation (HONO elimination) step for pure RDX. This reaction explains the early evolution of HCN from RDX-TAGzT mixtures compared to pure RDX and pure TAGzT samples, as shown in Figure 8-2. Direct reactions between RDX and NH<sub>3</sub>/N<sub>2</sub>H<sub>4</sub> were also investigated. These reactions were found to have high barriers and

probably do not play a significant role. The second group of reactions describes a new liquid-phase decomposition pathway for TAG<sup>+</sup> (P2) in the presence of RDX. The NO<sub>2</sub><sup>-</sup> anion formed from pathway P1 reacts with TAG<sup>+</sup> cation to form NH<sub>2</sub>NO<sub>2</sub>. An autocatalytic behavior of NO<sub>2</sub><sup>-</sup> is observed in this pathway. NH<sub>2</sub>NO<sub>2</sub> reacts with CN<sup>-</sup> to regenerate NO<sub>2</sub><sup>-</sup> and form NH<sub>2</sub>CN (INTM42A). This pathway supplements the nucleophilic substitution (S<sub>N</sub>2) by the CN<sup>-</sup> pathway for pure TAGzT. Pathways P1 and P2 are partly responsible for the early decomposition behavior of RDX-TAGzT mixtures, as shown in Figure 8-1. The third group of reactions describes the exothermic reactions among the decomposition products of RDX and TAGzT and plays an important role in the early decomposition of RDX-TAGzT mixtures. NH<sub>3</sub>, a decomposition product of TAGzT, can react with HONO, a decomposition product of RDX, to form N<sub>2</sub> and H<sub>2</sub>O. Similarly, N<sub>2</sub>H<sub>4</sub>, a decomposition product of TAGzT, can react with NO<sub>2</sub>, a decomposition product of RDX, to form HONO. HONO can then react with N<sub>2</sub>H<sub>4</sub> via multiple pathways to form N<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, NH<sub>3</sub>, and NO. These reactions explain the early evolution of N<sub>2</sub>O, H<sub>2</sub>O, NH<sub>3</sub>, and NO from RDX-TAGzT mixtures compared to pure RDX and pure TAGzT samples, as shown in Figure 8-2. The experimental species profiles shown in Figure 8-2 were obtained by reducing the FTIR data using the data-reduction model described in Section 2.3.

### 8.2.2 Gas-phase decomposition

Due to the liquid-phase decomposition of RDX and TAGzT, numerous liquid-phase decomposition product species also enter the gas phase along with RDX and TAGzT at the propellant surface. Hence, it is important to include decomposition reactions of all these species along with RDX and TAGzT. The updated gas-phase reaction mechanism for RDX described in CHAPTER 6 and the gas-phase decomposition mechanism for TAGzT provided by Kumbhakarna et al. [121] were included in the updated gas-phase mechanism for RDX-TAGzT mixtures. The updated gas-phase reaction mechanism for RDX includes the gas-phase decomposition reactions of both RDX and its liquid-phase decomposition products. The gas-phase reaction mechanism for TAGzT provided by Kumbhakarna et al. [121] includes oxidation reactions of two of the major decomposition products of TAGzT in the liquid phase, namely, hydrazine and NH<sub>3</sub>. The oxidation reactions were obtained from the work of Dean and Bozzelli [147] and Thaxton et al. [148]. Additional decomposition reactions for all the liquid-phase species (TAGzT products and RDX-TAGzT interaction products) which enter the gas phase were also added to the updated gas-phase mechanism for RDX-TAGzT mixtures. The updated gas-phase mechanism for an RDX-TAGzT mixture has 185 species and 608 reactions. Similar to the liquid phase, quantum chemical calculations were used to identify the elementary reactions in the gas phase. The calculations were performed at B3LYP/6-311++G(d,p) level of theory to determine the rate kinetics parameters [149].

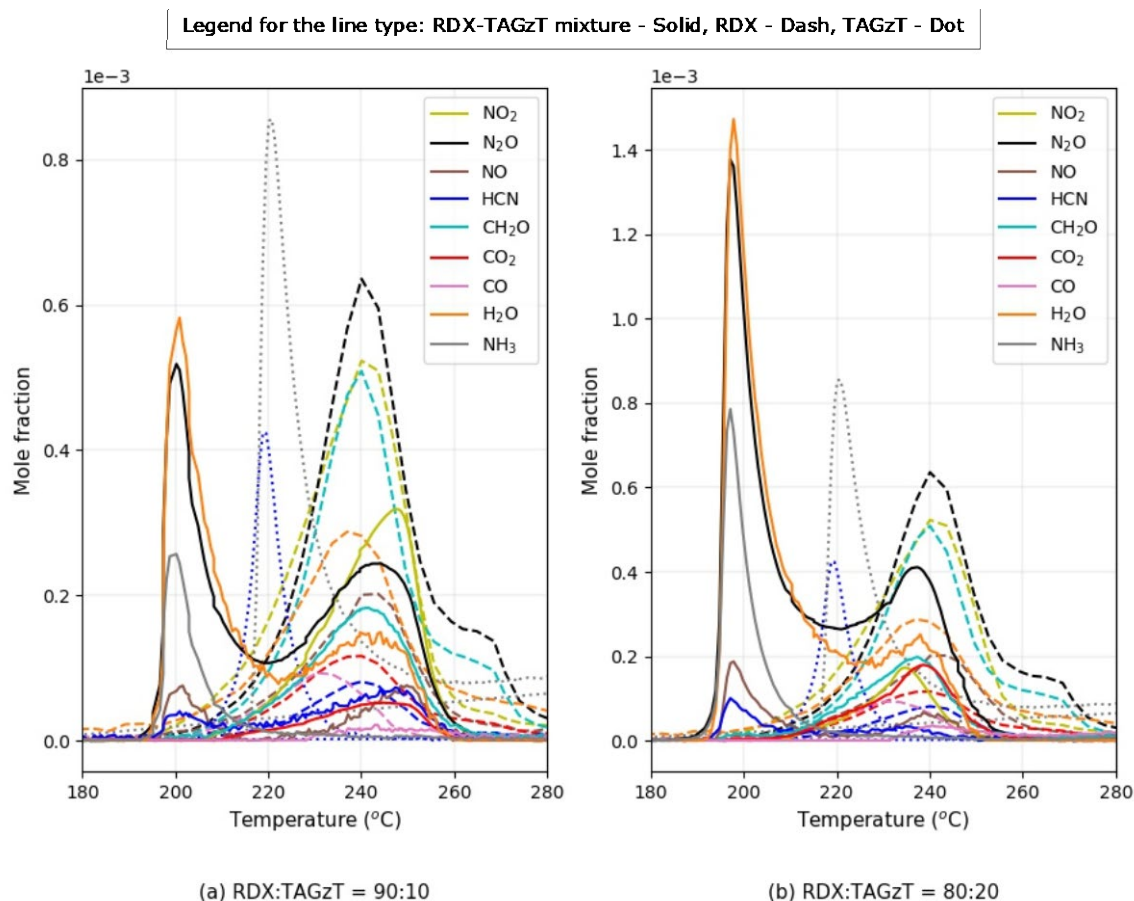


Figure 8-2. Species evolution during thermal decomposition of RDX, TAGzT, and RDX-TAGzT mixtures at 15 °C/min heating rate.

