Green Propellants

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Cover illustration: The crystal unit cell of ammonium dinitramide (ADN)
Per aspera ad astra
Abstract

To enable future environmentally friendly access to space by means of solid rocket propulsion a viable replacement to the hazardous ammonium perchlorate oxidizer is needed. Ammonium dinitramide (ADN) is one of few such compounds currently known. Unfortunately compatibility issues with many polymer binder systems and unexplained solid-state behavior have thus far hampered the development of ADN-based propellants.

Chapters one, two and three offer a general introduction to the thesis, and into relevant aspects of quantum chemistry and polymer chemistry.

Chapter four of this thesis presents extensive quantum chemical and spectroscopic studies that explain much of ADN’s anomalous reactivity, solid-state behavior and thermal stability. Polarization of surface dinitramide anions has been identified as the main reason for the decreased stability of solid ADN, and theoretical models have been developed to explain and predict the solid-state stability of general dinitramide salts. Experimental decomposition characteristics for ADN, such as activation energy and decomposition products, have been explained for different physical conditions. The reactivity of ADN towards many chemical groups is explained by ammonium-mediated conjugate addition reactions. It is predicted that ADN can be stabilized by changing the surface chemistry with additives, for example by using hydrogen bond donors, and by trapping radical intermediates using suitable amine-functionalities.

Chapter five presents several conceptual green energetic materials (GEMs), including different pentazolate derivatives, which have been subjected to thorough theoretical studies. One of these, trinitramide (TNA), has been synthesized and characterized by vibrational and nuclear magnetic resonance spectroscopy.

Finally, chapter six covers the synthesis of several polymeric materials based on polyoxetanes, which have been tested for compatibility with ADN. Successful formation of polymer matrices based on the ADN-compatible polyglycidyl azide polymer (GAP) has been demonstrated using a novel type of macromolecular curing agent. In light of these results further work towards ADN-propellants is strongly encouraged.

Keywords: Quantum chemistry, reaction kinetics, ammonium dinitramide, high energy density materials, rocket propellants, chemical spectroscopy, polymer synthesis.
List of Publications

This thesis is based on the following papers, referred to in the text by their Roman numerals I-X:

I. Dinitraminic acid (HDN) Isomerization and Self-Decomposition Revisited
   Martin Rahm and Tore Brinck

II. Novel 1,3 Dipolar Cycloadditions of Dinitraminic Acid:
    Implications for the Chemical Stability of Ammonium Dinitramide
   Martin Rahm and Tore Brinck

III. The Anomalous Solid State Decomposition of Ammonium Dinitramide: A
     Matter of Surface Polarization
    Martin Rahm and Tore Brinck

IV. On the Anomalous Decomposition and Reactivity of Ammonium and
    Potassium Dinitramide
    Martin Rahm and Tore Brinck

V. The Molecular Surface Structure of Ammonium and Potassium Dinitramide: A
   Vibrational Sum Frequency Spectroscopy and Quantum Chemical Study
   Martin Rahm, Eric Tyrode, Tore Brinck and Magnus Johnson
   Submitted for publication

VI. Kinetic Stability and Propellant Performance of Green Energetic Materials
    Martin Rahm and Tore Brinck

VII. Envisioning New High Energy Density Materials: Stability, Detection and
     Performance
    Martin Rahm, Adriana Trinchero and Tore Brinck

VIII. Experimental Detection of Trinitramide
     Martin Rahm, Sergey V. Dvinskikh, Istvan Furo and Tore Brinck
     Manuscript
IX. Tri-Block Copolymers of Polyethylene Glycol and Hyperbranched Poly-3-ethyl-(hydroxymethyl)oxetane Through Cationic Ring Opening Polymerization
Martin Rahm, Robert Westlund, Carina Eldsäter and Eva Malmström

X. Design of an Ammonium Dinitramide Compatible Polymer Matrix
Martin Rahm, Eva Malmström and Carina Eldsäter
*Manuscript*

This thesis contains unpublished results.

**Publications not included in this thesis:**

**Supramolecular Control in Carbohydrate Epimerization: Discovery of a New Anion Host-Guest System**
Hai Dong, Martin Rahm, Tore Brinck and Olof Ramström

**Phosphine-Catalyzed Disulfide Metathesis**
Rémi Caraballo, Martin Rahm, Pornrapee Vongvilai, Tore Brinck and Olof Ramström

**Diastereoselective One-Pot Tandem Synthesis of 3-Substituted Isoindolinones: a Mechanistic Investigation**
Marcus Angelin, Martin Rahm, Andreas Fischer, Tore Brinck and Olof Ramström

**Control of the Ambident Reactivity of the Nitrite Ion in Inversion Reactions**
Hai Dong, Martin Rahm, Lingquan Deng, Tore Brinck and Olof Ramström
*Submitted for publication*
Author’s Contributions

The following is a description of my contribution to Publications I to X, as requested by KTH.

Paper I-IV: I formulated the research strategies and performed the calculations. The manuscripts were written together with Tore Brinck.

Paper V: I formulated the research strategy together with the co-authors. I performed the crystallization work and the calculations. The manuscript was written together with Magnus Johnson.

Paper VI and VII: I formulated the research strategies, performed the calculations and wrote the manuscripts.

Paper VIII: I formulated the research strategy, performed the calculations and the synthesis. I wrote the manuscript.

Paper IX: I formulated the research strategy together with Eva Malmström, performed the experimental work and wrote the majority of the manuscript.

Paper X: I formulated the research strategy, performed most of the experimental work and wrote the manuscript.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACE</td>
<td>Activated chain end mechanism</td>
</tr>
<tr>
<td>ADN</td>
<td>Ammonium dinitramide</td>
</tr>
<tr>
<td>AM</td>
<td>Activated monomer mechanism</td>
</tr>
<tr>
<td>AN</td>
<td>Ammonium nitrate</td>
</tr>
<tr>
<td>AP</td>
<td>Ammonium perchlorate</td>
</tr>
<tr>
<td>COSMO</td>
<td>Conductor like screening model</td>
</tr>
<tr>
<td>DB</td>
<td>Degree of branching</td>
</tr>
<tr>
<td>DF</td>
<td>Degree of functionalization</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic surface potential</td>
</tr>
<tr>
<td>GAP</td>
<td>poly(glycidyl azide)</td>
</tr>
<tr>
<td>GEM</td>
<td>Green energetic material</td>
</tr>
<tr>
<td>GUDN</td>
<td>Guanylurea dinitramide</td>
</tr>
<tr>
<td>HDN</td>
<td>Dinitraminic acid</td>
</tr>
<tr>
<td>HEDM</td>
<td>High energy density material</td>
</tr>
<tr>
<td>HFC</td>
<td>Heat-flow calorimetry</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>I&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>Specific impulse</td>
</tr>
<tr>
<td>KDN</td>
<td>Potassium dinitramide</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix-assisted laser desorption ionization time-of-flight</td>
</tr>
<tr>
<td>MECP</td>
<td>Minimum energy crossing point</td>
</tr>
<tr>
<td>MNA</td>
<td>2-methyl-4-nitroaniline</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OB</td>
<td>Oxygen balance</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarizable continuum model</td>
</tr>
<tr>
<td>PEG</td>
<td>poly(ethylene glycol)</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TMPO</td>
<td>3-ethyl-3-(hydroxymethyl)oxetane</td>
</tr>
<tr>
<td>TNA</td>
<td>Trinitramide</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
</tr>
<tr>
<td>VSFS</td>
<td>Vibrational sum frequency spectroscopy</td>
</tr>
<tr>
<td>ZPE</td>
<td>Zero-point energy</td>
</tr>
</tbody>
</table>
# Table of Contents

Abstract  
List of Publications  
Abbreviations

1. Introduction ........................................................................................................... 1  
   1.1. The Need for Environmental Access to Space ............................................. 2  
   1.2. Ammonium Dinitramide (ADN) .................................................................. 3  
   1.3. Current and Future Uses of Dinitramide Salts ........................................... 4  
   1.4. The Aim of This Thesis ............................................................................... 5

2. Computational Chemistry ....................................................................................... 6  
   2.1. Introduction to Quantum Chemistry ............................................................. 6  
   2.2. The Born-Oppenheimer Approximation ....................................................... 7  
   2.3. The Antisymmetry Principle and Slater Determinants ............................... 8  
   2.4. Orbital Basis Functions ............................................................................. 9  
   2.5. Hartree-Fock Theory ................................................................................ 9  
   2.6. Electron Correlation and Post Hartree-Fock Methods .............................. 11  
   2.7. Density Functional Theory ...................................................................... 11  
   2.8. Molecular Thermodynamics ..................................................................... 14  
   2.9. Transition State Theory ........................................................................... 14  
   2.10. Applied Computational Chemistry .......................................................... 16

3. Polymer Chemistry .................................................................................................. 17  
   3.1. Hyperbranched Polymers ........................................................................... 17  
   3.2. Cationic Ring Opening Polymerization of Oxetanes .................................. 18  
   3.3. Polymer Networks ..................................................................................... 19

4. Decomposition and Reactivity of Dinitramide Salts ................................................. 20  
   4.1. Introduction ............................................................................................... 20  
   4.2. The Dinitramide Anion (DN⁻) .................................................................... 21  
   4.3. Dinitraminic Acid (HDN) .......................................................................... 22  
   4.4. ADN and KDN Clusters ............................................................................ 23  
      4.4.1. The Dimer Model ................................................................................. 23  
      4.4.2. Larger Clusters ................................................................................... 27  
   4.5. Vibrational Sum Frequency Spectroscopy Studies of ADN and KDN ....... 29  
   4.6. The Anomalous Behavior of Dinitramide Salts ......................................... 32  
   4.7. Compatibility Testing .............................................................................. 34  
   4.8. The Reactivity of ADN ............................................................................. 37  
   4.9. Stabilization of Dinitramide Salts ............................................................... 42  
   4.10. Summary and Conclusions ....................................................................... 45
5. Green Energetic Materials ......................................................... 46
  5.1. High Energy Density Materials (HEDMs) and Propulsion ............. 46
  5.2. Green Energetic Materials (GEMs) ........................................ 48
  5.3. Theoretical Results ........................................................... 49
    5.3.1. The trinitrogen dioxide anion (N(NO)$_2^-$) ......................... 50
    5.3.2. The 1-nitro-2-oxo-3-aminotriazene anion (NH$_2$-NN(O)N-NO$_2$) ... 51
    5.3.3. The pentazole anion (cyclo-N$_5^-$) ................................... 52
    5.3.4. The oxopentazole anion (cyclo-N$_5$-O) ............................. 53
    5.3.5. The 1,3-dioxopentazole anion (cyclo-N$_5$-O$_2$) .................... 53
    5.3.6. Trinitramide (N(NO$_2$)$_3$) .......................................... 54
  5.4. Experimental Detection of Trinitramide (TNA) .......................... 54
  5.5. Summary and Conclusions .................................................. 57

6. Polymer Synthesis .................................................................. 58
  6.1. Design of a Rocket Propellant Formulation ............................... 58
  6.2. poly-3-ethyl-3-(hydroxymethyl)oxetane (poly-TMPO) ................. 59
  6.3. Tri-block copolymers of poly-TMPO and PEG .......................... 60
  6.4. Copolymers of TMPO and THF and the curing of GAP ................. 62
  6.5. Summary and Conclusions .................................................. 65

7. Concluding Remarks .............................................................. 66

Acknowledgements ...................................................................... 67
References ................................................................................. 69
1. Introduction

The vastness of space has caught the imagination of people throughout history. This great frontier in human undertakings defines much of what remains, before we can truly master the natural world.

One of the first steps toward the heavens were made in 1687, when Sir Isaac Newton published *Philosophiæ Naturalis Principia Mathematica*,[1] by many considered the most important work in the history of science. In 1919 the pioneering Robert H. Goddard (Figure 1) published *A Method of Reaching Extreme Altitudes*.[2] Later, in 1926, he launched the world’s first liquid rocket, which was propelled by gasoline and liquid oxygen.

Since then the development of rocket propulsion, and the exploration of space, has literally skyrocketed. The short-term reasons for such endeavors are many and range from national pride, military superiority, and economic profit to scientific discovery. However, many agree that the exploration of space is more fundamental, and even necessary for the long-term survival of the species.[3-6] One can argue that the future of mankind will be written in the stars.

Near future interplanetary crafts are likely to be propelled by high-power plasma rockets[7,8] and ion engines.[9,10] Still, heavy earth orbit launchers and navigational thrusters are likely to rely on chemical propulsion for the foreseeable future.

To develop the chemical propulsion technologies of the future, new energetic materials, oxidizers and polymeric materials are needed. The creation of these requires the use of many theoretical and experimental tools made available in modern chemistry, such as quantum chemical calculations and powerful spectroscopic methods.

![Figure 1. Professor Robert H. Goddard (1882 - 1945) – A theorist and an engineer recognized as the father of modern rocketry.](image-url)
1.1. The Need for Environmental Access to Space

The space industry is growing worldwide and numerous telecommunication, research and surveillance satellites are commissioned every year.\textsuperscript{[11,12]} New manned shuttles and space exploration vehicles are being devised. Even space tourism is predicted to have a bright future.\textsuperscript{[13-15]} The large number of orbital launches in recent years (78 in 2009\textsuperscript{[11]}) has raised serious concerns regarding their environmental impact.

The vast majority of space launchers rely on solid rocket propellants in one or several of their stages. The main component of such a propellant is the oxidizing material, which typically is \textit{ammonium perchlorate} (AP, \(\text{NH}_4^+\text{ClO}_4^-\)). The remainder of the formulation consists of a fuel, commonly aluminum (Al) powder, and a polymer matrix. A standard AP-Al propellant has excellent performance characteristics, good thermal stability, as well as low friction and shock sensitivity. Unfortunately its combustion results in the formation of various chlorinated and hazardous exhaust products. As examples it can be mentioned that the European space launcher Ariane-5 and the newly developed Vega launcher contain 476 and 122 tons of AP-based propellant each.\textsuperscript{[16,17]} Upon launch this converts into the equivalence of 270 and 71 tons of concentrated hydrochloric acid respectively. The American space shuttle, due to be decommissioned and likely replaced by a similar system, contains 998 tons of AP-based propellant.\textsuperscript{[18]} This corresponds to 578 tons of concentrated hydrochloric acid.

Liquid state-of-the-art mono and bipropellants, needed in various navigational thrusters and rocket engines, are commonly based on \textit{hydrazine} (\(\text{N}_2\text{H}_4\)) derivatives such as mono methyl hydrazine (MMH) or unsymmetrical dimethyl hydrazine (UDMH). Hydrazine is unfortunately considered extremely toxic,\textsuperscript{[19,20]} which creates occupational hazards during handling and fueling.\textsuperscript{[21]}

The motivation and necessity of replacing AP and hydrazine-based formulations with more \textit{green propellants} is apparent, and considerable efforts toward this end have been pursued.\textsuperscript{[20,22-32]} Finding replacements has unfortunately proven a difficult challenge, primarily due to the small number of available and suitable oxidizing agents.