Most of the  $AzT^{2-}$  decomposes in the melt-layer due to the low-barrier decomposition reactions whereas the undecomposed  $TAG^+$  enters the gas phase in its neutral form, TAG. Similar to the liquid phase, gas-phase decomposition of TAG occurs via three competitive pathways labeled as pathways P3–P5 in CHAPTER 7. In pathway P3, an H atom is shifted in a TAG molecule with the help of another TAG molecule. The resultant intermediate undergoes three unimolecular steps to release  $NH_3$ ,  $N_2H_2$ , and  $NH_2NHCN$ . In pathway P4, TAG undergoes unimolecular dissociations to form  $N_2H_4$ , cyanamide (INTM 42A), and INTM 30A. INTM 30A readily reacts with  $NO_2$  to form  $N_2$  and HONO. In pathway P5, TAG dissociates to form cyanamide,  $NH_3$ , and  $N_2$ . Cyanamide acts as an autocatalytic agent in this pathway and reduces the barrier for TAG decomposition. Pathway P5 has smaller barriers compared to the pathways P3 and P4.

Apart from  $AzT^{2-}$ ,  $TAG^+$ , and TAG, the neutral liquid-phase decomposition products of TAGzT and RDX-TAGzT interaction reactions also enter the gas-phase at the propellant surface. Whereas, the charged liquid-phase decomposition products are unlikely to directly enter the gas phase and were assumed to convert to their corresponding stable neutral form at the interface. Elementary reactions for all such molecules which lead to the formation of final decomposition products were investigated and added to the updated gas-phase mechanism. For most of these species, their liquid-phase decomposition reactions were re-investigated in the gas-phase.

### 8.3 Results and discussion

The multi-phase combustion model was used to evaluate the combustion wave-structure of the RDX-TAGzT mixture in the pressure range of 10–90 atm. The high-pressure range was selected because of its relevance to the rocket motors. For all simulations an initial (unburnt) propellant temperature of 293

K was used. An RDX:TAGzT mass ratio of 75:25 was used for most of the model simulations because the corresponding experimental results are available from Mason et al. [130]. Burn rate, melt layer thickness, temperature profile, heat feedback from gas-to-liquid phase, overall heat release in the melt layer, and species evolution profiles in the gas and liquid-phase region were calculated. The effect of mixture composition was also studied by using the model for RDX:TAGzT mass ratio of 90:10. The results presented in this section demonstrate the significance of including the updated liquid- and gas-phase decomposition mechanisms, and the bubble formation phenomena in the melt layer.

The burn-rate variation with pressure is shown in Figure 8-3. The obtained burn-rates for the RDX-TAGzT 75:25 mixture is higher than pure RDX at all pressures. This result is in agreement with the experimental observations of Mason et al. [130]. Similar to the case of a monopropellant, the burn-rate of a pseudo-propellant also increases with an increase in pressure. This increase is due to the fast gas-phase exothermic reactions pressed near the propellant burn surface at high pressures which increases the heat feedback to the condensed phase. The early increase in temperature in the gas-phase at higher pressures can be observed in Figure 8-4. The model predictions for burn-rate are in excellent agreement with the experimental data of Mason et al. [130]. An improved match has been obtained compared to the earlier combustion model of Kumbhakarna et al. [27] where liquid-phase decomposition of RDX and TAGzT mixture was modeled using 8 global reactions. Figure 8-3 clearly indicates the significance of including a detailed liquid-phase reaction mechanism in a combustion model for a pseudo-propellant. The difference between the calculated burn-rates from the current model and Kumbhakarna et al. model [27] increases with pressure. This indicates that the effect of including a detailed liquid-phase reaction mechanism increases with pressure. This result is in agreement with the trend observed for RDX monopropellant (refer CHAPTER 6).

The burn rate is often expressed in the form,  $r_b = aP^n$ , where  $r_b$  is the burn-rate,  $a$  is the pre-exponential factor,  $P$  is the pressure and  $n$  is the pressure exponent. Using the current model, the pressure exponent for the RDX-TAGzT 75:25 mixture was found to be 0.856 and matches very well with the experimental values of 0.863 by Mason et al. [130]. The combustion model was also used to study an RDX-TAGzT mixture with a mass ratio of 90:10. The burn rate was found to be 2.4 cm/s at 90 atm. The corresponding burn-rate values for RDX and RDX-TAGzT (75:25) mixture were 2.04 cm/s and 2.82 cm/s, respectively. The results show that the burn-rate of the pseudo-propellant increases with an increase in the TAGzT mass percentage from 0 to 25. This agrees with the experimental results of Mason et al. [130].

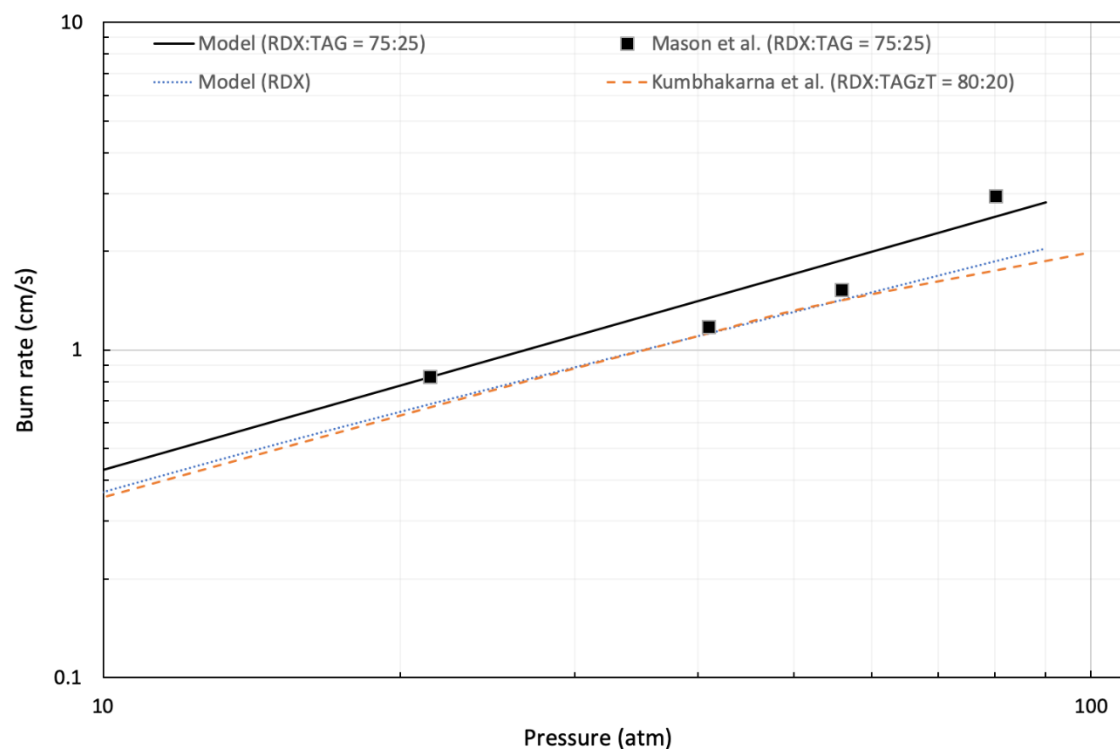


Figure 8-3. Variation of burn-rate with pressure for self-deflagration of RDX-TAGzT pseudo-propellant and RDX monopropellant. References are provided in text.

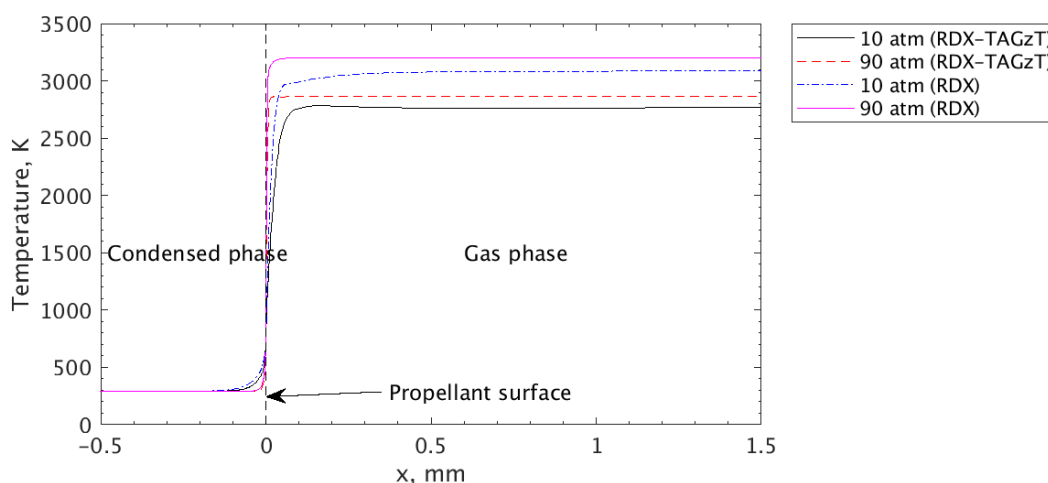


Figure 8-4. Temperature profiles for self-deflagration of RDX-TAGzT (75:25) pseudo-propellant and RDX monopropellant.

Figure 8-4 shows the temperature distribution during RDX-TAGzT (75:25 by mass) constant pressure combustion at 10 and 90 atm. RDX data is also provided for comparison. Similar to the case of RDX, with an increase in pressure, the temperature profile becomes steeper in both gas and condensed phases. Steep temperature profiles in the gas-phase at higher pressures explain the high burn-rates due to the increased conductive heat feedback from the gas phase to the melt layer. In the solid phase, exponentially increasing profiles were obtained whereas almost linear temperature profiles were obtained in the melt layer. Monotonously increasing temperature profiles were obtained in the gas phase. Similar to the case of self-deflagration of RDX, a two-stage flame structure in the temperature profile is not present for self-deflagration of the RDX-TAGzT mixture. It is also important to note that the final flame

temperature for the RDX-TAGzT mixture is lower than RDX at all pressures. This is due to the high nitrogen content of TAGzT which results in the formation of molecular nitrogen at a lower temperature.

Since the liquid-phase decomposition of TAGzT is more exothermic compared to RDX, the melt-layer thickness of the RDX-TAGzT mixture is smaller and the surface temperature is higher compared to RDX. For the RDX-TAGzT mixture, the melt-layer thick decreases from  $7.6\ \mu\text{m}$  to  $2.8\ \mu\text{m}$  when the pressure is increased from 10 to 90 atm. Whereas, the propellant surface temperature increases from 682 K to 790.3 K when the pressure is increased from 10 to 90 atm. The increase in surface temperature with pressure is due to the increase in heat feedback from the gas phase.

For an RDX-TAGzT mixture, the extent of decomposition in the melt layer can be represented by the mass fractions of RDX,  $\text{TAG}^+$ , and  $\text{AzT}^{2-}$  at the propellant surface. In the presence of bubbles at the propellant surface, a weighted mass fraction of RDX was calculated. Due to the small reaction barriers,  $\text{AzT}^{2-}$  completely decomposes in the melt layer at both 10 atm and 90 atm pressures. For a 75:25 RDX-TAGzT mixture, the RDX mass fraction at the propellant surface is 0.729 and 0.714 at 10 atm and 90 atm, respectively. The  $\text{TAG}^+$  mass fraction at the propellant surface is 0.048 and 0.047 at 10 atm and 90 atm, respectively. Note that most of the  $\text{TAG}^+$  only converts to TAG due to the presence of  $\text{CN}^-$  in the melt layer. Similar to the case of RDX monopropellant, the current results show that with an increase in pressure the extent of decomposition slightly increases in the melt layer. This behavior is the combined effect of an increase in propellant surface temperature and a decrease in melt layer thickness with an increase in pressure. Moreover, at higher pressures, the vaporization tendency of the liquid-phase decomposition products decreases. Hence, these products remain dissolved and participate in secondary decomposition reactions.

For an RDX-TAGzT mixture, the extent of bubble formation in the melt layer with pressure follows the same trend as in the case of RDX monopropellant. With an increase in the pressure, the fractional volume of bubbles decreases. 1.2% and 0.6% void fraction values were obtained for 10 atm and 90 atm, respectively. Bubble formation only becomes dominant at low pressures ( $\sim 1$  atm).

Figure 8-5 shows the mole fraction profiles of the major species in the gas-phase region for self-deflagration of 75:25 RDX-TAGzT mixture at 10 and 90 atm. Experimental gas-phase species profiles are not yet available in the literature for comparison. Similar to RDX monopropellant, a two-stage flame structure is obtained in the species profiles. A comparison with RDX results (shown in Figure 6-9) shows a change in the composition of the final gas-phase decomposition products ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and  $\text{N}_2$ ). The mole fractions of  $\text{N}_2$  and  $\text{H}_2$  increase whereas mole fractions of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  decrease on addition of TAGzT to RDX. The mole fraction of  $\text{CO}$  remains almost the same. The relative concentrations of these species govern the final flame temperature. The high nitrogen content of TAGzT is responsible for the changed final decomposition product composition and decreased flame temperature (refer Figure 8-4).

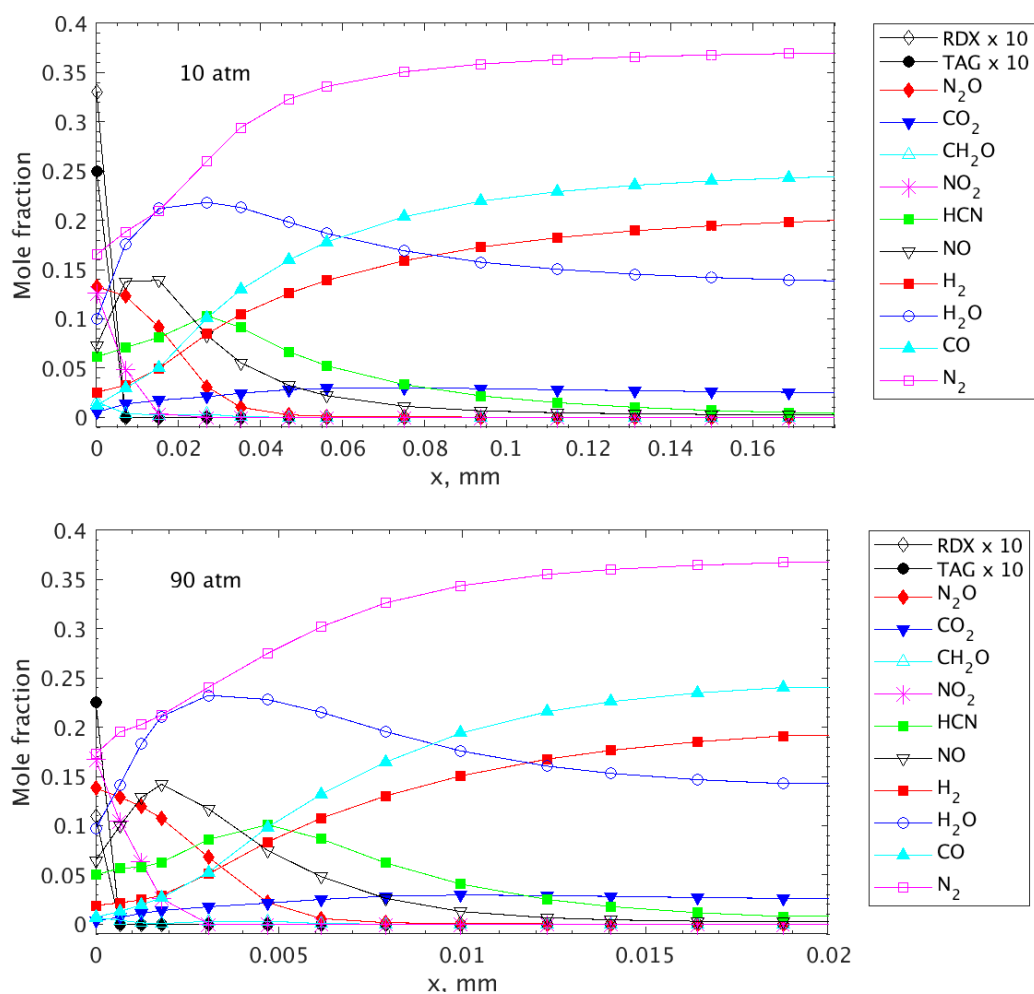


Figure 8-5. RDX-TAGzT (75:25 by mass) flame structure in the gas phase.