\textit{Hydrazinium nitroformate} (HNF, \(\text{N}_2\text{H}_5^+\text{C(NO}_2)_3^-\)) is one oxidizer that is being seriously considered as a replacement for both AP and hydrazine.\textsuperscript{[20,27,30,33-35]} However, despite significant advances in recent years, there are several issues that argue against the use of HNF. There are unresolved problems concerning thermal stability and friction sensitivity, as well as various compatibility problems.\textsuperscript{[27,28,35]} HNF is also expensive to produce and due to its carcinogenic hydrazine base not strictly a green propellant.

\textit{Ammonium nitrate} (AN, \(\text{NH}_4^+\text{NO}_3^-\)) is a highly stable and cheap oxidizer, as well as a commonly used soil fertilizer. Unfortunately AN is non-ideal in propellant formulations for several reasons. It exhibits poor performance due to a relatively low energy content and an inability to effectively combust aluminum. It also provides insufficient propellant burn rates. AN also has many different crystal phases, which transform into one another, close to ambient temperatures. This causes inhomogeneity in solid formulations, which can lead to cracks and bubbles.\textsuperscript{[36]}

\textit{Hydroxylammonium nitrate} (HAN, \(\text{NH}_2\text{OH}^+\text{NO}_3^-\)) is primarily considered a possible hydrazine monopropellant replacement. It has as of yet not reached practical applicability due to problems regarding ignition catalysts, complicated combustion mechanisms, high sensitivity and material incompatibility.\textsuperscript{[32]}
Ionic liquids typically show substantial advantages over common solvents, such as high stability, low toxicity, good solvent characteristics, and virtually no vapor pressure. Unconventional propellants based on energetic ionic liquids have been proposed.\cite{37,38}

In addition to the above-mentioned possibilities there exist a number of high energy density materials (HEDMs) that are possible propellant components. Some of these are discussed in a later chapter. The bulk of this thesis however, is focused on the energetic salt ammonium dinitramide (ADN, \(\text{NH}_4^+\text{N(NO}_2\text{)}_2^-\)), which is proposed as the main oxidizing agent in future rocket propellants.

1.2. Ammonium Dinitramide (ADN)

Ammonium dinitramide (ADN, \(\text{NH}_4^+\text{N(NO}_2\text{)}_2^-\), Figure 2, Table 1)\cite{39} is a chlorine free oxidizer that has been considered a possible AP replacement for the last 20 years.\cite{23} ADN was secretly discovered in 1971\cite{40} in the former USSR, and is believed to have been used in operational missile systems.\cite{41} Its rediscovery in 1989\cite{42} by US scientist initiated worldwide civil and military interest.

ADN has several advantages over AP; it contains no chlorine and produces no hazardous combustion products. The absence of chlorine also enables a low-signature (no smoke) combustion when combined with a suitable fuel. Furthermore, the dinitramide anion is more energetic, which enable higher performances than AP-based propellants. It has been estimated that if a propellant formulation based on ADN were to replace today’s AP-based propellants the lift capacity of space launchers would increase by approximately 8%.\cite{31}

![Figure 2. Ammonium dinitramide (ADN)](image_url)

ADN is a colorless salt that becomes yellowish when non-dry. \(\alpha\)-ADN has a monoclinic crystal structure, in the \(\text{P2}_1/c\) space group.\cite{43} A second monoclinic high-pressure phase, \(\beta\)-ADN, has been reported over 2 GPa.\cite{44} ADN is highly soluble in polar solvents whilst non-soluble in most low-polarity solvents.\cite{45} Due to its high hygroscopicity, ADN dissolves itself if the relative humidity exceeds 55 \%.\cite{46,47} Similar to all dinitramide salts ADN is photosensitive, and should not be subjected to excessive UV light.\cite{48,49}

There are several ways of synthesizing ADN, using standard industrial chemicals. For instance, nitration of primary amines, or ammonia, using mixed acids or other nitration agents, such as \(\text{NO}_3\text{BF}_3\) or \(\text{N}_2\text{O}_5\).\cite{41,48} Since 1996 ADN is produced in larger scale, at a pilot plant operated by Eurenco Bofors in Karlskoga, Sweden.
1.3. Current and Future Uses of Dinitramide Salts

Aside from their fairly obvious potentials in rocket propellants, explosives and pyrotechnics, dinitramide salts have been suggested for use in a wide range of applications.\(^5\) The potassium salt of dinitramide (KDN) is due to the high electrical conductivity of its combustion products considered a possible plasma-forming fuel in future magnetohydrodynamic (MHD) generators.\(^5\)

Lithium dinitramide (LiDN) is reported an effective electrolyte additive in electrochemical cells (batteries), using lithium cathodes, where it significantly reduces self-discharge rates.\(^5\) Due to a high solubility in lipophilic media, the use of dinitramide salts of biologically active cations holds promise in a variety of medical fields including pharmaceuticals, drug delivery, medical imaging and diagnostics.\(^5\)

There are also synthetic possibilities, where the dinitramide molecule can be used in forming new compounds.\(^5\)

The first commercial use of dinitramides was in gas generators for air bags.\(^5\) In this application, the ADN precursor guanylurea dinitramide (GUDN) is used. More recently, an extra pure ADN-synthesis has enabled the development of a liquid ADN-based monopropellant.\(^6\) The propellant, which significantly outperforms corresponding hydrazine propellants, is currently being tested in the navigational thrusters of the Swedish PRISMA satellite, now in low earth orbit. The satellite is meant to demonstrate green propellant technology and formation flying in space.\(^6\)

Unfortunately the development of a solid ADN-based propellant, required in the main stages of heavy space launchers, has proven a considerable challenge. Primarily this is due to ADN’s unexplained reactivity towards many commonly used polymer binder systems, as well as its anomalous solid-state behavior.

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### Table 1. Properties of ADN

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>124.07 g/mol</td>
</tr>
<tr>
<td>Density of solid (25 °C)</td>
<td>1.81 g/cm(^3)</td>
</tr>
<tr>
<td>Density of liquid (100 °C)</td>
<td>1.56 g/cm(^3)</td>
</tr>
<tr>
<td>Melting point</td>
<td>93 °C</td>
</tr>
<tr>
<td>Heat of formation</td>
<td>-35.4 kcal/mol</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>101.3 kcal/mol</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>1.8 J/g</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>+25.79 %</td>
</tr>
<tr>
<td>Critical relative humidity</td>
<td>55.2 %</td>
</tr>
<tr>
<td>Friction sensitivity</td>
<td>72 N</td>
</tr>
<tr>
<td>Impact sensitivity</td>
<td>5 Nm</td>
</tr>
<tr>
<td>Electrostatic discharge sensitivity</td>
<td>0.45 J</td>
</tr>
<tr>
<td>UV absorption maxima in water</td>
<td>214 and 284 nm</td>
</tr>
<tr>
<td>Solubility in water at 20 °C</td>
<td>357 g in 100 g solvent</td>
</tr>
<tr>
<td>Solubility in butyl acetate at 20 °C</td>
<td>0.18 g in 100 g solvent</td>
</tr>
<tr>
<td>Solubility in dichloromethane at 20 °C</td>
<td>0.003 g in 100 g solvent</td>
</tr>
</tbody>
</table>
1.4. The Aim of This Thesis

The overall aim of this work has been the development of new high-performance, and more environmentally friendly, solid rocket propellant formulations, and in particular the use of ADN in such. However, some of this work also applies to liquid formulations. The initial aim has been towards fundamental understanding of decomposition mechanisms, kinetics, solid-state behavior, and the reactivity of the ADN salt. A number of related energetic compounds have been approached both theoretically and experimentally. Finally, a number of polymeric systems have been synthesized and tested for use with ADN.

Chapter 4 is the largest of this thesis, and is focused on understanding the behavior of dinitramide salts, and in particular ADN. The chapter initially describes quantum chemical studies on self-decomposition and reactivity. The focus then shifts to more experimental aspects, including thermal compatibility studies and spectroscopic measurements. Stabilization of dinitramide salts is also addressed.

Chapter 5 summarizes the theoretical work done on a set of promising energetic molecules, most of which hitherto are unknown in the condensed phase. The chapter also covers the successful synthesis of one of these compounds.

Chapter 6 deals with the synthesis and testing of polyoxetane-based materials, meant for use as matrices and as curing agents in solid rocket propellant formulations.
2. Computational Chemistry

This chapter provides a brief introduction to some of the theories behind computational chemistry. The text assumes a basic knowledge of quantum mechanics and a familiarity with operators and matrix notations. Atomic units are used throughout. Several textbooks\cite{61-64} are recommended for a more in depth description.

2.1. Introduction to Quantum Chemistry

The particle-wave duality of both matter and light is a fundamental law of nature that became evident during the last century. In 1900 Planck offered an explanation for the quantization of black body radiation (light).\cite{65} Later de Broglie showed that matter exhibits both particle and wave characteristics.\cite{66} The failure of classical Newtonian mechanics in describing the smallest scales of reality resulted in the development of quantum mechanics (QM). Today the development of applied QM-methodology has enabled predictions of physical and chemical properties from first principles.

The fundamental postulate of quantum mechanics is that a microscopic system is completely described by the so-called wave function, $\Psi$, and that any physical observable of that system can be represented by applying a suitable mathematical operator. The famous Schrödinger equation\cite{67} considers the total energy of the system, and writes as,

$$\hat{H}\Psi = E\Psi$$ \hspace{1cm} (2.1)

where $\hat{H}$ is the Hamiltonian operator and $E$ the corresponding eigenvalue (the energy of the system). An important property of a wave function is that if multiplied with its complex conjugate ($\Psi^*$) and integrated over a space it provides the particle probability in that space. In order for a wave function to be a suitable description of a real system it needs to be well behaved, and uphold several criteria. For one, the particle density of a bound particle must equal 1 when integrated over all space,

$$\int_{-\infty}^{\infty} |\Psi(r,t)|^2 \, dr = 1.$$ \hspace{1cm} (2.2)

As there exists a complete (possibly infinite) set of orthonormal wavefunctions that satisfy the Schrödinger equation, an arbitrary function $\Phi$ can be written as a linear combination of these,

$$\Phi = \sum_i c_i \Psi_i.$$ \hspace{1cm} (2.3)
It can be shown that the energy resulting from an incomplete expansion, i.e. a non-exact wave function, $\Phi$, always is higher than the lowest possible (i.e. ground state) energy of the system ($E_0$), that is,

$$\frac{\int \Phi \hat{H} \Phi^* \, dr}{\int \Phi \Phi^* \, dr} = \frac{\langle \Phi | \hat{H} | \Phi^* \rangle}{\langle \Phi | \Phi^* \rangle} \geq E_0. \quad (2.4)$$

This is referred to as the variational principle, which can be used to estimate the quality of a calculated trial wave function.

For most common purposes when quantum mechanics is applied on chemical systems the time-independent non-relativistic Schrödinger equation is used. For a many-body $N$-electrons and $M$-nuclei system the corresponding Hamiltonian operator writes as,

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2\mu_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i<j}^{N} \sum_{A=1}^{M} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B=A}^{M} \frac{Z_A Z_B}{r_{AB}} \quad (2.5)$$

Where $i$ and $j$ runs over electrons, $A$ runs over nuclei, $r_{ij}$, $r_{iA}$ and $r_{AB}$ are the distances between the corresponding particles, $Z_A$ is the charge of nuclei $A$, $\mu_A$ is the mass of nuclei $A$, and $\nabla^2$ is the Laplacian operator,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \quad (2.6)$$

The first two terms of equation (2.5) describes the kinetic energy of the electrons and nuclei, respectively. The third term equates the Coulomb attraction between nuclei and electrons, whilst the last two accounts for repulsion between electrons and nuclei, respectively.

The problem at the heart of computational chemistry is many-body interactions. Since each individual particle experience a potential from every other particle the Hamiltonian operator (2.5) depends on the coordinates of all particles, and the Schrödinger equation (2.1) quickly becomes very cumbersome. In fact it is impossible to solve exactly for any but a two-particle system such as the hydrogen atom (H) or the helium cation (He$^+$). In order to analyze a system of meaningful size from first principles, a series of approximations are introduced.

### 2.2. The Born-Oppenheimer Approximation

One of the most important simplifications to the Hamiltonian operator is undoubtedly the Born-Oppenheimer approximation. It is made possible by the significantly larger masses of nuclei, compared to electrons, which means that the latter move much faster than the former. As a consequence, the electrons can be regarded as moving in a field of fixed nuclear charges. After removing the constant all-nuclear parts from equation (2.5), the electronic Hamiltonian can be written as,
The resulting electronic Schrödinger equation is now only dependent on the electronic coordinates,

$$
\hat{H}_{el} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}}.
$$  \hspace{1cm} (2.7)

The electronic wave function still depends on the fixed nuclear coordinates, and so does the electronic energy.

It should be noted that without the Born-Oppenheimer approximation the fundamental chemical concept of an electronic potential energy surface (PES, c.f. section 2.9) would be meaningless. Equilibrium between different molecular structures, such as reactants and transition states in transition-state theory (TST, c.f. section 2.9) would not be possible. Luckily, the Born-Oppenheimer approximation is well justified, in all but a few cases.

### 2.3. The Antisymmetry Principle and Slater Determinants

The antisymmetry principle (or Pauli exclusion principle) is a consequence of relativistic quantum mechanics, and states that electronic wave functions must be antisymmetric with respect to the interchange of coordinates of any two electrons. In other words, the sign of the wave function must change when two electrons switches place,

$$
\Phi(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N) = -\Phi(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N).  \hspace{1cm} (2.10)
$$

In order to construct a many-electron wave function from a set of spin orbitals that uphold the antisymmetry principle, a Slater determinant is typically used,

$$
\Phi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N)
\end{array} \right|.
$$  \hspace{1cm} (2.11)
where $1/\sqrt{N!}$ is a normalization factor, and $x_N$ are the three spatial coordinates and the single spin coordinate of electron $N$. Exchanging two rows of the determinant corresponds to interchanging the position of two electrons. This will also change the sign of the determinant.

2.4. Orbital Basis Functions

The so-called basis set approximation enables construction of the spatial parts of the spin orbitals using linear combinations of a finite number of known spatial basis functions $(\phi_\mu(r), \mu = 1, 2, \ldots, M)$, where $M$ is the number of basis functions and $c_{\mu i}$ are expansion coefficients,

$$\psi_i(r) = \sum_{\mu=1}^{M} c_{\mu i} \phi_\mu(r).$$  \hspace{1cm} (2.12)

In order to use equation (2.12) to formulate molecular orbitals a suitable basis is required. For this purpose linear combinations of Gaussian type orbitals (GTOs) are typically employed,

$$GTO(r, \theta, \phi) = N e^{-\zeta^2 l_0^2} Y_{l,m}(\theta, \phi).$$  \hspace{1cm} (2.13)

Here $\zeta$ (zeta) describes the “spread” of the function, which will vary depending on the shape of the orbital. $N$ is a normalization factor, $l$ is the spin angular momentum quantum number, $m$ is the magnetic quantum number, $a_0$ is the Bohr radius (0.5292 Å), and $Y_{l,m}(\theta, \phi)$ are the spherical harmonics. The quality, or size, of a basis set is in principle determined by the number of GTOs included in the basis set expansion.