Figure 8-5 also shows that as the pressure increases, the shape of gas-phase species profiles remains almost the same but are compressed in the spatial dimension. At higher pressures, the exothermic gas-phase reactions occur very close to the propellant surface which increases the heat feedback and hence the burn rate. On closer inspection of the RDX flame structure, it can be noted that the relative ratio of  $NO_2:N_2O$  at the propellant surface increases with pressure. A similar trend is also present in the case of RDX.

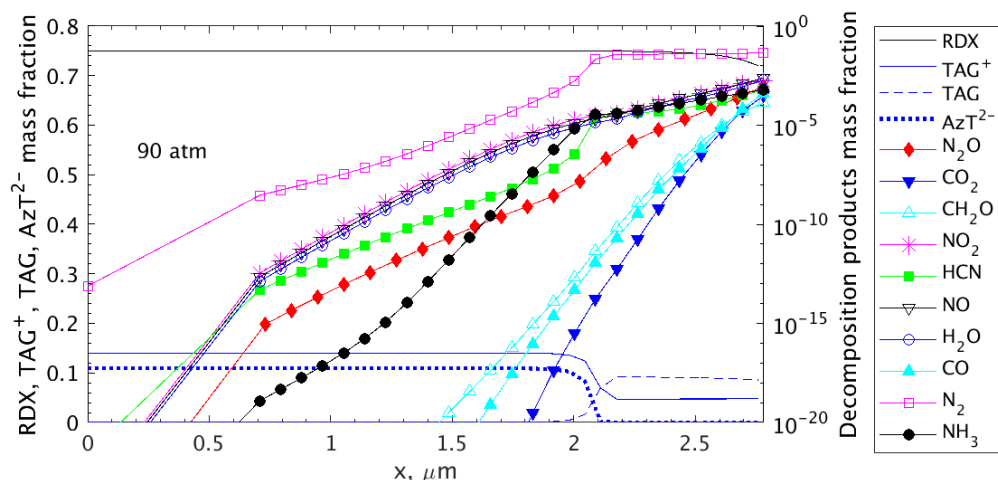


Figure 8-6. Species profiles in the liquid-phase volume fraction of the melt layer during self-deflagration of 75:25 RDX-TAGzT mixture at 90 atm.

Figure 8-6 shows the mass fraction profiles of the major reactant and product species in the melt layer for self-deflagration of 75:25 RDX-TAGzT mixture at 10 and 90 atm. Similar to the liquid-phase thermal decomposition results of TAGzT (refer Figure 7-1), a two-stage decomposition process is also present in the melt layer of the RDX-TAGzT combustion wave. This behavior is likely due to the low-barrier decomposition pathways of  $AzT^{2-}$ . Early growth of  $N_2$  and HCN concentration in the melt layer supports this inference.

The heat feedback from gas-to-liquid phase ( $\dot{q}_g$ ) and overall heat release in the melt layer ( $\dot{Q}_c$ ) were also evaluated using the combustion model.  $\dot{q}_g$  values of 182.4 and 1216.5 cal cm<sup>-2</sup> s<sup>-1</sup> were obtained at 10 atm and 90 atm, respectively.  $\dot{Q}_c$  values of 250.9 and 927.3 cal cm<sup>-2</sup> s<sup>-1</sup> were obtained at 10 atm and 90 atm, respectively. Experimental data is not available in the literature for comparison. The computed values indicate an increase in the heat feedback from the gas phase and heat release in the melt layer with an increase in pressure. Unlike the case of RDX monopropellant, the heat release in the melt layer due to the liquid-phase decomposition reactions is of the order of the heat feedback from the gas phase even at the high pressure (90 atm). This clearly indicates the significance of including both liquid- and gas-phase decomposition mechanism in the combustion model of RDX-TAGzT pseudo-propellant.

## 8.4 Conclusions

In this study, both liquid- and gas-phase decomposition mechanisms for an RDX-TAGzT mixture were developed using a combined computational and experimental approach. Special efforts were made to understand the chemical interaction between RDX and TAGzT in both the phases. A recently developed multi-phase combustion model for constant pressure self-deflagration of RDX was further improved to simulate pseudo-propellant combustion. Similar to the monopropellant model, the current model also accounts for both liquid- and gas-phase decomposition reactions along with bubble formation in the melt layer. The model was used to estimate the RDX-TAGzT flame structure in a pressure range of 10–90 atm. An excellent agreement was achieved with the experimental burn-rate data. The results indicate that approximately 2.8% of the initial mass of RDX decomposes in the melt layer at 10 atm, and increases to about 4.8% at 90 atm. Comparison of these values with the case of RDX monopropellant shows that the extent of RDX decomposition in the liquid phase increases due to the presence of TAGzT. The liquid-phase decomposition mechanism developed in this study explains the chemical interaction between RDX and TAGzT. Specific elementary reactions have been found out which are responsible for the enhanced decomposition. The low reaction barriers associated with these reactions support the enhanced decomposition. Since significant amount of decomposition occurs in the liquid phase, it is important to include detailed liquid-phase chemical kinetics along with detailed gas-phase chemical kinetics in the combustion models.

## CHAPTER 9

### INVESTIGATION OF THERMAL DECOMPOSITION PROCESSES OF HMX AND TAGzT MIXTURES USING THERMOLYSIS EXPERIMENTS AND QUANTUM CHEMICAL CALCULATIONS

#### 9.1 Introduction

HMX-TAGzT mixtures were studied by Flanagan et al. [150] using mass spectroscopy and gas chromatography techniques at moderate and high temperatures using a high heating rate (2000 K/s). High temperature pyrolysis experiments suggested that the combustion of HMX is modified primarily by  $\text{NH}_3$ , which is a decomposition product of TAGzT. Hence, it is evident that the presence of TAGzT significantly impacts the decomposition characteristics when mixed with RDX or HMX. 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  $\sim 70$  K higher than RDX). Such a difference in melting temperatures may affect the thermal decomposition characteristics of RDX and HMX in mixtures with TAGzT.

In this chapter, using TGA/DSC coupled with FTIR spectroscopy, the thermal decomposition characteristics of HMX-TAGzT mixtures are studied at low and moderate temperatures (373-673 K) using low heating rates. Previous studies involving RDX/HMX and TAGzT mixtures were primarily studied by performing experiments. Here-in along with experiments, quantum chemical (QC) calculations are performed to identify important reactions responsible for increased rate of HMX decomposition in presence of TAGzT.

#### 9.2. Details of experimental studies

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) combined with FTIR spectroscopy were used to perform thermal decomposition studies of HMX and TAGzT mixtures. For each experiment, approximately 1 mg of the mixture 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. 151. The spectral transmittance data obtained from FTIR are analyzed following previously used procedures [151] to calculate the mole fraction of several IR-active gaseous species released during decomposition.

#### 9.3 Details of quantum chemical (QC) calculations

The Gaussian 16 [152] program package was used to study reactions involving the two components of TAGzT and their 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 [153,154]. 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 [98]. In most cases, the CBS-QB3 compound method was also used based on input geometry and frequency calculations from B3LYP/6-311++G(d,p). To consider condensed-phase reactions, the CPCM solvation model [155] was used along with acetonitrile as the solvent.

#### 9.4. 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, experiments were performed 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.

#### 9.4.1 Results from TGA and DSC studies

The thermolysis experiments showed that mass-loss and heat release took place in two major exothermic steps for all three mixture ratios and heating rates. Figure 9-1 (a) and (b) show the comparison of TGA mass loss and DSC profiles at three different heating ratios (15, 20 and 25 K/min) for the 90-10 mixture ratio. The first mass loss amounts to  $\sim 10\%$ , which is believed to be largely the wt% of TAGzT added in the mixture. Figure 9-1 (a) shows that depending on the heating rate used, the first phase of decomposition starts at  $\sim 483$  K. It is to be noted that as the heating rate is reduced, decomposition starts at a lower temperature and vice-versa. This trend also applies to the other HMX-TAGzT mixture mass ratios of 80-20 and 70-30. As heating rate is reduced, the mixture is exposed to lower temperatures for a longer period of time, which increases the extent of sample sublimation and/or solid-phase reactions, leading to start of mass loss earlier than that at higher heating rates. After completion of first mass loss near  $\sim 500$  K, the second phase of major mass loss begins at  $\sim 553$  K, immediately after a very small endothermic peak due to melting of HMX 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. [123].

In addition to the above-mentioned two major mass loss steps, 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. 9-1 (a) that even before HMX melts at  $T = 553$  K,  $\sim 7$ – $8\%$  of mass loss due to decomposition of HMX has already taken place for the 90-10 mixture mass ratio. However, the extent of mass loss of HMX is not significant ( $\sim 2\%$  at  $25$  K/min to  $\sim 3.7\%$  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  $\sim 4$ – $5\%$  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 has a measurable effect on the mass loss of HMX.

The comparison of TGA/DSC curves for 90-10 mixture ratio with that of pure HMX and TAGzT is shown in Fig. 9-2 for a heating rate of  $15$  K/min. From the figure, it is evident that the endothermic peak at  $553$  K corresponds to the melting of HMX. It is noted that the presence of TAGzT in the mixture did not

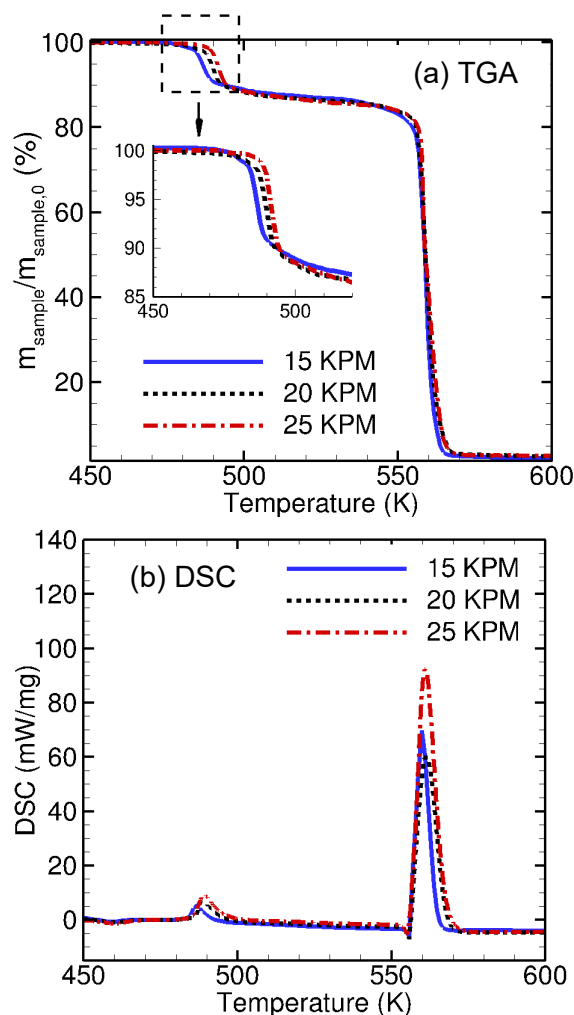


Figure 9-1. TGA and DSC results for HMX-TAGzT (90-10) mixture for three heating rates.

alter the melting point of HMX. Furthermore, 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 temperature of initiation of decomposition of individual ingredient in the 90-10 mixture ratio.

The TGA and DSC thermal decomposition behavior of the three different mixture ratios of HMX-TAGzT as well as pure HMX are shown in Fig. 9-3. Similar to the HMX-TAGzT (90-10) mixture results discussed above, two major mass loss steps are observed for the 80-20 and 70-30 mixture mass ratios. For the 80-20 case, 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 higher. For the HMX-TAGzT (80-20) mixture ratio, the mass loss during this intermediate phase of decomposition ranges from ~10% at 25 K/min to ~25% at 15 K/min.

For the 70-30 mass mixture ratio, the early interaction between HMX and TAGzT is even stronger. As can be observed from the figures, mass loss during the first phase of decomposition for 70-30 is significantly higher than that of the initial wt% of TAGzT in the mixture (~60% mass loss). This indicates that along with TAGzT, HMX in the 70-30 mixture decomposes significantly during the first phase of mass loss in the temperature range of ~473-493 K.

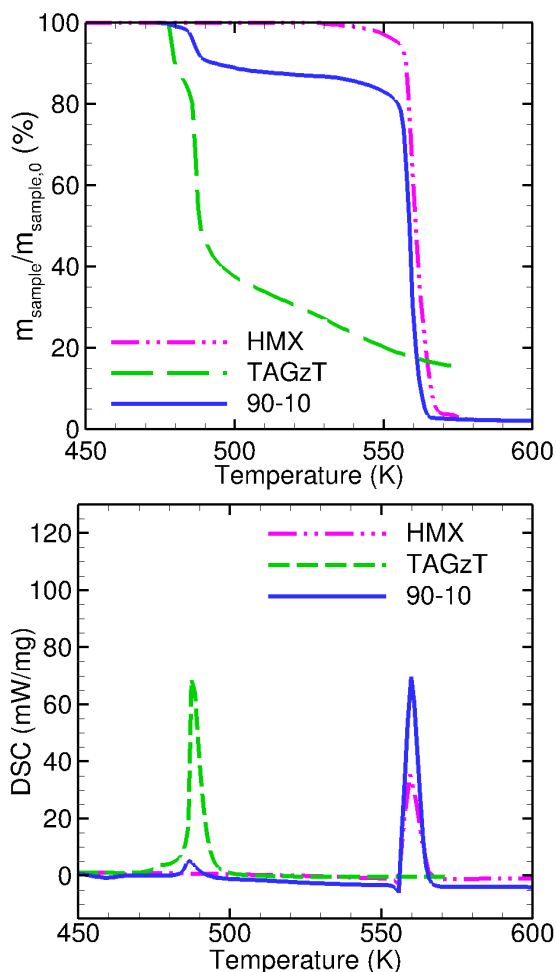


Figure 9-2. Comparison of TGA and DSC results for HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT (15 K/min).