2.5. Hartree-Fock Theory

In the Hartree-Fock approximation a set of spin orbitals, $\chi_a$, are used to construct a single determinant, which is the best approximation to the ground state wave function, described by the electronic Hamiltonian $\hat{H}_{el}$ (2.7). The optimal ground state wave function is found by minimizing the energy, according to the variational principle (2.4). The Hartree-Fock equation can be written as a set of one-electron eigenvalue equations,

$$\hat{f}(i) \chi_a = \epsilon_a \chi_a$$ \hspace{1cm} (2.14)

where $\hat{f}(i)$ is the one-electron Fock-operator defined as,

$$\hat{f}(i) = \hat{h}(i) + v(i)^{HF}$$

$$= -\frac{1}{2} \nabla_i^2 - \sum_A Z_A \frac{1}{r_{iA}} + \sum_{b}[\hat{J}_b(i) - \hat{K}_b(i)]$$ \hspace{1cm} (2.15)
in which $\hat{H}(i)$ is an operator describing non-interacting electrons in a field of fixed nuclear charges, and $v(i)^{\text{nr}}$ accounts for electron-electron interaction through a one-electron average potential. $\hat{J}_a(i)$ is the Coulomb operator, which describes the potential on electron $i$ from an electron in $\chi_b$, i.e. classical Coulomb repulsion. When summed over all electrons it gives an average contribution,

$$\hat{J}_b(i) = \int |\chi_b(j)|^2 \frac{1}{r_{ij}} d\mathbf{x}_j. \quad (2.16)$$

The non-classical exchange operator $\hat{K}_b(i)$ is a consequence of the antisymmetry of the wave function. It can be defined by its operation on spin orbital $\chi_a$,

$$\hat{K}_b(i)\chi_a(i) = \left[ \int \chi_b^*(j) \frac{1}{r_{ij}} \chi_a(j) d\mathbf{x}_j \right] \chi_b(i). \quad (2.17)$$

In this way Hartree-Fock can treat electron-electron interactions in an average way. Self-interaction with the same spin orbital ($a=b$) is cancelled out,

$$[\hat{J}_a(i) - \hat{K}_a(i)] \chi_a(i) = 0. \quad (2.18)$$

As the $\hat{J}_b(i)$ and $\hat{K}_b(i)$ operators are functionally dependent on the spin orbitals, the Hartree-Fock equation is dependent on its solution, and needs to be solved iteratively. To do this all $N$ one-electron Hartree-Fock equations are combined into an equation of matrices, the Roothan-Hall equation,

$$\mathbf{FC} = \mathbf{SCE} \quad (2.19)$$

where $\mathbf{F}$ is the matrix containing the Fock operators, $\mathbf{C}$ is the basis set coefficient matrix, $\mathbf{S}$ is the overlap matrix, and $\mathbf{E}$ is the diagonal energy eigenvalue matrix. The optimization procedure, which is called the self-consistent field (SCF) method, starts by guessing a set of coefficients. From this the Fock matrix is constructed, and diagonalized. This leads to a new set of coefficients, which in turn provides an improvement to the Fock matrix. The procedure is repeated until the energy is minimized and the system has reached self-consistency. The final energy expression of a Hartree-Fock calculation writes as,

$$E = \sum_{a=1}^{N} h_a + \frac{1}{2} \sum_{a}^{N} \sum_{b=a}^{N} (J_{ab} - K_{ab}) + V_{ab} \quad (2.20)$$

where the term $\frac{1}{2}$ corrects for the double counting of electron-electron interactions. To conclude, Hartree-Fock theory treats electron interactions in an average way, and the cumbersome $N$-electron problem is elegantly reduced to $N$ one-electron problems.
2.6. Electron Correlation and Post Hartree-Fock Methods

Despite several approximations in the Hartree-Fock method it usually accounts for approximately 99% of the total energy (given a large enough basis set). Unfortunately it is the last 1% that determines the outcome of many chemical transformations. The difference is referred to as the missing correlation energy.

To improve on the Hartree-Fock wave function, and thus include more of the electron correlation, there are several alternatives. Either the number of determinants used to construct the wave function is increased. This is the case in the configuration interaction (CI) and coupled cluster (CC) methods. Another possibility is the introduction of a perturbed Hamiltonian, e.g. using Möller-Plesset perturbation theory (MP2 and MP4).

Unfortunately Post Hartree-Fock methods are very computationally demanding. Whilst Hartree-Fock can be used on hundreds of atoms, chemical accuracy (< 1 kcal/mol error) is only possible for ca 10 to 20 atoms using more advanced wave function based methods.

For very high accuracy calculations in this thesis, the composite method CBS-QB3\(^{[71,72]}\) has typically been employed. CBS-QB3 is based on coupled cluster (CCSD(T)) energies, which are extrapolated to the basis set limit using second and fourth order Möller-Plesset perturbation theory (MP2 and MP4) calculations and empirical corrections. The method has a reported mean average deviation of 0.87 kcal/mol, when benchmarked against the G2 test set.\(^{[71]}\)

2.7. Density Functional Theory

In a theorem presented by Hohenberg and Kohn it is shown that the energy and all properties of the ground state can be obtained from the electron density ρ(r).\(^{[73]}\) This proof constitutes the basis for density functional theory (DFT), which has lead to a revolution within computational chemistry and physics.

As noted in the previous sections of this chapter, the complexity of a wave function increases rapidly with an increasing number of electron coordinates. This prohibits high-level calculations on larger systems. Since only three spatial coordinates (x, y, z = r) are needed to define the density, this problem is in principle circumvented in DFT. The density remains a function of only three coordinates, irrespective of the number of electrons.

Because of this, the ultimate goal in DFT development is to find the exact density functional \(F[\rho]\) that can connect the electron density with the energy of a system. The second Hohenberg-Kohn theorem\(^{[73]}\) states that any trial electron density will return a energy that is equal to or higher than the ground state energy. In other words, DFT is subjected to the variational principle.

Although the exact form of \(F[\rho]\) is unknown it is, similarly to Hartree-Fock, composed of a summation of different terms: the kinetic energy of electrons \(T[\rho]\), the electron-nuclei attraction \(V_{ni}[\rho]\), and the electron-electron repulsion \(V_{ee}[\rho]\), which can be divided into Coulomb \(J[\rho]\) and exchange \(K[\rho]\) parts,
\[ F[\rho] = T[\rho] + V_{\text{ex}}[\rho] + J[\rho] + K[\rho]. \] (2.21)

The nuclear-nuclear repulsion remains a constant within the Born-Oppenheimer approximation.

The \( V_{\text{ex}}[\rho] \) and \( J[\rho] \) functionals can be expressed classically using Coulomb interactions between the charge clouds at \( \rho(\mathbf{r}) \) and \( \rho(\mathbf{r}') \), and the fixed nuclear charges,

\[
V_{\text{ex}}[\rho] = -\sum_{A=1}^{M} \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r},
\]

\[
J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'.
\] (2.22)

Unfortunately it is difficult to construct functionals that accurately describe the remaining exchange and kinetic terms. As a consequence, and as suggested by Kohn and Sham (KS) in 1965, modern DFT methods have reverted back to using orbitals to describe the electron density,

\[
\rho_{\text{approx}} = \sum_{i=1}^{N} |\phi_i^{KS}|^2.
\] (2.23)

In the Kohn-Sham formalism a large part of the density functional is exactly known. The bulk of the kinetic energy is calculated from a reference state of non-interacting electrons,

\[
T_{\text{ref}}[\rho] = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i^{KS} | \nabla_i^2 | \phi_i^{KS} \rangle.
\] (2.24)

All remaining unknown terms, namely the exchange and correlation energy inherent in the kinetic energy and the electron-electron interactions, are combined into a separate term, the exchange correlation functional, \( E_{\text{XC}}[\rho] \),

\[ F[\rho] = T_{\text{ref}}[\rho] + V_{\text{ex}}[\rho] + J[\rho] + E_{\text{XC}}[\rho]. \] (2.25)

Since the exchange-correlation energy is small compared to the other exactly known terms, the accuracy of Kohn-Sham DFT becomes less sensitive to errors in the used functional, as compared to orbital free DFT.

Several approximations to the \( E_{\text{XC}}[\rho] \) functional have been presented. In the Local Spin Density Approximation (LSDA) \( E_{\text{XC}}[\rho] \) is divided into an exchange part and a correlation part, and approximated using expressions valid for a uniform electron gas (i.e. a slowly varying function),

\[
E_{\text{X}}^{\text{LSDA}}[\rho_\alpha \rho_\beta] = -\frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} \int \left( \rho_\alpha^{1/3}(\mathbf{r}) + \rho_\beta^{1/3}(\mathbf{r}) \right) d\mathbf{r}.
\] (2.26)

For this specific case, the form of the exchange functional is known.
The analytical expression for the corresponding correlation part is unknown. However, the functional $E_{CVN}^{\text{VR}}[\rho]$ has been successfully estimated by fitting values from accurate quantum Monte-Carlo simulations of an electron gas at different densities.\textsuperscript{75,76}

In the \textit{Generalized Gradient Approximation} (GGA), the first derivative of the electron density is introduced as a correction to the LSDA model. In the popular GGA exchange functional $B88$ an empirical parameter $\beta$ is used, which is derived from experimental data for the rare gas atoms.\textsuperscript{77}

$$E_{x}^{\text{B88}}[\rho] = E_{x}^{\text{LSDA}}[\rho] + \Delta E_{x}^{\text{B88}}$$

$$\Delta E_{x}^{\text{B88}} = - \beta \rho^{1/3} \left( \frac{|\nabla \rho|}{\rho^{4/3}} \right)^2$$

A corresponding popular GGA approach to the correlation energy is the LYP functional, which has been obtained after fitting four variables to experimental data on Helium.\textsuperscript{78}

A significant improvement to the accuracy of DFT is realized when considering functionals that include some extent of exact exchange (analogous to Hartree-Fock exchange). The most famous of many such \textit{hybrid functionals} is undoubtedly B3LYP,\textsuperscript{79} which has been the standard method for optimizing geometries throughout this thesis,

$$E_{xc}^{\text{B3LYP}} = aE_{xc}^{\text{HF}} + (1-a)E_{xc}^{\text{LSDA}} + b\Delta E_{x}^{\text{B88}} + c\Delta E_{c}^{\text{LYP}} + (1-c)E_{c}^{\text{VRN}}.$$ \hspace{1cm} (2.28)

In B3LYP the three parameters $a$, $b$ and $c$ have been optimized against experimental data on a large set of atomization energies, ionization potentials and proton affinities, and the amount of exact exchange ($a$) amounts to 20 percent.\textsuperscript{79} B3LYP has a reported mean average deviation of 4.1 kcal/mol, when benchmarked against the G3/05 test set.\textsuperscript{80}

In more recent hybrid functionals improved treatment of electron correlation is achieved using inclusion of second order perturbation corrections. One such functional that has been used actively in this thesis is B2PLYP,\textsuperscript{81} which has a reported mean absolute deviation of 2.5 kcal/mol, when tried against the G3/05 test set.\textsuperscript{82}

There are several known limitations to DFT that apply in certain situations. \textit{Self-interaction error}, i.e. an electron’s non-physical interaction with itself, is especially problematic in many pure DFT functionals. The self-interaction of electrons can lead to a preference for delocalization of the electron density that sometimes results in unrealistic energies. This is especially a case of concern for systems with loosely bound electrons, such as anions with low electron affinities, and transition states. This effect can result in large errors for several types of calculations, e.g. bond dissociation energies, excitation energies, or when considering charge-transfer processes.
Fortunately these artifacts are mitigated to a large extent in hybrid functionals that include some amount of exact exchange. Despite this, DFT calculations should preferably be compared to more rigorous wave function based methods when in doubt.

To conclude, modern DFT methods enables calculations on large systems at a computational cost similar to that of Hartree-Fock. The accuracy of these calculations is in many cases comparable to high-level wave function based methods.

2.8. Molecular Thermodynamics

To connect calculated electronic energies of single molecules with macroscopic observables such as enthalpy ($H$), entropy ($S$), or Gibbs free energy ($G$), partition functions are introduced. A partition function is defined as a probability-weighted sum of energy states,

$$ q = \sum_{i=\text{states}} e^{-\epsilon_i/k_bT}. $$

(2.29)

The microscopic partition function ($q$) includes all electronic, translational, rotational and vibrational energy levels of one molecule. The corresponding partition function for a macroscopic system ($Q$), consisting of $N$ such non-interacting identical particles, is given by

$$ Q = \frac{q^N}{N!}. $$

(2.30)

The translational and rotational energy levels can be calculated from the mass of the particle in question, and the temperature. The vibrational energy levels can be calculated from the second derivate of the Hamiltonian energy expression (the Hessian). Explicit knowledge of $Q$ then enables straightforward calculation of the above-mentioned physical quantities $H$, $S$ and $G$,

$$ H = k_bT^2\left(\frac{\partial \ln Q}{\partial T}\right)_v + k_bTV\left(\frac{\partial \ln Q}{\partial V}\right)_T $$

$$ S = k_bT^2\left(\frac{\partial \ln Q}{\partial T}\right)_v + k_b\ln Q $$

(2.31)

$$ G = H - TS = k_bTV\left(\frac{\partial \ln Q}{\partial V}\right)_T - k_bT\ln Q. $$

2.9. Transition State Theory

Transition state theory (TST) is a hybrid quantum-classical approach for treating the kinetics of chemical reactions. The central assumption is that the rate of a chemical transformation is determined by a transition state (TS), which is in thermodynamic equilibrium with the reactant species,

$$ [A] + [B] \rightarrow [TS]^\dagger \rightarrow [P] $$

(2.32)
A transition state constitutes a saddle-point on the multi-dimensional potential energy surface (PES) on which the system evolves. More precisely it is a minimum in all but one coordinate, the reaction coordinate (Figure 3). The equilibrium constant $K^\ddagger$ corresponds to the free energy difference ($\Delta G^\ddagger$) between reactant and transition state, and can be calculated using quantum chemical methods,

$$K^\ddagger = e^{-\Delta G^\ddagger/RT}.$$  \hspace{1cm} (2.34)

**Figure 3.** Chemical reactions occur on a potential energy surface (PES). The transition state (TS) geometry corresponds to the highest point on the most optimal PES path between reactant and product.

The TST approach implies that the rate of reaction is only dependent on the highest and lowest points on the PES along the reaction coordinate. For this reason the movement between reactant and TS can be treated classically. As the minima and maxima on the PES are treated quantum mechanically, the dynamics of perpendicular coordinates are partly taken into account by considering the vibrational modes of the different states.

By assuming equilibrium between all states, their average occupation can be described using a Boltzmann distribution and the rate constant for a reaction calculated using the Eyring equation,

$$k_{rate} = k_bT \frac{e^{-\Delta G^\ddagger/RT}}{h}.$$  \hspace{1cm} (2.35)
where $k_b$ and $h$ are the Boltzmann and Planck constants, respectively. $\kappa$ is the transmission coefficient, which is used to correct for re-crossing and tunneling effects. By setting $\kappa$ to unity and using an accurate value of $\Delta G^\ddagger$, TST provides an upper limit to the real rate, and works well for most ordinary chemical transformations at decent temperatures. However, there are cases where TST is inadequate, two examples being inter-system crossing reactions (e.g. in photochemistry), and tunneling.