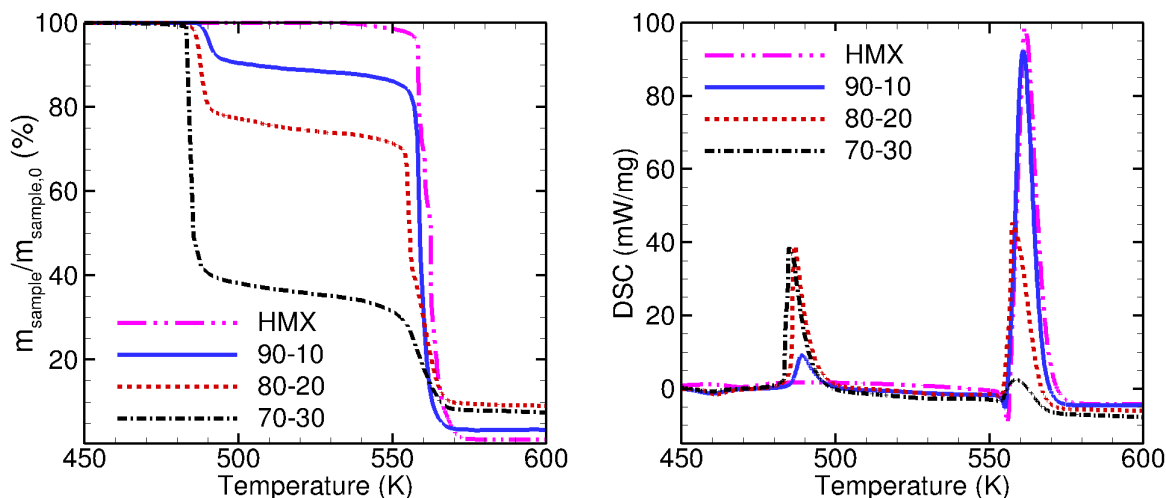


Figure 9-3. TGA and DSC results for HMX and HMX-TAGzT mixtures at different mass ratios (25 K/min).

### 9.4.2 Results for species profiles of evolved gases

Along with mass loss results from TGA/DSC studies, we also obtained FTIR spectra which provide information on IR-active gaseous species evolved during experiments for wavenumbers ranging from 600-3750  $\text{cm}^{-1}$ . By performing a data reduction on the acquired FTIR spectra using the HITRAN database [156], the partial pressure or mole fraction of gaseous species are calculated and shown in Fig. 9-4. The mole fraction of gaseous species released during decomposition of pure TAGzT and HMX are also provided in Fig. 9-4. Mole fraction of each gaseous species released during decomposition of the 90-10 mixture is also compared against pure HMX, which is shown in Fig. 9-5. It can be observed from the above figures that the trend of  $\text{NH}_3$  and  $\text{HCN}$  evolution during TAGzT decomposition has changed significantly compared to pure TAGzT. In pure TAGzT,  $\text{HCN}$  evolves first followed by  $\text{NH}_3$  approximately after 20 K when  $\text{HCN}$  release during decomposition is almost ceased. Furthermore, the mole fraction of  $\text{HCN}$  released during pure TAGzT decomposition is much larger than that of  $\text{NH}_3$  and occurs over a shorter temperature interval (473-493 K) compared to  $\text{NH}_3$ , which is released slowly throughout TAGzT decomposition. Unlike pure TAGzT, the release of  $\text{NH}_3$  and  $\text{HCN}$  occurs simultaneously for the 90-10 mixture, but the mole fraction of  $\text{NH}_3$  released is much larger than that of  $\text{HCN}$ . 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.

Furthermore, from the Fig. 9.4, it can be observed that during the first major mass loss step,  $\text{NH}_3$ ,  $\text{HCN}$  and  $\text{N}_2\text{O}$  are released along with a few other species (possibly an azide and hydrazine, as well the non-IR-active  $\text{N}_2$ ). It is clear that  $\text{N}_2\text{O}$  must arise from an interaction between TAGzT and HMX, or their products. Hence, from the species profiles, it is evident that in addition to TAGzT, HMX also undergoes decomposition to some extent during the first phase of mass loss. As a result, TAGzT and its decomposition products react with HMX. Once the first mass-loss step ends by  $\sim 500$  K, the strength of  $\text{N}_2\text{O}$  peak starts diminishing significantly and no peaks corresponding to  $\text{NH}_3$  and  $\text{HCN}$  exist, which indicates that TAGzT in the mixture has already undergone almost complete decomposition during the first mass loss step. However, the presence of  $\text{N}_2\text{O}$  indicates that HMX undergoes continuous decomposition very slowly even after TAGzT is consumed. Other than  $\text{N}_2\text{O}$ , no new peaks are observed in the spectra till  $\sim 548$  K when decomposition products of HMX, such as  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{HCN}$  are identified. The intensity of these peaks further increases and few more new peaks ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{NO}$ ) are observed once HMX melts at 553 K. The FTIR spectra obtained during liquid-phase decomposition of HMX-TAGzT 90-10 mixture at 553 K is similar to that obtained from decomposition of pure HMX.

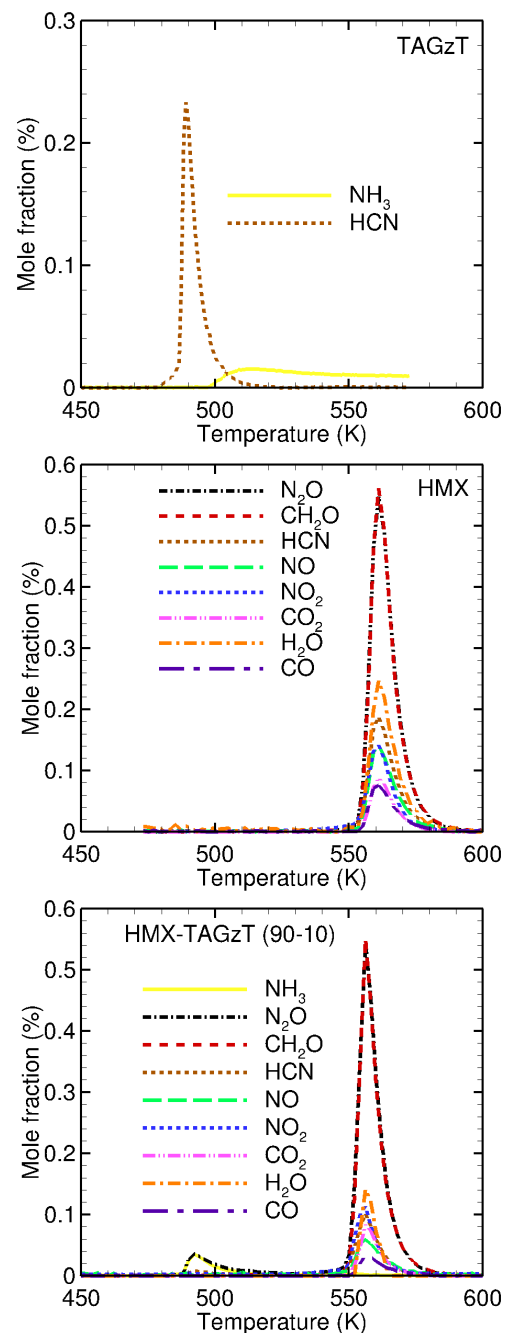


Figure 9-4. Comparison of mole fractions of evolved IR-active species deduced from FTIR transmission spectra during decomposition of HMX-TAGzT (90-10) mixture with pure HMX and pure TAGzT (25 K/min).

Although decomposition of TAGzT has been impacted significantly by the presence of HMX, the temperature peak of maximum condensed-phase decomposition of HMX is reduced by about 5K in the presence of TAGzT. It can be observed from Fig. 9-4 that among the gaseous species released during condensed-phase decomposition of pure HMX,  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  are the primary ones (mole fraction  $\sim 0.6\%$ ). In addition to  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$ , mole fraction of other gaseous species released ( $\text{HCN}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ) are in the range of  $\sim 0.1$ - $0.2\%$  with  $\text{H}_2\text{O}$  having the highest mole fraction ( $\sim 0.2\%$ ) and  $\text{CO}$  being the lowest ( $<0.1\%$ ). It should be noted that  $\text{N}_2$  is the purge gas in TGA-IR transmission chamber, and thus represents the remainder is the mole fractions. Similar trend of gaseous species evolution after HMX melts is observed for the 90-10 mixture as well. The only difference is that the gaseous species evolution starts a little early at  $\sim 548$  K for 90-10 mixture compared to pure HMX for which it starts at  $\sim 553$  K. Thus, it can be concluded that although TAGzT decomposition products react with solid-state or dissolved HMX during first phase of mass loss to accelerate the rate of HMX decomposition, there remains some effect of TAGzT products on condensed-phase HMX decomposition. 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 [146].

The mole fractions of each gaseous species released during decomposition of HMX-TAGzT (80-20) and (70-30) mixtures are shown in Figs. 9-5 and 9-6, respectively. It can be observed from these 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, but to a much larger extent. However, regarding decomposition of HMX in the mixture, there exists significant differences among the mixture ratios. Although the trend of species evolution remains similar with  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  being the primary gaseous species released and  $\text{CO}$  having the lowest mole fraction among all species, the mole fraction of gaseous species released during the second stage of the expected condensed-phase HMX decomposition has reduced significantly compared to 90-10 mixture. Furthermore, from TGA curve in Fig. 9-3 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.

The trend is similar for the 70-30 mixture, but the amount of HMX decomposed during the first stage is very significant and surprising. From these FTIR species profiles, it can be observed that during the first phase of decomposition, in addition to  $\text{N}_2\text{O}$ , additional species are detected corresponding to HMX decomposition, including  $\text{HCN}$ ,  $\text{NO}$ ,  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , along with TAGzT decomposition products  $\text{NH}_3$  and  $\text{HCN}$ . The presence of  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  confirms that the ring opening of HMX has taken place during the first mass loss step even before the melting temperature is reached. Similar to HMX-TAGzT (90-10) and (80-20) mixtures, it is noted that  $\text{N}_2\text{O}$  vanishes after the first phase of decomposition and also the amount of  $\text{N}_2\text{O}$  formed diminishes significantly. In addition to  $\text{N}_2\text{O}$ , IR-active species are again detected near  $\sim 540$  K when

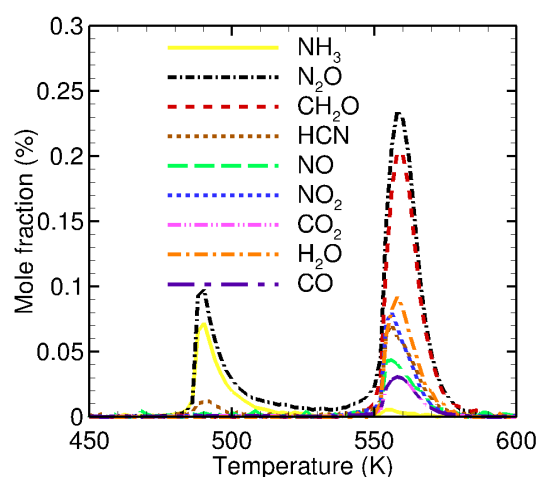


Figure 9-5. Mole fraction of gaseous species released during decomposition of HMX-TAGzT (80-20) mixture (25 K/min).

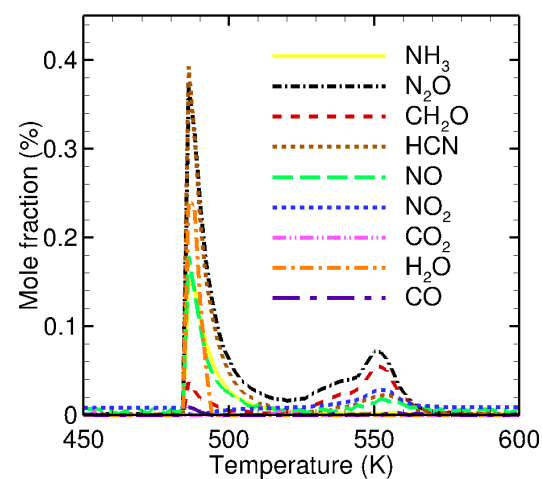


Figure 9-6. Mole fraction of gaseous species released during decomposition of HMX-TAGzT (70-30) mixture (25 K/min).

CH<sub>2</sub>O and HCN are detected. 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, is significantly less than that of observed for the HMX-TAGzT (80-20) and (90-10) mixtures. From the above discussion, it is evident that using different HMX-TAGzT mixture ratios, the extent of decomposition of HMX can be greatly affected.

#### 9.4.3 Results from quantum chemical calculations

Using QC calculations, Patidar et al. [123] concluded that initiation of HMX decomposition occurs via a unimolecular reaction to form HONO and a cyclic intermediate (INT249a; 249 is the molecular weight) having forward free energy barrier of 180 kJ/mol. The molecular structure of INT249a is provided in Fig. 9-7. HONO is a very reactive species and participates in many different bimolecular reactions. It can undergo a self-reaction to form ONNO<sub>2</sub>, or NO and NO<sub>2</sub>, it can react with INT249a formed

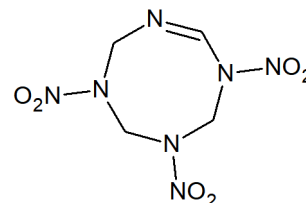


Figure 9-7. Molecular structure of INT249a

during initiation to produce ring-opening, forming CH<sub>2</sub>O, N<sub>2</sub>O, and other species. HONO can also react with other decomposition products via several reactions [123]. 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 observed below 555K. For temperatures below 555K, initiation of HMX decomposition is likely to involve both TAGzT and its decomposition products. In this work, using QC calculations, we studied assisted HONO elimination and other 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 CN<sup>-</sup>, TAG, N<sub>2</sub>, NH<sub>3</sub>, HCN, N<sub>2</sub>H<sub>4</sub> and many other intermediates [34] during the first mass-loss step. However, during this phase of decomposition, HMX in the mixture remains largely in its solid state as it melts at ~553 K. Therefore, condensed-phase TAGzT decomposition products are most likely to undergo surface reactions with that of crystals of solid-state HMX in the mixture. However, in this work, we considered HMX to be in a “molten” condensed phase in order identify relevant reaction pathways. Although this is an approximate approach for studying the interaction of TAGzT decomposition products with HMX, it provides a qualitative idea about important low barrier pathways that help explain the observed products.

Based on our earlier works on TAGzT decomposition [134, 142], ring-opening of AzT<sup>2-</sup> releasing N<sub>2</sub> is the initiation of decomposition with a forward free energy barrier of 157 kJ/mol. Subsequent reactions involving the corresponding di-anion have very low barriers. The global reaction involving the AzT<sup>2-</sup> di-anion can be written as  $\text{AzT}^{2-} \rightarrow 4\text{N}_2 + 2\text{CN}^-$ ,  $\Delta H_{\text{rxn}} = -473$  kJ/mol, and as such very exothermic. Both anionic species in this reaction play important roles in the decomposition of HMX. In Table 9-1, we show the results from our calculations. Both the AzT<sup>2-</sup> di-anion and the CN<sup>-</sup> anion could play very important roles in the initiation of decomposition of TAGzT as the barriers of the bimolecular reactions **R1** and **R2** are below the barrier for unimolecular decomposition mentioned previously. Furthermore, the produced NO<sub>2</sub><sup>-</sup> anion can also accelerate the decomposition of HMX via the formation of *cis*-HONO shown by reaction **R3**. Autocatalytic reactions are also important as shown by reaction **R3**, and to a lesser extent by **R4**. Reactions **R5** and **R6** show that HONO-elimination can be assisted by ammonia and hydrazine, by reducing the strain associated with the direct HONO-elimination reaction. The rates of the latter two reactions are increased by effects from symmetry. It should also be pointed out that an equilibrium also exists between NO<sub>2</sub><sup>-</sup> and HONO via proton transfer from TAG<sup>+</sup>. The Gibbs free energy change of such reactions are on the order of 40 to 50 kJ/mol. Although the equilibrium constant appears to be quite low, the consumption of HONO is very fast in reactions with many different species, such as N<sub>2</sub>H<sub>4</sub> and TAG.