2.10. Applied Computational Chemistry

Provided that an adequate electronic description (wave function) can be devised, it is in principle possible to calculate any physical observable of a real molecular system. Some typical calculations that have been used in this thesis are named below. Additional details on their accuracy and methodology can be found in papers I-VIII, or in the literature citations provided.

Electronic structure calculations, i.e. geometry optimizations, single-point energy calculations, and frequency analyses have primarily been performed using the Gaussian,[83] Turbomole,[84] and ORCA[85] program suits. The effects of solvation have been modeled implicitly using the PCM and COSMO methods.[86]

Harmonic vibrational spectra (IR and Raman) have typically been calculated at the B3LYP/6-31+G(d,p) level using analytical force constants. Electronic transitions with corresponding oscillator strengths (UV/VIS) have been calculated at the td-B3LYP[87]/6-31+G(d,p) and CC2[88]/aug-cc-p-VTZ levels of theory. Nuclear magnetic resonance (NMR) spectra have been estimated from shielding tensors obtained using the Gauge-Independent Atomic Orbital (GIAO)[89] protocol on B3LYP/6-311++G(3df,2pd) wave functions.

Properties such as heats of sublimation and vaporization and density have been estimated from a statistical analysis of the electrostatic potential (ESP) on the molecular surface, using parameterized relationships.[90-92] Properties such as density and lattice energy of solids have also been calculated from molecular volumes, which can be estimated from the electron density.[92-95]

Finally, theoretical rocket propellant performances have been calculated using NASA’s CEA code.[96,97] The latter calculations are purely thermodynamic in nature (no quantum mechanics), and based on known equation of states for a large database of compounds.
3. Polymer Chemistry

This chapter is meant to provide a brief introduction to some aspects of hyperbranched polymers and cross-linked polymer matrices. The field of polymer chemistry is vast, and more detailed coverage can be found elsewhere.\cite{98,99}

3.1. Hyperbranched Polymers

Despite that the possibility of making hyperbranched polymers was theorized as early as 1952,\cite{100} it was not until 1978 that the first material was reported.\cite{101} Since then, much attention has been given to perfectly branched, and close to monodisperse systems, so-called dendrons and dendrimers.\cite{102,104} Such macromolecules exhibit very unique properties compared to linear systems, due to their well-defined globular shape. Today these types of materials have been evaluated for use in a wide range of areas and applications, such as drug delivery,\cite{105} photosensitizers,\cite{106} catalysis,\cite{107} energy conversion,\cite{108} sensors,\cite{109} and various other nano-technologies.\cite{110} The main drawbacks of these materials are the costly, and often time-consuming, step-wise synthesis and the need for extensive purification.

In contrast, irregular hyperbranched polymers are typically easy, fast and cheap to attain. Similar to monodisperse dendrimers their properties are correlated to their globular shape, which gives rise to a low viscosity (due to lack of chain entanglements).\cite{111} Similar is also the large concentration of functional groups, which typically enables straightforward and diversified functionalization. The obvious downside with irregular hyperbranches is the much poorer structural control, which limits their use in certain fields, such as medicine and nano-technology.

There are several ways of generating hyperbranched structures, typically using step-growth polycondensation of AB$_x$ type monomers (Figure 4), self-condensing vinyl polymerization of AB’ monomers, or ring-opening polymerization of latent AB$_x$ monomers.\cite{112} One important measure of the structure of these materials is the degree of branching (DB),\cite{113} which ranges from zero for a linear polymer, to one in a perfect dendrimer. DB is defined as a quota between dendritic ($D$), linear ($L$) and terminal ($T$) units,

\[
\text{Degree of Branching (DB)} = \frac{D + T}{D + T + L}.
\]  

(3.1)
3.2. Cationic Ring Opening Polymerization of Oxetanes

In cationic ring opening polymerization (CROP) cyclic monomers are added to a growing chain through step-wise ionic propagation. CROP is possible through two competing mechanisms, whose relative significance is determined by the chemistry of the monomer as well as reaction conditions (Figure 5). In the activated chain end mechanism (ACE) the cation is situated on the chain end of the propagating polymer, whereas in the activated monomer mechanism (AM) the charge is instead present on the free monomer (Figure 5)\textsuperscript{[114,115]} Oxetane-type monomers are the ones most important to this thesis, and will be used as examples.

For oxetanes the AM mechanism generally results in a lower degree of cyclic oligomers and a narrower polydispersity. AM is favored by a low instantaneous concentration (high conversion) of the monomer, and a high concentration of hydroxyl groups in the reaction mixture. The AM mechanism enables the formation of hyperbranched structures if the monomer is multifunctional, e.g. has additional hydroxyl groups.

CROP is performed under acidic conditions, and Brønstedt or Lewis acids such as BF$_3$ or different onium salts of BF$_4^-$, PF$_6^-$ or SbF$_6^-$ anions typically initiate the polymerization of oxetanes.

Figure 4. Schematic representation of an irregular hyperbranched polymer formed using homopolymerization of an AB$_2$ monomer.

Figure 5. Cationic ring opening polymerization of oxetane proceeds through the activated chain end (ACE) and activated monomer (AM) mechanisms.
3.3. Polymer Networks

There are in principle two ways of turning generic polymers into solid plastics. In the first, polymer chains are cross-linked physically, either by reactions between groups on the different chains, or by the addition of a curing agent that bridges several chains and interconnects them. Such processes are typically irreversible, and produce thermoset plastics. Any kind of reaction that forms covalent bonds can in principle be utilized for this purpose.

The other alternative is thermoplastic materials, whose formation in contrast is reversible with heat. In such materials the polymer chains are held together by weaker secondary interactions, such as hydrogen bond, dipole-dipole, and hydrophobic interactions. This has the advantage that the plastic material can be melted and reused a large number of times. On the other hand thermoplastic materials typically exhibit poorer dimensional stability under stress, and at elevated temperatures.

Elastomers are plastic materials that show both viscous and elastic properties (viscoelastic). This allows adaptation (elongation) upon stress, and rapid relaxation back to the initial state after the stress is removed. Depending on the type of material, elastomers can reversibly relax from an extension of up to 1000%. However, when the temperature creeps too low the materials become brittle and glass-like. This transformation occurs at the glass transition temperature ($T_g$), which is an important material characteristic.
4. Decomposition and Reactivity of Dinitramide Salts

(Papers I-VI)

In order to facilitate new technologies based on dinitramide salts, fundamental understanding of the chemistry behind their decomposition and reactivity is necessary. This chapter intends to provide an overview of the theoretical and experimental studies done on ADN and potassium dinitramide (KDN, K\textsuperscript{+}N(NO\textsubscript{2})\textsubscript{2}\textsuperscript{-}) in the work leading up to this thesis. The chapter begins with a thorough walk-through of relevant experimental background information, and continues by explaining the different types of theoretical models used to describe the behavior of solid and liquid dinitramide salts. Thermal stability, decomposition routes, reactivity and stabilization of DN-salts are covered. Spectroscopic investigations of ADN and KDN are also presented.

4.1. Introduction

Many dinitramide salts exhibit what is known as anomalous solid-state decomposition. This manifests itself as faster decomposition in the solid state compared to liquid state, acceleration of decomposition within a small temperature range corresponding to the melting point of the eutectic mixture with the nitrate salt, and instantaneous inhibition of accelerated decomposition with the addition of water.\textsuperscript{[116-118]} The behavior has been reported for a range of salts, including salts from metal ions such as Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+} and Cs\textsuperscript{+}.\textsuperscript{[116]} Interestingly, the dinitramide salts of guanidine\textsuperscript{[43,116]} and guanylurea\textsuperscript{[119]} show no anomalous behavior.

In regards to the anomalous decomposition of dinitramide salts, ADN holds an intermediate position, exhibiting accelerated decomposition only close to the melting point of the eutectic with nitrate at 60 °C.\textsuperscript{[117,118]} The initial activation energy for ADN is highly dependent on experimental conditions and it is typically reported to be between 29 - 42 kcal/mol.\textsuperscript{[41,48,116,118,120,121]} Under vacuum or after significant drying (<0.1 % water) decomposition accelerates, and the barrier is around 30 kcal/mol. A barrier close to 40 kcal/mol is usually seen in non-dry samples, and at atmospheric pressure.\textsuperscript{[116,118,120,121]} ADN have been reported to decompose into numerous products such as N\textsubscript{2}O, NO\textsubscript{2}, NO, NH\textsubscript{4}+NO\textsubscript{3} (AN), HNO\textsubscript{3}, N\textsubscript{2}, HONO, H\textsubscript{2}O and NH\textsubscript{3}.\textsuperscript{[41,44,118,120,122,123]} The relative amounts of these compounds vary depending on the extent of reaction, temperature and pressure. Reported products also depend on the detection capacity of the instruments used in each study.

Initial ADN decomposition gases have been analyzed with time resolved transmission FT-IR spectroscopy at low and high temperatures.\textsuperscript{[121]} Based on this study, it was proposed that decomposition occurs mainly through two pathways,\textsuperscript{[121,124]} one that operates at low temperatures and produces NO\textsubscript{2} as the initial product,

\[
N(NO_2)_2 \rightarrow NO_2^+ + NNO_2^-
\]  
(4.1)
and another that becomes important at higher temperatures (≈150 °C) and produces mainly N₂O,

\[ \text{N(NO}_2)_2 \rightarrow \text{NO}_3^- + \text{N}_2\text{O}. \]  (4.2)

Surface effects and dinitramide distortions have been speculated to provide an explanation for the anomalous decomposition of ADN and dinitramide metal salts. The dinitramide anion, which is typically semi-planar and resonance stabilized, was suggested to be less stable in the solid state due to a non-symmetrical geometric and electronic structure.\[118\] The structural and electronic distortions of the dinitramide anion in different salts have been analyzed by spectroscopic and theoretical methods.\[125,126\]

The simplicity of the potassium cation makes KDN a less complicated compound to analyze, compared to ADN. Hydrogen bonding and proton transfer, possible in ADN, cannot exist in KDN. However, extensive differential scanning calorimetry (DSC) studies have shown that KDN exhibits complicated eutectic, fusion, and liquefaction processes in the solid state.\[127\] It has been concluded that the decomposition processes of KDN are highly topochemical, with accelerated decomposition following smaller particle sizes and cracking of crystals.\[127\] This is indicative of surface chemistry and similar to observations on ADN.\[116\]

The activation barrier for decomposition of KDN under moist air has been estimated to 41 kcal/mol using a manometric procedure.\[116\] KDN’s initial decomposition barrier (1 % decomposed) under closed vacuum has been reported to be 37.5 kcal/mol when using thermobalance measurements.\[128\] In its solid state, KDN primarily breaks down into K⁺NO₃⁻ and N₂O. NO and NO₂ are also observed.\[127,129\]

### 4.2. The Dinitramide Anion (DN⁻)

If one considers the isolated dinitramide anion (DN⁻, N(NO₂)₂⁻, c.f. 1 in Figure 6) in gas phase, the best \textit{ab initio} estimates of its decomposition barrier is 46.1 kcal/mol (enthalpy of activation, CBS-QB3 level, Figure 6 and Paper IV). The reaction proceeds through an internal transition state (TS₁, Figure 6), which transforms the dinitramide anion into an NO₃⁻ anion and nitrous oxide (2). Several groups have previously reported calculations on this transition state, at lower levels of theory.\[130-132\]

The dissociation enthalpy for homolytic cleavage of the nitrogen-nitrogen bond (Eq. 4.1) is as high as 49.7 kcal/mol at the CBS-QB3 level. The corresponding energy barriers for both reactions are 44.8 (Eq. 4.1) and 47.0 kcal/mol (Eq. 4.2) at the B2PLYP/aug-cc-pVTZ level.

It is clear that using a single dinitramide anion for modeling ADN stability results in unrealistically high decomposition barriers. The model is insufficient for describing proper kinetics of solid-state dinitramide salts. This is also in accordance with X-ray diffraction data and computational work, which has shown a single ion to be an insufficient model for recreating experimental dipole moments.\[126\]
Figure 6. Concerted NO₂-transfer in the dinitramide anion can produce NO₃⁻ and N₂O. Energies in kcal/mol are calculated at the CBS-QB3 level.

Since all calculations up to this point only had regarded gas-phase reactions, the effect of a more polar surrounding was investigated using implicit solvation models (Paper VI). The effect of a low polarity solvent (THF) proved significant. The lowest decomposition route changed to a homolytic bond cleavage reaction, in which NO₂ radicals and NNO₂⁻ radical anions were formed (Figure 7). The enthalpy of activation for this process was estimated to 42 kcal/mol, which is in close agreement with experimental data available for several non-dry dinitramide solids, as well as dinitramide melts.\(^{[116]}\) However, these calculations do not explain the anomalous behavior, i.e. the even lower barriers at low humidity and pressure.

Figure 7. Decomposition of the dinitramide anion (1) in gas-phase and in THF solution. Energies in kcal/mol are calculated at the CBS-QB3 level.

4.3. Dinitraminic Acid (HDN)

In an effort to combine experimentally determined activation energies and final products in a viable theoretical explanation several groups (including our own, Paper I) have invoked the conjugate acid of the dinitramide anion (HDN, HN(NO₂)₂, c.f. 4 in Figure 8).\(^{[130-134]}\) On the basis of comparison with ammonium nitrate it was argued that ADN can decompose via HDN, which forms through sublimation of the salt, or proton transfer in the crystal.

The latest high-level calculations on the gas-phase stability of HDN give an enthalpy of activation of 36.5 kcal/mol for its decomposition (c.f. Figure 8, and Paper I). In comparing the obtained activation energies with experiments, HDN appears
inadequate in explaining the energetics of solid-state dinitramide salt decomposition (which should be in the vicinity of \(\Delta H^\ddagger \approx 30 \text{ kcal/mol}\)).

In addition to having high barriers, there are several other facts that argue against the importance of HDN formation. Firstly, HDN has a reported pK\(_a\) of -4.9\(^{135}\), a value in good agreement with earlier theoretical estimates (pK\(_a\) \(\approx -5.6\)^{136}). Consequently, it is one of the most acidic inorganic species known, and unlikely to exist in any but under extreme conditions, e.g. strong acid or vacuum. Secondly, the sublimation enthalpy of ADN has been indirectly obtained from experimental data and found to be 44 kcal/mol.\(^{130}\) This significant energy barrier likely negates the possibility for HDN formation in a solid-gas interface. Thirdly, the kinetic isotope effect for the decomposition of ADN has been measured to 1.38.\(^{118}\) This low value, which corresponds to a non-primary kinetic isotope effect, proves that the process does not include proton transfer in the rate-determining step. Finally, the characteristic anomalous behavior of metal dinitramides (such as KDN) cannot be explained by the existence of HDN, since such compounds do not contain any hydrogen atoms. The relevance of HDN in different media is discussed in section 4.8.

**Figure 8.** Self-decomposition of HDN (4) can proceed through homolytic nitrogen-nitrogen bond cleavage in an HDN proton transfer isomer (5). The process generates HNO\(_3\) and N\(_2\)O (8). Energies in kcal/mol are calculated at the CBS-QB3 level.

4.4. ADN and KDN Clusters

4.4.1. The Dimer Model

In looking beyond the isolated dinitramide molecule, and considering larger system, conformers of the ADN dimer, i.e. (NH\(_4\))^\(+\)N(NO\(_2\))\(_2\)_2 (Paper III and IV) were investigated. The ADN dimer is the smallest system where the salt can exist in ionic form (no HDN formation). Due to the high surface to volume ratio in the dimer, the dinitramide anions experience a lower degree of coordination than in solid ADN. This is a similar situation to dinitramide anions situated on the surface of a crystal. KDN have also been analyzed in parallel to the work on ADN (Figure 9).
Interestingly, conformations that have one dinitramide anion coordinated at only one NO$_2$ group are energetically favored over conformations with a more symmetrical coordination. Dinitramide anions that have an unsymmetrical coordination of counterions become polarized. The polarization reduces the electron resonance stabilization of the anion, which results in partial weakening of one nitrogen-nitrogen bond (c.f. $r_{NN}$ in Figure 9). As a consequence, the dinitramide anion becomes distorted and transforms from a semi-flat structure (e.g. 9 and 13) into a twisted conformation (e.g. 10 and 16).

Figure 9 shows some of the computed dimer systems, where the nitrogen-nitrogen bond lengths ($r_{NN}$) are given together with the dihedral N-N-N twist angle ($\phi$) and relative energies. Despite being lower in energy (i.e. more thermodynamically favored), the elongated nitrogen-nitrogen bonds in the less symmetrical conformers of ADN (10 and 12) and KDN (14, 16) indicate that the structures also are more reactive.

Figure 10 shows a proposed decomposition mechanism for the ADN dimer in conformation 10. The barrier for dissociation of a dinitramide anion into a NO$_2$ radical and a NNO$_2$ radical anion is lowered by a staggering 13.3 kcal/mol compared to the same reaction in the gas phase. If one assumes the first step (10 $\rightarrow$ 17) to be irreversible (due to loss of NO$_2$), it becomes rate-determining. The reduced barrier corresponds to an increase in rate by almost ten orders of magnitude compared to the...
gas-phase. The initial step is quickly followed by the release of N₂O through TS3, and the formation of a complexed OH radical in 18. At this point the OH radicals are likely to act as scavengers of NO₂ radicals (making the initial step irreversible). The combination of 18 and NO₂ produces the final decomposition product ammonium nitrate (AN) in 19. In total, the process is greatly thermodynamically favored, with a relative Gibbs free energy of close to -50 kcal/mol.

The direct formation of nitrate through a concerted process, analogous to TS1, was also investigated in the dimer model (TS4). The polarization of the perturbed anion had the effect of lowering TS1 with almost 6 kcal/mol, giving an enthalpy barrier of 39.1 kcal/mol and a free energy barrier of 40.2 kcal/mol.

![Diagram of decomposition mechanisms](image)

Figure 10. Proposed decomposition mechanisms for solid state ADN. Energies in kcal/mol are relative to 10 unless otherwise stated and calculated at the B2PLYP/aug-cc-pVTZ level.

By using the dimer model it was noted that water could be formed through an almost barrierless process (18 → 20). In this reaction, a proton on ammonium is transferred to the hydroxyl radical, at the same time as the dinitramidide anion is oxidized to a radical (TS5). Because the constituents of the formed cluster 20 are uncharged, there are considerably weaker electrostatic forces holding it together, and its
thermodynamically favored breakup releases a large number of gaseous products (21). The dinitramide radical (21), which is formed in this process, was predicted to decompose primarily through homolytic bond dissociation of its nitrogen-nitrogen single bond requiring an enthalpy of activation of 20.1 kcal/mol (Figure 11 and Paper IV). The dinitramide radical can also decompose in the presence of other radicals through the formation of various trinitramide (TNA, N(NO₂)₂) isomers (25 and 26). The stability of TNA is addressed in greater detail in Paper VIII, and in Chapter 5.

The formation and decomposition of the dinitramide radical 21 (in the way described here) explains both the formation of water, as well as ammonia and several NOₓ species that have been observed experimentally.\[118,120,121,124,137,138\]

![Figure 11. Three decomposition routes available to the dinitramide radical (21). Energies are calculated at the B2PLYP/aug-cc-pVTZ and CBS-QB3 levels.](image)

When the lowest energy conformer of the KDN dimer is analyzed in the same way as ADN, a similar polarization effect is observed (Figure 12). Also in this case the dominating decomposition pathway is homolytic cleavage of a polarized and distorted dinitramide anion into a NO₂ radical and a NNO₂⁻ radical anion (16 → 27). The activation enthalpy for this step is calculated to be 36.0 kcal/mol. Thus, the polarization
phenomenon reduces the barrier by 11.0 kcal/mol compared to the gas phase. This corresponds to an increased decomposition rate by almost eight orders of magnitude.

Similar to the case of ADN and its complexed OH radical in 18, the oxygen radical of 28 will act as a NO$_2$ scavenger. The thermodynamic equilibrium between 27 and 28 ($\Delta\Delta G = 0$ kcal/mol) and the very large driving force favoring product formation (28 $\rightarrow$ 29, $\Delta G = -68.9$ kcal/mol) ensures the irreversibility of the initial step (16 $\rightarrow$ 27). As for the case of ADN, the direct transformation into nitrate, possible through TS10, appears less likely in the modeled scenario as the barrier amounts to 43.9 kcal/mol.

**Figure 12.** Proposed decomposition mechanisms for solid state KDN. Energies in kcal/mol are relative to 16 unless otherwise stated and calculated at the B2PLYP/TZVP(2d)+ level.

4.4.2. Larger Clusters

In order to better address issues such as long range coulombic interactions on real ADN and KDN crystal surfaces and the effect of increased ion coordination and hydrogen bonding, the calculations were expended to larger clusters containing 12 dinitramide anions (Paper III and IV). Both clusters of ADN and KDN were obtained after optimization from their respective X-ray crystal structures.$^{[43]}$

In analogy to what is observed in the dimer models, distorted and polarized dinitramide conformations also form spontaneously on the surface of the larger clusters (Paper III and IV). Due to the larger amount of coordinating cations in these systems, the polarization effect is enhanced, which can be seen when observing the dihedral twist angles.

In ADN, the initial dissociation (likely to be rate-determining) is lowered with 3 kcal/mol compared to the dimer. This is not likely to change much with further expansion of the system. Hence, our best estimate of ADN’s initial decomposition barrier is obtained by correcting the dimer calculations by 3 kcal/mol, resulting in a
barrier of approximately 30 kcal/mol. This is in very good agreement with what is seen experimentally, in the case of dry samples or vacuum.\textsuperscript{[118,120,121]}

For KDN, the polarization phenomenon appears to reach its maximum already in the dimer model, as further expansion into larger clusters has limited effect. Thus, the initial decomposition barrier for KDN is estimated to 36 kcal/mol.

To further validate the full mechanism outlined with the ADN dimer model, all reaction steps were re-analyzed using a model of double size, the ADN tetramer (Figure 13). The results of the tetramer studies were in agreement with the results obtained with the dimer model. Compared to the dimer, the tetramer resembles the 12-unit cluster (Paper IV) to a greater extent, as the polarized dinitramide anion is coordinated by hydrogen bonds from three ammonium cations instead of two. Due to the enhanced polarization induced by the extra hydrogen bond, the enthalpy of activation for the concerted pathway is lowered by an additional 1.5 kcal/mol, relative to the dimer, and becomes 37.6 kcal/mol (TS 12). This value would possibly be reduced further in an even larger system. However, the difference relative the dominating dissociative pathway (NO\textsubscript{2} formation) is unlikely to shrink below 6 kcal/mol. This is in agreement with experimental results, which detect NO\textsubscript{2} at considerably lower temperatures than N\textsubscript{2}O.\textsuperscript{[121,124]} The direct dissociation pathway (30 → 31) is lowered by close to 3 kcal/mol, compared to the dimer, and reaches an enthalpy of activation close to 30 kcal/mol. Thus, the tetramer model results in the same activation barrier as the much larger 12-unit cluster (Paper III and IV).

In the later steps of the decomposition mechanism, the tetramer model appears to support the formation of water and dinitramide radicals to a greater extent than in the dimer. For instance, in the second step (TS11), a double proton transfer and simultaneous electron transfer directly produce water (instead of a hydroxyl in to the dimer) and a bound dinitramide radical. Several isomers then exist (32-34), where the radical is complexed in different ways (either to ammonia, or water), or sits on the hydroxyl. Ammonia, water and NO\textsubscript{x} gasses are expected when the product clusters dissociate. Similar to the case in the dimer model, ammonium nitrate (35) can easily form in the presence of nitrogen dioxide.
**Figure 13.** Proposed decomposition pathways for solid state ADN. Energies in kcal/mol are relative to 30 unless otherwise stated and calculated at the B2PLYP/TZV(2d,2p)+ level.

4.5. Vibrational Sum Frequency Spectroscopy Studies of ADN and KDN

As it is likely that surface chemistry plays an important role for the chemical reactivity and stability of both ADN and KDN, detailed knowledge of their molecular surface structure is important. To verify the theoretical predictions regarding polarized dinitramide anions, described in the previous sections, both salts were investigated using Vibrational Sum Frequency Spectroscopy (VSFS, Paper V).

VSFS is a coherent second order nonlinear laser spectroscopy technique, which can be used to investigate the molecular structure of interfaces that are accessible by a laser. The second order nature of VSFS enables it to only detect molecules with a net orientation. Thus, it only probes the very few molecules residing at the interface between two centrosymmetric media, such as a gas/liquid or a liquid/solid boundary. The technique involves a visible laser beam at a fixed frequency and a tunable infrared (IR) laser beam, which results in the generation of a beam having a frequency equal to the sum of the frequencies of the incident beams. The beam induces IR and Raman anti-Stokes transitions in the surface molecules, which requires the molecular
vibrations to be both IR and Raman active in order to generate a signal in the sum frequency spectrum. The underlying theories behind VSFS are outlined elsewhere.\textsuperscript{139-143}

To enable a clear identification of polarized surface dinitramides, a large frequency shift of a vibrational mode compared to the corresponding signal originating from non-polarized molecules is preferable. Furthermore, the vibrational mode(s) used for identification should not be close to, or overlap, with bands from the nitrate decomposition products, which are presumed to partly occupy the surface. The vibrational mode most suitable for this purpose turned out to be the symmetric and out of phase NO\textsubscript{2} stretch, $\nu_s$(NO\textsubscript{2}), of the dinitramide anion (Figure 14). Since this mode includes a significant amount of antisymmetric N-N-N stretching, it is sensitive to changes in the N-N bond strength. As demonstrated in the previous sections of this chapter, the N-N bond strength changes dramatically in going from a non-polarized to a polarized dinitramide anion. Consequently, a relative shift of approximately +55 cm\textsuperscript{-1} can be expected for the $\nu_s$(NO\textsubscript{2}) mode, in ADN (Figure 14).

Orientation-averaged VSFS-like spectra were theoretically obtained for a large number of ADN, AN, KDN and KN clusters by multiplying IR and Raman intensities obtained at the B3LYP/6-31+G(d,p) level (Paper V). The average sum frequency intensity of the $\nu_s$(NO\textsubscript{2}) stretch of polarized dinitramide anions was projected to be significantly higher than most other bands.

Crystals of ADN and KDN were obtained after crystallization in 2-propanol. Some crystals were stored in saturated solution, whereas others were stored under air. Different conditions (such as ambient and N\textsubscript{2} atmosphere) were also tried during SF acquisition. In addition to the VSFS studies, bulk IR and Raman measurements were made on ADN, KDN, AN and KN crystals (Figure 15). Published experimental IR and Raman data was also employed to facilitate the assignment of the SF peaks.\textsuperscript{144,145}

The surface of KDN was found to be rough and partly covered with a thin layer of KN, which due to its low thickness was not detectable by infrared and Raman spectroscopy (Paper V). This is in agreement with observations done by XPS.\textsuperscript{127} In contrast, no conclusive signature of AN was observed on the surface of ADN. Instead, ADN exhibits an extremely inhomogeneous surface on which polarized dinitramide anions are present (Figure 16). However, as previously mentioned, it is well established that the main solid-state decomposition product of both ADN and KDN is nitrate.\textsuperscript{144,118,120,123} Because the formation of AN is known to occur, the observed peaks at 1345 and 1050 cm\textsuperscript{-1} in Figure 16 are likely to originate at least partly from AN.
Figure 14. The frequency of the symmetric and out of phase NO$_2$ stretching mode of the dinitramide anion is blueshifted when the anion is polarized (twisted). Harmonic vibrational frequencies have been calculated at the B3LYP/6-31+G(d,p) level, and scaled by 0.97 to fit experimental data of the 1200 cm$^{-1}$ band.$^{[144]}$

Figure 15. Bulk Raman and IR spectra of ADN, KDN, AN, and KN crystals.

Due to the random nature of the ADN surfaces, quantitative measurements were impossible to perform. No correlation between preparatory methods and peaks could be found, and the spectra in Figure 16 have been chosen to show all encountered signals.
The peaks at ~1180 and ~1210 cm\(^{-1}\) originate from the symmetric NO\(_2\) stretching vibration (out of phase) of ADN, \(\nu_s(\text{NO}_2)\).\textsuperscript{[144,145]} Good agreement with the computed spectra indicate that the peaks at ~1243 and ~1271 cm\(^{-1}\) originate from the same vibration in polarized anions. A thorough discussion surrounding the peak assignments for both ADN and KDN is given in Paper V.

The theoretical and experimental observations of polarized dinitramide anions on disordered surfaces of ADN are of great importance for understanding the chemical stability and reactivity of the ADN salt. As unwanted decomposition is likely to be highly topochemical, these results will facilitate a more efficient tailoring of surface-active polymer support, stabilizers and/or coatings for ADN.

Figure 16. Four selected VSF spectra of ADN that show proof of a highly disordered surface, where polarized dinitramide anions are present in different conformations.

4.6. The Anomalous Behavior of Dinitramide Salts

The anomalous behavior of dinitramide salts is loosely defined as faster decomposition of the salts in the solid state compared to liquid state, acceleration of decomposition at the melting point of the eutectic mixture with nitrate, and instantaneous inhibition of accelerated decomposition with the addition of water.\textsuperscript{[116-118]} The combined studies in this thesis have led to a plausible explanation to the anomalous behavior.
After performing a range of high-level computational studies it can be concluded that the decomposition barrier of an unperturbed dinitramide anion, is around 40-42 kcal/mol in polar and non-polar solvent. This value for the barrier is similar for symmetric non-polarized (i.e. bulk-like) clusters of ADN and KDN in gas-phase. The average value of 41 kcal/mol is in agreement with values obtained for several dinitramide metal salts, both in the solid state, and in a molten state.\textsuperscript{116} The value is also in agreement with non-dry ADN under atmospheric conditions.\textsuperscript{118,120}

An accelerated decomposition, with a corresponding activation barrier of approximately 30 kcal/mol for ADN, and 36 kcal/mol for KDN, is explained by a situation where the dinitramide ion is polarized due to favorable interactions with its surrounding counterions (section 4.3 - 4.4, Papers III and IV). This effect is especially pronounced when the respective solids are subjected to a surrounding with weak interactions to the surface, such as a vacuum, or a non-polar environment. Nevertheless, the experimental VSFS results of the previous section have shown that polarized structures are to expect even under ambient conditions. With this in mind, the known stabilizing effect of water is easily understood. Water has been shown to stabilize ADN by several orders of magnitude, using implicit and explicit solvation modeling of dinitramide clusters (Papers III and IV). This is in agreement with experimental findings.\textsuperscript{118}

Theoretical modeling and spectroscopic measurements (section 4.5, Paper V) have shown that surfaces of ADN and KDN are highly complex. Pure dinitramide surfaces are unlikely to exist for longer time periods, especially under drying conditions. A pacifying layer of nitrate covers the surface of KDN. ADN appears to have both AN and dinitramide present on its irregular surface. As speculated in earlier literature,\textsuperscript{116,118} the occurrence of nitrate-dinitramide mixtures is a likely explanation for the accelerated decomposition of ADN at 60 °C, and KDN at 109 °C. However, as bulk and sub-surface Raman and IR measurements show no sign of nitrate in either salt, the anomalous acceleration likely arise due to melting processes on the surfaces of the solid salts.