A reaction between TAG and HONO is likely to be responsible for the simultaneous appearance of N<sub>2</sub>O and NH<sub>3</sub>, as shown in Fig. 9-5. Slightly less of NH<sub>3</sub> is quantified compared to N<sub>2</sub>O in the gas phase. It

could be caused by numerical difficulties in capturing the fine rotational-line structure in the spectral range of 900-1,000  $\text{cm}^{-1}$ , which is used in the data reduction, or over lapping of spectral lines of  $\text{N}_2\text{H}_4$ , which has a similar fine line structure as that of  $\text{NH}_3$ . It could also be caused by protonation of  $\text{NH}_3$  forming  $\text{NH}_4^+$ , and thus remaining in the condensed phase. No other species follow this behavior, and as such it is expected that both species are formed in a reaction and thus responsible for the observed trend. In Table 9-1, we show the reaction sequence releasing  $\text{N}_2\text{O}$  and  $\text{NH}_3$  by reactions **R7**, **R8** and **R9**. First, HONO reacts with TAG, with subsequent proton transfer to release the  $\text{N}_2\text{O}$  and  $\text{NH}_3$ . In these experiments,  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  readily evaporate, and they may not contribute significantly in the condensed-phase reactions. The evidence that **R10** and **R11** may not contribute to the simultaneous appearance of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  via **R12** - **R14** is that no water is detected, unless the 70-30 case is considered. In a combustion application, however, the residence time of  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  in the condensed-phase region would increase and reactions **R10** and **R11** are likely to play an important role.

Table 9-1. Gibbs free energy barrier  $\Delta G$  in forward (*f*) and backward (*b*) direction and enthalpy of reaction (kJ/mol).

| No. | Reaction                                                                                                                                    | $\Delta G_f$ | $\Delta G_b$ | $\Delta H_{rxn}$ |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------|--------------|--------------|------------------|
| R1  | $\text{HMX} + \text{AzT}^{2-} \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{AzT}^-$                                                | 154          | 248          | -41              |
| R2  | $\text{HMX} + \text{CN}^- \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{HCN}$                                                      | 115          | 232          | -52              |
| R3  | $\text{HMX} + \text{NO}_2^- \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{cis-HONO}$                                               | 159          | 227          | -3               |
| R4  | $\text{HMX} + \text{TAG} \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{TAG}^+$                                                     | 122          | 241          | -54              |
| R5  | $\text{HMX} + \text{NH}_3 \leftrightarrow \text{INT249a} + \text{trans-HONO} + \text{NH}_3$                                                 | 175          | 263          | -29              |
| R6  | $\text{HMX} + \text{N}_2\text{H}_4 \leftrightarrow \text{INT249a} + \text{trans-HONO} + \text{N}_2\text{H}_4$                               | 175          | 263          | -29              |
| R7  | $\text{TAG} + \text{cis-HONO} \leftrightarrow \text{HOC}(\text{N}(\text{NO})\text{NH}_2)(\text{NHNH}_2)_2$                                  | 148          | 151          | -62              |
| R8  | $\text{TAG} + \text{trans-HONO} \leftrightarrow \text{HOC}(\text{N}(\text{NO})\text{NH}_2)(\text{NHNH}_2)_2$                                | 154          | 154          | -59              |
| R9  | $\text{HOC}(\text{N}(\text{NO})\text{NH}_2)(\text{NHNH}_2)_2 \leftrightarrow \text{OC}(\text{NHNH}_2)_2 + \text{N}_2\text{O} + \text{NH}_3$ | 33           | 341          | -213             |
| R10 | $\text{N}_2\text{H}_4 + \text{cis-HONO} \leftrightarrow \text{NH}_2\text{NHNO} + \text{H}_2\text{O}$                                        | 153          | 236          | -86              |
| R11 | $\text{N}_2\text{H}_4 + \text{trans-HONO} \leftrightarrow \text{NH}_2\text{NHNO} + \text{H}_2\text{O}$                                      | 152          | 232          | -83              |
| R12 | $\text{NH}_2\text{NHNO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O} + \text{N}_2\text{O} + \text{NH}_3$                         | 144          | 325          | -149             |
| R13 | $\text{NH}_2\text{NHNO} + \text{cis-HONO} \leftrightarrow \text{cis-HONO} + \text{N}_2\text{O} + \text{NH}_3$                               | 58           | 239          | -149             |
| R14 | $\text{NH}_2\text{NHNO} + \text{NH}_3 \leftrightarrow \text{NH}_3 + \text{N}_2\text{O} + \text{NH}_3$                                       | 58           | 239          | -149             |
| R15 | $\text{HMX} + \text{NO}_3^- \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{HNO}_3$                                                  | 187          | 227          | +14              |
| R16 | $\text{RDX} + \text{NO}_3^- \leftrightarrow \text{INT175} + \text{NO}_2^- + \text{HNO}_3$                                                   | 153          | 218          | -10              |
| R17 | $\text{HMX} + \text{DAG} \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{DAG}^+$                                                     | 123          | 230          | -36              |
| R18 | $\text{HMX} + \text{MAG} \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{MAG}^+$                                                     | 114          | 226          | -47              |
| R19 | $\text{HMX} + \text{G} \leftrightarrow \text{INT249a} + \text{NO}_2^- + \text{G}^+$                                                         | 123          | 232          | -44              |

In view of the potential reactions from  $\text{CN}^-$ ,  $\text{AzT}^{2-}$ , and TAG, as shown by **R1**, **R2** and **R4**, we also include additional reactions given by **R15** – **R19**. Here the strong bases of diaminoguanidine (DAG), (mono-) aminoguanidine (MAG), and guanidine (G) may be protonated via H-abstraction reactions similar to **R4**. Barriers are very similar to **R4**. Similarly, the nitrate anion can also play a role as shown by **R15**, but the barrier is higher compared to the nitrite anion listed by reaction **R3**. With symmetry effects the barrier becomes close to the HONO-elimination reaction for HMX; **R15** is endothermic but exergonic, meaning it is favorable in the forward direction. For RDX, however, the nitrate anion abstracting an H-atom has a barrier about 8 kJ/mol lower compared to the HONO-elimination reaction shown by **R16**. Thus, mixing these two nitramines with ionic compounds could lower the decomposition temperatures to a significant effect, as shown by the nitramine-TAGzT mixtures considered in this project.

## 9.5 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 550K. 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, the TAGzT and its decomposition products react with solid-state HMX in the mixture to release  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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 QC calculations, we identified important pathways through which HMX can decompose in the presence of TAGzT decomposition products. It has been observed that the  $\text{AzT}^{2-}$  dianion and  $\text{CN}^-$  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 154 and 115 kJ/mol, respectively. Therefore, compared to the barrier involved during unimolecular decomposition of HMX forming HONO during initiation (180 kJ/mol), the barrier of HONO formation pathway from HMX in presence of TAGzT is reduced by ~65 kJ/mol. In addition, several other HONO formation reactions involving TAGzT decomposition products are studied having barrier lower than 167 kJ/mol. By performing QC calculations along with experiments, this work provides a detailed understanding of the thermal decomposition behavior of HMX-TAGzT mixtures at low heating rates.

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1. L. Patidar, S.T. Thynell, Quantum mechanics investigation of initial reaction pathways and early ring-opening reactions in thermal decomposition of liquid-phase RDX, *Combust. Flame*. 178 (2017) 7–20.
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