There is irrefutable experimental evidence showing the existence of surface processes. For instance, the decomposition rates of dinitramide salts are known to accelerate with grinding of crystals.\textsuperscript{116,127} Grinding increases the overall surface area, and creates new non-decomposed surfaces of dinitramide. As speculated in earlier work,\textsuperscript{116} the formation of eutectic mixtures is also accompanied by an increased number of crystal defects. This will likely reduce the stability of the dinitramide ions bordering to such defects. The dependence on pressure and the stabilizing effect of water vapor also supports the importance of surface processes.

It is noted that the NNO$_2^-$ radical anion, which is formed in the initial steps of KDN’s and ADN’s decomposition (and likely many other dinitramide salts), is charge-topologically similar to the nitrate ion (Paper IV). An ADN-NNO$_2$NH$_4$ mixture is likely to exhibit similar physical properties to ADN-AN (e.g. close to identical melting points). Since the NNO$_2^-$ radical anion is significantly less stable than both nitrate and dinitramide, it decomposes very quickly. During its short existence, it and its immediate surroundings constitute an ADN-AN imitating ADN-NNO$_2$NH$_4$ mixture. As such a phase is likely to melt close to the eutectic point, it will add to the overall acceleration of decomposition in this temperature range. However, it should be noted
that no experimental data is known for $\text{NNO}_2\text{NH}_4$, and that its physical properties and importance are speculative at this point.

The anomalous acceleration at the eutectic temperature only occurs at that specific temperature, and not above. The constitution of ADN and AN at the eutectic point is reported to be a 1:2 ratio.\[^{118}\] Thus, a crude sketch of the binary eutectic system can be devised from the melting points of ADN and AN (Figure 17). The phase changes inherent in pure AN have been omitted. The accelerated decomposition at the eutectic temperature is likely due to the necessary phase changes (melting) that need to occur when the system resides in this temperature (see horizontal solidus line in Figure 17). Such processes will create new interfacial surfaces and crystal defects where polarized dinitramides can form and accelerate decomposition. The effect is likely to be observed largely irrespective of the concentration of AN in the system. The decrease in rate, when increasing the temperature above the eutectic temperature, is explained by a system in equilibrium (no phase changes). Crystallization of ammonium nitrate on the surface can also act stabilizing. The decomposition barrier for any co-existing liquid ADN-AN-phase will be similar to bulk ADN, i.e. ca 40-42 kcal/mol.

![Figure 17](image)

*Figure 17.* A rough sketch of the ADN-AN eutectic system. Accelerated decomposition at specifically 60 °C is explained by melting processes. A pacifying AN-phase is expected to form if the concentration of nitrate in the surface composition exceeds ~67 %.

### 4.7. Compatibility Testing

To acquire a more fundamental understanding of which specific chemical groups that are ADN-compatible, a systematic heat-flow calorimetry (HFC) study was performed. The analysis was done according to STANAG 4582,\[^{146}\] where the heat-flow due to decomposition is measured at 75 °C for 19 days, and where a value below 63.1 μW/g is used as a criteria for sufficient stability. By assuming first order decomposition
kinetics, it can be estimated that a free energy of activation needs to exceed roughly 34 kcal/mol in order for a compound to be classified as non-reactive towards ADN under these conditions. This approximate value is important in later comparisons with calculated reaction barriers (section 4.8).

A known ADN-compatible solvent, dimethylformamide (DMF, 41), was used to dissolve ADN together with each compound to be tested. Approximately 200 mg of prepared solution was used in every test, of which circa 20-30 mg were ADN, and an equal amount the corresponding test compound. The results of the study are shown in Figure 18.

In addition to this test set, there are a large number of other substances that have been tested over the years. However, since such tests have been performed differently (e.g. bulk mixing of solid polymers, instead of molecules in a solvent medium), they are not included. Unfortunately, the knowledge of such tests is also to some extent classified, and has not been fully disclosed to the author of this thesis.

As partly presented in Paper IX and X, several polymers have been analyzed during the course of this project. The energetic poly(glycidyl azide) polymer (GAP) as well as the energetic polymer poly-3-methyl-3-(nitratomethyl)oxetane (poly-NIMMO) are previously known to be ADN compatible. In addition to these materials, hyperbranched poly-3-ethyl-(hydroxymethyl)oxetane (poly-TMPO) was shown to be surprisingly compatible. A number of different copolymers of TMPO and THF also exhibit good stability towards ADN. Different alkyne-functionalized versions of poly-TMPO and poly-TMPO-co-poly-THF have also been analyzed, with varying results (Paper X). As seen in Figure 18 it is difficult to draw any obvious conclusions regarding trends or reasons for or against compatibility.

The ether functionality is deemed stable when present in a small molecule in solution (40), and when incorporated into polymers such as GAP, NIMMO and poly-TMPO, but incompatible when present in a larger poly ethylene glycol (PEG) chain (Paper IX).

It is noteworthy that carboxylic acid groups appear thermally stable with ADN, when present in solution (38). This goes against the premise that acidity (although weak in this case, $pK_a = 4.8$) is of importance for ADN’s stability. It can also be concluded that hydroxyl groups, which are present in various alcohols and polymers known to work well with ADN, are compatible.

Amines were shown to be incompatible in two of the investigated substances. However, the amine functionality is present in several stable dinitramide salts, such as guany lurea dinitramide (GUDN), as well as known ADN stabilizing agents, such as 2-methyl-4-nitroaniline (MNA). Dimethyl amides proved exceedingly stable when present in the solvent DMF (41), whilst incompatible when situated next to a phenyl group (54). Azides are undoubtedly thermally stable together with ADN, as shown both with our test substance 1-hydroxy-3-azidopropane (37) and with azide-containing polymers (e.g. GAP).
It can be concluded that the ADN-compatibility of some functional groups depends heavily on their physical environment. For instance, hydroxyls, amines and ethers behaves differently when present in a small molecule in solution, compared to when embedded in a macromolecule. As will be strongly indicated in the next section of this chapter, the ammonium cation is one likely cause for the wide range of incompatibility that plagues ADN. The surrounding environment needs to discourage exchange of protons, by strongly binding to the surface of ADN. To facilitate this the surrounding should preferably be polar in nature, and capable of hydrogen bond donation. This will
stabilize surfaces of ADN, and discourage the formation of HDN and ammonia. At the same time the surrounding should not enable ADN to become partly solvated, as this likely creates new reaction centers at the ADN-polymer interface. As ADN predominantly exists as clusters in medium and low-polarity solvents (that have surfaces), the above reasoning also applies to such solutions.

4.8. The Reactivity of ADN

This section of the chapter aims to explain some of the observed HFC results, using quantum chemical calculations. Work primarily focused on dinitraminic acid (HDN) is presented first. This is followed by a theoretical investigation into the likelihood of HDN’s formation from ADN in different media. Finally, other alternative explanations to the reactivity of ADN are addressed.

Because of the dinitramide anion’s high inherent stability, it is difficult to imagine how it can be directly responsible for the large range of incompatibility issues concerning ADN and various chemicals. Initial calculations on the addition of the anion to olefinic double bonds, through 1,3-cycloaddition and direct nucleophilic attack, resulted in unreasonably high activation barriers (> 40 kcal/mol), both in gas-phase and in solution.

In Paper II the reactivity of HDN (4) was investigated with respect to its hitherto unknown 1,3-dipolar cycloaddition reactions with olefinic double bonds (Figure 19). The reactivity of eight different double bonds, with varying electron affinity, was modeled with HDN, and compared to the known 1,3-dipoles azide and nitrile oxide.

Electron-rich double bonds, such as vinyl ethers, were predicted to be substantially more reactive than more electron-poor ones, such as acrylates. The reactivity difference could be explained using frontier molecular orbital theory, in which the reactivity trend is primarily determined by the overlap of the HOMO and LUMO orbitals of the reacting species.

Initially, the results of Paper II were considered promising, as they provided a plausible mechanism for the known incompatibility of ADN and vinyl ethers, a functionality that is present in certain polymer cross-linking agents. Unfortunately, experimental testing with increasingly electron-poor bonds, e.g. in acrylates, provided no improvement to the ADN-compatibility (section 4.7). Although the reactivity towards vinyl ethers could be explained, it was concluded that other mechanisms also needed to be considered.

HDN has been reported to add to activated olefinic double bonds through Michael-type reactions in benzene.\textsuperscript{[147]} 2-propanal, methyl vinyl ketone and phenyl vinyl ketone were shown to react rapidly, but the more electron-poor double bonds of acrylonitrile and methyl acrylate proved non-reactive.\textsuperscript{[147]}

In an effort to explain this reactivity, a number of model compound were analyzed in gas-phase using B3LYP/6-31+G(d,p) and CBS-QB3 calculations. Figure 20 shows the theoretical justification for the reported experimental findings. The reactions proceed through a type of concerted 1,4-conjugate addition, in which the carbonyl oxygen of the olefin accepts a proton from HDN, as the center nitrogen of the dinitramide attacks the β-carbon. Subsequent keto-enol tautomerization gives the final products, which have been identified by \textsuperscript{1}H-NMR.\textsuperscript{[147]}
When a lone aldehyde or ketone neighbors the double bond, the basicity of the carbonyl is sufficient to make the reaction proceed rapidly. However, when an electronegative group or element, such as oxygen, neighbors the carbonyl the activation energy rises significantly, and hinders the reaction (Figure 20).

This specific reactivity of HDN, which is now rationalized by theoretical models, is intriguing and can possibly be utilized in synthesizing a range of new organic dinitramide derivatives.
However, just as the relevance of HDN can be questioned in regards to ADN’s self-decomposition and solid-state anomalous behavior, its role in ADN’s incompatibility issues primarily depends on its possibility to spontaneously form from ADN, in meaningful quantities. The \( pK_a \) of HDN is \(-4.9\). Thus, the presence of HDN in a polar surrounding should be insignificant. To shed light on the actual relevance of HDN in different media, a PCM-B3LYP investigation was performed, including all relevant species. It is important to remember that the PCM method provides fairly poor accuracy in certain cases. Consequently, the presented values in Figure 21 are only rough estimates.

Figure 21 shows calculated relative free energies and enthalpies for the acid-base equilibrium of ADN in gas-phase (\( \varepsilon = 0.0 \)), THF (\( \varepsilon = 7.58 \)) and water (\( \varepsilon = 78.4 \)). It is noteworthy that the sublimation enthalpy of ADN, which has been indirectly obtained from experimental data and found to be 44 kcal/mol, is in fairly good agreement with our calculated value for the tetramer cluster. As can be expected, the sublimation energy approaches the real value, with increasing size of the theoretical model.

Figure 21 shows that the predominant form of ADN in gas-phase (1 atm), is ionic, and present in the form of clusters. The existence of positive and negative ionic gas-phase clusters has been verified experimentally, using mass and collision induced dissociation (CID) spectroscopy. HDN is expected to be thermodynamically viable in small amounts, especially at pressures lower than 1 atm (Figure 21). However, the high sublimation energy presents a significant barrier for this transformation, and experimental detection of gas-phase HDN is usually achieved under extreme circumstances, such as ion or laser bombardment of a solid sample. In addition, as shown in section 4.4, the anomalous solid-state behavior of ADN, with barriers close to 30 kcal/mol, can only be explained with an ionic model (and not with HDN).

As HDN is unlikely to form in meaningful quantities in the gas-phase, its concentration in more polar media will be even scarcer. In THF the predominant form will be clusters of ADN, whilst HDN will exist on a scale of a few ppb. In water, the free ions will dominate, and HDN will be virtually non-existing (K \( \approx 7*10^{-12} \)). This is in agreement with aqueous experiments on HDN.

From the mechanistic calculations on clusters of ADN, it was realized that various radicals form during the thermal decomposition reactions (section 4.4 and Paper IV). These species, including OH, NO\(_2\), NO\(_3\) and N(NO\(_2\))\(_2\) (e.g. 21-24), can be strongly bound in spin delocalized complexes with water and ammonia, as well as stabilized by electrostatic interactions with the surrounding bulk. Upon solvation of such a contaminated ADN salt, radicals will be released to the surrounding environment, and initiate various harmful decomposition processes (Paper IV).
Figure 21. The acid-base equilibrium of ADN in different media, calculated at the PCM-B3LYP/6-31+G(d,p) level. \( N = 2, 3 \) and 4 denotes ADN clusters of increasing size in the gas-phase.

It is also conceivable that the semi-stable trinitramide (TNA, Paper VIII) forms during some of the decomposition routes. It, or more likely its decomposition products, could then be present during decomposition of ADN. The standard method for analyzing the purity of ADN is high-pressure liquid chromatography (HPLC) and UV-spectroscopy in water. As TNA decomposes rapidly in polar solvents and ambient temperatures (Paper VIII), it would not appear in such analyses. Regardless of the method of detection the existence of TNA has been shown difficult to prove even at higher concentrations, and it is unlikely to be detected in ADN if present.

The most likely explanation to the wide range of compatibility issues of ADN is realized when considering conjugate additions of the ammonium-dinitramide ion pair to various double bonds. Figure 22 shows some of the investigated reactions with vinyl and carbonyl double bonds. Non-substituted alkenes are predicted to be kinetically stable with respect to dinitramide addition, with free energy barriers exceeding 40 kcal/mol. This is in agreement with the HFC study. The reactivity between ADN and electron-poor double bonds, such as acrylates, can be understood by ammonium-mediated 1,4-conjugate addition of the dinitramide anion to the \( \beta \)-carbon (c.f. TS19 in Figure 22). The observed reactivity of ADN towards ketones can also been explained by a similar 1,2-addition to the carbonyl carbon (c.f. TS21 in Figure 22).
Figure 22. Conjugate additions of the ammonium-dinitramide ion pair to vinyl and carbonyl carbons explain much of ADN’s reactivity. Energies in kcal/mol (1 M) are calculated at the B3LYP/6-31+G(d,p) level. X means little or no reaction after 19 days at 75 °C.

For simplicity, the energies in Figure 22 are shown relative to HDN and ammonia. If the transition state energies are instead taken relative clusters of ADN (dimer or trimer), the enthalpy barriers ($\Delta H^\ddagger$) rise due to the higher stability of the clusters. However, the rate-determining free energies of activation ($\Delta G^\ddagger$) remain very similar due to smaller entropic effects. The cost of forming HDN and ammonia from ADN varies between media, and this energy should be added to the presented gas-phase barriers to obtain more realistic values (Figure 21). As the free energy cost of HDN formation is in the vicinity of 10 kcal/mol in low polarity surroundings (Figure 21), free energy barriers of approximately 30 kcal/mol can be estimated for most reactions shown in Figure 22. Such barriers are sufficiently low to explain much of the observed incompatibility at 75 °C (Figure 18, section 4.7).

Due to the tedious procedures associated with transition state optimization in solution (e.g. using PCM), the transition states shown in Figure 22 have only been investigated in the gas-phase. However, as most enthalpy barriers are very low, despite the presence of the in gas phase unfavorable ionic dinitramide, any additional solvation effects are unlikely to reduce the rates of reaction significantly.

To conclude this section, the dinitramide anion (1) is deemed relatively un-reactive by itself, and even though the conjugate acid (HDN, 4) might influence the reactivity of ADN, its importance appears unjustified. One possible explanation to the range of incompatibility of ADN is the presence of complexed radical decomposition intermediates. However, a more likely explanation, for much of the observed reactivity, is ammonium-mediated conjugate addition of the dinitramide to vinyl and carbonyl.
double bonds. HDN formation is not a prerequisite for such processes, however its importance over-all cannot be completely ruled out. HDN remains one possible explanation for ADN’s reactivity towards vinyl ethers, with which it can react through 1,3-dipolar cycloaddition reactions.

4.9. Stabilization of Dinitramide Salts

One of the primary conclusions regarding the stability of dinitramide salts is the importance of maintaining electron delocalization in the anion. Polarized dinitramides, primarily present at interfaces, reduce the stability of ADN under non-polar, dry and vacuum conditions. The known stabilizing effect of dinitramide salts by small amounts of water has been explained using implicit and explicit solvation of clusters (Papers III and IV). Higher activation barriers in dinitramide melts and solutions, compared to the solid state, support this notion.

The importance of maintaining resonance stabilization of dinitramide anions, e.g. by hydrogen bond donation, indicate that surface-active species can act as stabilizing agents for dinitramide salts, and especially ADN. Amines as well as compounds containing hydroxyl groups are predicted to generally function towards this end. Furthermore, suitable inert compounds with strong polar or ionic character likely assist in this manner. This is in agreement with the known pacifying effect of nitrate, on the surface of solid ADN and KDN, as well as the effect of potassium phosphate, ammonium fluoride$^{[118]}$ and the effect of several other compounds mentioned later in this section.

One drastic way of removing the issue of polarization of the dinitramide altogether is to change the counterion. If chosen carefully, this can also remove many ammonium-catalyzed reaction pathways (section 4.8).

If the dinitramide anion is strongly locked in a flat geometry, e.g. through hydrogen bonding from a matching counterion, the stability of the anion increases significantly. One clear example of this is realized by comparing the crystal structures of ADN and guanylurea dinitramide (GUDN), shown in Figure 23. The crystal stabilization of the dinitramide anion in GUDN is astounding, and the activation energy has been measured to 66.2 kcal/mol.$^{[119]}$ This value can be compared to approximately 40 kcal/mol seen in most moist, solvated, or otherwise stabilized forms of metal and ammonium dinitramides, or 30 kcal/mol in dry ADN.

Figure 23. Destabilization and stabilization of the dinitramide anion through crystal lattice effects is clearly illustrated in the crystal unit cells of ADN and GUDN, respectively.
The activation barrier for molten dinitramide salts, i.e. of anions avoid of crystal effects, is approximately 40 kcal/mol.\textsuperscript{[116]} Compared to this base value, dinitramide anions in solid ADN can experience a destabilization due to polarization of up to 10 kcal/mol (Papers \textbf{III} and \textbf{IV}). In the same fashion, metal dinitramides, such as KDN are destabilized by roughly 4 kcal/mol (Paper \textbf{IV}). As already mentioned, polarization-negating counterions, such as guanyl urea (GU), act in the opposite way, and can stabilize dinitramide anions by as much as 26 kcal/mol.\textsuperscript{[119]}

In other words, the activation barrier for thermal decomposition of dinitramide salts roughly correlates as,

\[
\Delta E^\ddagger = 40 + \Theta^\pm
\]  

(4.3)

where \(\Theta^\pm\) denotes the stabilizing or destabilizing effect of a counterion in the solid state (in kcal/mol). As already shown for the case of potassium and ammonium, \(\Theta^-\) can be accurately calculated using quantum chemical methods. For GUDN \(\Theta^+\) can be accurately reproduced by approximating it to the binding enthalpy of HDN in the gas-phase (Figure 24).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure24.png}
\caption{Stabilizing counterion effects (\(\Theta^+\)) can be approximated to the binding enthalpy of HDN to a base in gas-phase (\(\Delta H\)). Energies (kcal/mol, 1 atm) are calculated at the B3LYP/6-31+G(d,p) level.}
\end{figure}

It is clear that the nature of the counterion is paramount for the stability of the dinitramide anion. Future research into novel dinitramide counterions is encouraged and should utilize the presented stability correlation.

When concerned about the stability (and reactivity) of ADN, it as also advisable to consider the possible formation of radicals. It is clear from the mechanistic investigations on ADN’s decomposition (section 4.4, and Papers \textbf{III} and \textbf{IV}), that many different radical species can be formed. This suggests that antioxidants should be potent as ADN stabilizers.

Finally, one can consider basicity, which by many has been assumed the most important property of an ADN stabilizer.\textsuperscript{[117,118]} However, as already discussed at lengths in this thesis, the justification for HDN formation is poor, and possible base stabilization of ADN is only deemed relevant in the most non-polar of environments.

Several compounds have been tried experimentally with ADN in efforts aimed at finding suitable stabilizers.\textsuperscript{[117,118,148,149]} Different amines, such as hexamine, diphenylamine, 2-nitro-diphenylamine, 2-methyl-4-nitroaniline (MNA) and ammonia
have all generated positive effects.\textsuperscript{117,118,149} Amides as well as various inorganic salts have been shown effective in the molten\textsuperscript{149} and in the solid state.\textsuperscript{118} Perhydro-1,3,5-triazine-2,4,6-trion, commonly known as Verkades superbase,\textsuperscript{150,151} is reported a good stabilizer for ADN.\textsuperscript{117} Methylidiphenyl urea (Akardit II) has also shown stabilizing properties.\textsuperscript{152}

One plausible explanation for the stabilizing effect of these compounds is that they can form complexes with free radicals, i.e. act as radical-traps, or “radical-stabilizers”. This has already been demonstrated theoretically possible for ammonia (c.f. 33 in Figure 13).

Several compounds have been analyzed for their ability to complex the dinitramide radical (21). Interestingly, hexamine (71) and MNA (72), two of the most successful ADN stabilizers, proved among the best in this respect (Figure 25). Complexation enthalpies between 12 and 14 kcal/mol effectively raises the decomposition barrier for the dinitramide radical (21) above 30 kcal/mol. Although promising, the low-level DFT-B3LYP energies presented here should preferably be validated against higher-level calculations.

Figure 25. The ADN-stabilizing effect of hexamine and MNA, as well as other similar basic amino-compounds, can be explained by their ability to bind free radicals. Energies (kcal/mol, 1 M) are calculated at the B3LYP/6-31+G(d,p) level.

Aside from the theoretical justification for the radical-trap nature of these stabilizers, there is also experimental evidence. MNA is known to stabilize nitrocellulose, which decompose through the formation of NO\textsubscript{X} gases (radicals). Furthermore, the depletion of MNA has been reported to track decomposition of ADN, whilst pushing the decomposition onset to a higher temperature.\textsuperscript{153} It is also known that nitrogen oxides can oxidize amines.\textsuperscript{149} Consequently, it is reasonable to assume that the ADN-stabilizing effect of amines\textsuperscript{117,118,148,149} is due to their reducing ability, rather than their basicity.
To summarize, it is postulated that dinitramide salts, and in particular ADN, can be stabilized in several different ways:

- By mitigating the polarization of dinitramides at surfaces and interfaces. Suggestively using surface-active species that can adhere to protruding dinitramides using dipolar, ionic or hydrogen bond interactions.
- By changing the cationic counterion to one that does not aid the reactivity of the dinitramide anion, and preferably reduces the polarization effect.
- By the pacification of formed free radicals, using radical-complexation and reducing agents.

4.10. Summary and Conclusions

This chapter has covered the efforts to decipher the decomposition kinetics, solid-state behavior, reactivity and stabilization of dinitramide salts, and in particular ADN. Polarized and distorted dinitramide anions protruding from solid surfaces explain the low decomposition barriers seen under dry and low-pressure conditions. Vibrational sum frequency spectroscopy measurements on KDN indicate predominantly nitrate on the surface. ADN, however, proved to have a much more chaotic surface structure, in which micro domains of both AN and ADN exists. The theoretically predicted polarized dinitramide anions were detected. ADN’s anomalous acceleration of decomposition at the eutectic temperature of 60 °C is explained by phase changes occurring due to the coexistence of ADN and AN.

The reactivity of ADN towards several chemical groups and materials has been investigated using heat-flow calorimetry. The effect of changing the physical and chemical surroundings was seen to affect the reactivity of several functionalities. The reactivity towards different vinyl and carbonyl carbons can be theoretically explained by ammonium mediated conjugate addition reactions.

Finally, it is concluded that stabilization of the dinitramide anion is possible by counteracting polarization, for instance through the donation of hydrogen bonds from counterions or surfactants, and by the trapping of radical intermediates using suitable amine functionalities. Future research into novel dinitramide salts and ADN stabilizers could benefit greatly by properly considering the presented methodologies and results.
5. Green Energetic Materials

(Papers VI - VIII)

This chapter of the thesis summarizes the work done a range of novel energetic materials. These studies were in part encouraged by the high energy content and stability of the dinitramide anion (1), which led to a search for new oxygen and nitrogen rich compounds with similar advantageous properties. The chapter begins with a brief introduction into well-known energetic materials and selected key concepts. The main theoretical findings are presented. Finally, the synthesis of trinitramide (TNA) is addressed.

5.1. High Energy Density Materials (HEDMs) and Propulsion

The concept of HEDMs encompasses a wide range of substances, some of which are purely theoretical. Aside from conventional chemicals, substantially higher energy densities can be realized through exotic physics, e.g. in metallic hydrogen, nuclear isomers, fission, fusion, and antimatter. However, in this thesis, the term HEDM refers to energetic molecules that stores and releases their energy purely through the making and breaking of chemical bonds. The primary uses of such HEDMs are as secondary explosives and in propellant applications. Traditional hydrogen, nitrogen and carbon (HNC) substances within this class of compounds are 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and the more recent 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) (Figure 26).

These compounds derive most of their energy from a high heat of formation ($\Delta H_f$), a quantity strongly coupled to the nitrogen content of a molecule. In essence, this is due to the large difference in bond strength between nitrogen-nitrogen single ($\approx 38$ kcal/mol) and double ($\approx 100$ kcal/mol) bonds, compared to the triple bond of molecular nitrogen ($\approx 228$ kcal/mol). This large thermodynamic driving force for molecular nitrogen production also explains the inherent instability of many nitrogen rich compounds. In addition to nitrogen content ring strains also add to the energy of an HEDM. This is especially apparent in the cage-structure of the famous CL-20 molecule (Figure 26).
For an HEDM to perform well in a propellant formulation, its combustion upon firing needs to generate a high specific impulse ($I_{sp}$).[^97] The specific impulse, or effective exhaust velocity (Ns/kg = m/s), is defined as the thrust divided by the average mass flow through a rocket engine, and corresponds to performance per mass of propellant,

$$I_{sp} = \frac{F_{thrust}}{m}. \quad (5.1)$$

To some extent the specific impulse depends on the average molecular weight of the decomposition products, in the mass flow leaving the rocket engine. Small molecules carry most of the combustion energy as kinetic energy, whilst larger more complex molecules become vibrationally excited, thus reducing the performance of the propellant. For this reason proper combustion of a rocket propellant is desirable, and high combustion temperatures ($T_c$) usually accompany well performing propellants. Unfortunately, higher temperatures can become a concern when metals, such as aluminum, are being combusted. Existing highly aluminized propellants exhibit combustion temperatures up towards 3600 K.[^155] State-of-the-art materials used in the throat and nozzle of rocket engines fail at approximately 2500 K. Higher temperatures can be managed using regenerative cooling, film cooling, or ablative protection. However, combustion temperatures above 5000 K are unrealistic in practice.[^156]

Most propellant formulations include an oxidizer component and a fuel component. As common oxidizers have very low enthalpies of formation, they add little to the overall energy of the propellant. It is instead through combustion of the fuel (e.g. a metal) that the majority of energy is released. Many HEDMs, e.g. HMX and RDX, are not suitable for this purpose, since their typical negative oxygen balance (O.B., %) prohibit a complete combustion of themselves, or any additional fuel. Instead such compounds are employed as high explosives, or energetic additives. A compound that has the ability to combust itself completely without external oxygen is in this thesis referred to as having a perfect oxygen balance.

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm$^3$)</th>
<th>$\Delta H_f$ (kcal/mol)</th>
<th>Oxygen balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>1.78</td>
<td>-16</td>
<td>-74.0</td>
</tr>
<tr>
<td>RDX</td>
<td>1.82</td>
<td>+16</td>
<td>-21.6</td>
</tr>
<tr>
<td>HMX</td>
<td>1.91</td>
<td>+18</td>
<td>-21.6</td>
</tr>
<tr>
<td>CL-20</td>
<td>2.04</td>
<td>+100</td>
<td>-11.0</td>
</tr>
</tbody>
</table>

Figure 26. Some of the most important HEDMs in use today, together with selected characteristics.

[^97]: http://example.com
[^155]: http://example.com
[^156]: http://example.com
5.2. Green Energetic Materials (GEMs)

This part of the thesis is focused on a series of possible green energetic materials (GEMs) that, compared to common high explosives, have high oxygen balances. The investigated carbon free materials, which in a sense can be regarded either as energetic oxidizers or oxygen-rich high explosives, are predicted to be better-suited propellant components compared to classical HEDMs.

The combination of high inherent energies in the GEMs with high oxygen balances leads to better performances whilst reducing the necessity of metal fuel. The lessened need for metal fuel significantly reduces combustion temperatures, and enables both lighter and cheaper constructions as well as reduced smoke formation upon firing.

The classification as green can obviously not be certain until a compound has been successfully synthesized in bulk, and subjected to a thorough toxicity study. Nevertheless the halogen and metal-free nature of all the investigated compounds is encouraging. In addition advanced thermodynamical modeling have shown that all compounds decompose to harmless compounds such as water, molecular nitrogen and carbon dioxide when properly combusted in a rocket engine.

The stability of the dinitramide anion, and other related high-energy compounds, is correlated to several key electronic and physical properties:

- Weak nitrogen-nitrogen and nitrogen-oxygen single bonds can be strengthened by electron delocalization, resulting in partial double bond character and increased stability. This can typically be achieved through two ways:
  - Resonance stabilization between $sp^2$-hybridized nitrogen and oxygen. Lewis resonance structures should allow alternating negative and positive charges.
  - Aromaticity, or resonance, in cyclic systems that have $4n+2$ π electrons ($n = 0, 1, 2 \ldots$).
- A more planar molecular structure enhances electron delocalization and strengthens bonds. In addition such structures increase the chance of forming sheet-like crystal structures, which are believed to lower impact sensitivity.
- Specific interactions between ion pairs are often paramount for the inherent stability of each ionic constituent. Charged species are in many cases also necessary to allow for efficient electron delocalization.

Six ionic compounds have been analyzed in greater detail (Figure 27), the dinitramide (1), trinitrogen dioxide (75), 1-nitro-2-oxo-3-aminotriazene (76), pentazole (77), oxopentazole (78), and 1,3-dioxopentazole (79) anions. The neutral trinitramide (TNA, 25) was also subjected to an extensive study.
Figure 27. Investigated GEMs together with their nitrogen-nitrogen bond lengths (in Ångström), after optimization at the B3LYP/6-31+G(d,p) level of theory.

5.3. Theoretical Results

The main theoretical results of Papers VI-VIII are shown in Table 2 and Figure 28. The attribute of highest concern is naturally the kinetic stability. This has been estimated in the gas-phase and in a low polarity solvent (THF) after carefully considering several different decomposition routes for each compound. The individual compounds 75-79 and 25 are discussed in subsections 5.3.1 – 5.3.6. The majority of the investigated GEMs are ionic, and requires a counterion. Thus, in the estimations of several material properties, such as density, solid-state heat of formation and propellant performance, the corresponding ammonium salts were considered.
Table 2. Calculated properties of selected energetic materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>O.B. (%)</th>
<th>$\Delta H_{\text{Gas}} / \Delta H_{\text{Exp}}$ (kcal/mol)</th>
<th>Density$^\text{[a]}$ (g/cm$^3$)</th>
<th>$\Delta H_{\text{Exp}}$ (kcal/mol)</th>
<th>$A_{\text{Exp}}$ (nm)</th>
<th>$E_{\text{Exp}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N(NO$_2$)$_2$ - NH$_4$</td>
<td>+ 25.8</td>
<td>46.1 / 42.1</td>
<td>1.8 (1.81)</td>
<td>-36.2 (-35.4)</td>
<td>279 (0.11)</td>
<td>4.4</td>
</tr>
<tr>
<td>75 N(NO)$_2$ - NH$_4$</td>
<td>± 0.0</td>
<td>$&gt;$27.9 / $&gt;$27.5$^\text{[b]}$</td>
<td>1.6</td>
<td>2.9</td>
<td>271(0.40)</td>
<td>3.1</td>
</tr>
<tr>
<td>76 N$_5$O$_3$H$_2$ - NH$_4$</td>
<td>± 0.0</td>
<td>38.9 / 41.1</td>
<td>1.7</td>
<td>32.6</td>
<td>-</td>
<td>3.3</td>
</tr>
<tr>
<td>77 N$_5$ - NH$_4$</td>
<td>- 36.4</td>
<td>27.8 / 28.7</td>
<td>1.5</td>
<td>47.9</td>
<td>-</td>
<td>4.7</td>
</tr>
<tr>
<td>78 N$_2$O - NH$_4$</td>
<td>- 15.3</td>
<td>30.1 / 31.5</td>
<td>1.6</td>
<td>45.6</td>
<td>240 (0.20)</td>
<td>3.8</td>
</tr>
<tr>
<td>79 N$_2$O$_2$ - NH$_4$</td>
<td>± 0.0</td>
<td>27.8 / 28.9</td>
<td>1.7</td>
<td>44.3</td>
<td>284 (0.16)</td>
<td>3.7</td>
</tr>
<tr>
<td>25 N(NO$_3$)$_3$</td>
<td>+ 63.2</td>
<td>27.6 / 20.2</td>
<td>2.0</td>
<td>48.4</td>
<td>279 (0.02)</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] Experimental data from reference [48] is given within parenthesis.
[b] Calculated at the CC2/aug-cc-pVTZ level in gas-phase. Oscillator strengths are given within parenthesis.
[c] Adiabatic ionization energies are calculated at the B2PLYP/aug-cc-pVTZ level, with thermodynamic corrections from B3LYP/6-31+G(d) frequency analyses.
[d] Rough estimate, possibly considerably more stable.

Figure 28. Theoretical rocket propellant performance for the ammonium salts of 1, 75-79 and perchlorate (AP) when combusting aluminum. Conditions at maximum performance are shown within parenthesis. Polymer support has been omitted.

5.3.1. The trinitrogen dioxide anion (N(NO)$_2^-$)

The trinitrogen dioxide anion (75) constitutes a nitrogen rich compound with a strong GEM potential. The existence of 75 in gas-phase has been confirmed by several experimental studies.[157-160] Surprisingly, experimental estimates into the stability of 75 are in disagreement. Reported experimental stabilities range from 46 kcal/mol[159] to 30 kcal/mol,[160] 18 kcal/mol[160] and 5 kcal/mol.[161] Unfortunately, several low-level quantum chemical studies on the molecule have failed to adequately reproduce these values, which has confused the situation considerably.[158,160,162-164]

The potential energy surface surrounding 75 is rich in possibilities (Paper VI). After careful investigation it was realized that the most likely rate-determining step for decomposition is homolytic bond dissociation, forming nitrous oxide and a hyponitrite triplet anion (Figure 29). This process requires a spin-forbidden transition from the
singlet into the triplet surface. The minimal energy crossing point (MECP) on the seam of crossing of the intersecting surfaces were optimized at the B3LYP/6-31+G(d) level. Adapted frequency analysis at the same level of theory also provided an enthalpy correction. Single point calculations at higher levels of theory (e.g. CCSD(T)), together with a rough estimate of the kinetic penalty due to surface crossing, provided a corresponding “room temperature barrier” value that exceeds 27.9 kcal/mol. Implicit COSMO calculations on MECP1 indicated a similar stability in solution.

Due to the complexity of the bond breaking process, a multi-reference method, such as CASSCF or MR-CI, should preferably be employed to obtain more accurate estimates. Such calculations would need to be combined with implicit or explicit solvation modeling to acquire solution kinetics. With that said, the calculations presented in Paper VI offer strong support and complement to the experimental findings, and it is deemed likely that 75 is sufficiently stable for bulk synthesis at manageable temperatures.

In addition, a straightforward method for detecting 75 has been indentified. Strong photon absorption at approximately 270 nm should be detectable using UV spectroscopy. $\Delta H_f^{\text{gas}}$ of ammonium trinitrogen dioxide was calculated to 2.9 kcal/mol, a value that is significantly higher than the -35.4 kcal/mol of ADN. The ammonium salt has a perfect oxygen balance, and is expected to provide excellent propellant performance.

\[
\begin{align*}
\text{O}^&-N\equiv N\equiv N\equiv O & \quad \text{(75)} \\
\Delta H &= 0.0 \\
\Delta G &= 0.0 \\
\end{align*}
\]

\[
\begin{align*}
\text{MECP1} & \quad \Delta H^\dagger = >27.9 (>27.5) \\
\text{N}_2\text{O} + \text{NO}^- & \quad \Delta H = 27.9 (3.6) \\
\Delta G &= 20.0 (-2.3) \\
\end{align*}
\]

**Figure 29.** The primary self-decomposition pathway of the trinitrogen dioxide anion (75) is homolytic bond dissociation. Relative energies (kcal/mol) in THF are shown within parenthesis.

### 5.3.2. The 1-nitro-2-oxo-3-aminotriazene anion (NH$_2$NN(O)N-NO$_2^-$)

The conceptual design of the spectacular anion 76 arose from a series of studies on dinitramide-related compounds. Preliminary results point to an exceptional kinetic stability, which rivals that of 1. The free energy barrier believed to be rate-determining in decomposition (TS22, Figure 30) is projected as high as 36.9 kcal/mol in the gas-phase, and 44.8 kcal/mol in a low-polarity solvent. The high stability can be attributed to the inclusion of an electron donating amine group, which strengthens the electron resonance. When combined with an ammonium counterion 76 has a perfect oxygen balance. The salt is expected to have a density close to that of ADN, whilst greatly outperforming all other investigated ionic compounds as rocket propellants. The synthesis of 76 will no doubt be a significant challenge for any experimentalist. If successfully made however, it will likely constitute a highly efficient low-sensitivity GEM or HEDM.
5.3.3. The pentazole anion (cyclo-\(\text{N}_5^-(\text{c})\))

The pentazole anion (77) has primarily been included in this thesis as a reference to the oxo-substituted pentazolates (78 and 79). The compound is likely to decompose through a well-studied concerted cleavage into dinitrogen gas and azide (TS23, Figure 31). The process is predicted to have a free energy barrier for decomposition of 25.2 kcal/mol in the gas-phase. This value is in good agreement with previous high-level ab initio studies.\[165,166\] A slight stabilization is expected in solution, where the barrier rises to 26.1 kcal/mol.

The pentazole anion has no allowed electronic transitions, and has proven difficult to detect experimentally. However, 77 has been detected in the gas-phase using mass spectroscopy, following extensive theoretical and experimental efforts.\[166,167\] Despite this breakthrough no successful bulk synthesis has been presented, and the detection of 77 in solution by NMR spectroscopy has proved to be difficult.\[168-173\]

Ammonium pentazole (\(\text{NH}_4\text{N}_5\)) is predicted to perform quite poorly as a rocket propellant. This is primarily due to the salts negative oxygen balance, which hinders effective combustion of any additional fuel. This would, however, change in an all-nitrogen propellant, or in a formulation with oxygen-rich additives.

The pentazole group is a pseudohalide and, like the azido ligand, promises rich reaction chemistry. For example, transition metal adducts might be excellent burn rate modifiers, catalysts, or ingredients for gas generators. As the anion is isoelectronic with cyclopentadiene (cyclo-\(\text{C}_5\text{H}_5\)), one can envision a wealth of inorganic ferrocene-type chemistry. When synthesized it will constitute a highly valuable reagent toward futuristic HEDMs, such as neutral nitrogen allotropes.

Previous successful attempts to detect 77 have been based on laser fragmentation of aryl pentazoles.\[166,167\] Other possible approaches to the bulk synthesis of 77 include nucleophilic substitution and electrochemical oxidation of aryl pentazoles.

**Figure 30.** Primary self-decomposition pathway of the 1-nitro-2-oxo-3-aminotriazene anion (76). Relative energies (kcal/mol) in THF solvent are shown within parenthesis.

$$\text{\begin{align*}
    &\text{H} - \text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \\
    &\text{N} - \text{N} - \text{N} - \text{N} - \text{N} - \\
    &76
\end{align*}}$$

\[\Delta H = 0.0 \quad \Delta G = 0.0\]

**Figure 31.** Primary self-decomposition pathway of the pentazole anion. Relative energies (kcal/mol) in THF solvent are shown within parenthesis.
5.3.4. The oxopentazole anion \((\text{cyclo-N}_5\text{-O}^-)\)

In agreement with what has been suggested, but contrary to earlier calculations,\textsuperscript{[174]} the addition of oxygen to the pentazole ring do increase its kinetic stability. The rate-determining free energy barrier for decomposition of \(78\) (TS\textsubscript{24}, Figure 32) has been calculated to 28.9 kcal/mol. In solution the barrier rises to 30.3 kcal/mol, and \(78\) is predicted to be roughly 1200 times more stable than \(77\). A likely explanation to the stabilization is an increased separation of the \(\pi\) and \(\sigma\) electron systems of the nitrogen ring.\textsuperscript{[174]}

\(78\) has several advantages to \(77\) in addition to the higher stability. Strong UV absorbance at 240 nm enables straightforward detection upon synthesis, the density of the ammonium salt is also found to be higher than the parent analogue \(77\), and the propellant performance is significantly increased (Figure 28). The synthesis of \(78\) can possibly proceed through selective N-oxidation of aryl pentazoles, or by oxidation of \(77\).

![Figure 32](image)

**Figure 32.** Primary self-decomposition pathway of the oxopentazole anion (78). Relative energies (kcal/mol) in THF solvent are shown within parenthesis.

5.3.5. The 1,3-dioxopentazole anion \((\text{cyclo-N}_5\text{-O}_2^-)\)

The di-oxo substituted pentazole \((79)\) also exhibits an increased stability compared to \(77\), however less so than \(78\). The rate-determining free energy barrier of decomposition, leading to dinitrogen gas and \(75\), is predicted to be 26.9 kcal/mol in the gas-phase, and 28.0 kcal/mol in solution (TS\textsubscript{25}, Figure 33). Also this compound is deemed of higher interest than \(77\) based on its higher density, easier detection (UV absorption at 284 nm), and outstanding performance when used in a rocket propellant (Figure 28). Similar to \(78\), \(79\) could possibly be made by the selective N-oxidation of aryl pentazoles, or by oxidation of \(77\).

![Figure 33](image)

**Figure 33.** Primary self-decomposition pathway of the 1,3-dioxopentazole anion (79). Relative energies (kcal/mol) in THF solvent are shown within parenthesis.
5.3.6. Trinitramide (N(NO$_2$)$_3$)

The neutral trinitramide (TNA, 25) molecule was initially identified as a possible decomposition intermediate of dinitramide salts (Figure 11). Due to promising theoretical predictions of its stability it was subjected to a deeper study (Paper VIII). The molecule has previously been considered in a number of low-level theoretical studies.$^{[175-178]}$ The existence of an N$_2$O$_6$ intermediate has also been speculated to explain observed decomposition kinetics of HDN in nitric acid.$^{[135]}$

TNA is predicted to decompose through TS7 (Figure 34), which corresponds to a free energy of activation of 27.9 kcal/mol in the gas-phase, and approximately 20-22 kcal/mol in solution. The low barrier heights make preparation and handling of TNA cumbersome. However, if proper low-temperature methods are devised it could prove useful in cryogenic propulsion engines.

The molecule’s predicted solid-state heat of formation (48.4 kcal/mol), together with its high oxygen balance enables very favorable performance characteristics as a rocket propellant oxidizer. TNA is expected to provide specific impulses (Ns/kg) comparable to both liquid oxygen-liquid hydrogen and AP/Al references. Due to a high density, a TNA propellants is expected to provide a roughly 30 % higher density impulse (Ns/L) than liquid oxygen, a 16-20 % improvement to N$_2$O$_4$ when combusting hydrogen rich fuels, and a 19 % increase as compared to AP, when combusting aluminum.

![Figure 34](image)

**Figure 34.** Primary self-decomposition pathway of trinitramide (25). Relative energies (kcal/mol) in THF solvent are shown within parenthesis.

5.4. Experimental Detection of Trinitramide (TNA)

Two possibly routes to the synthesis of 25 were outlined and investigated theoretically (Paper VIII). First, the electrochemical oxidation of the dinitramide anion, 1, in the presence of N$_2$O$_4$,

\[
\text{N(NO}_2\text{)}_2^-(\text{I}) \xrightarrow{\text{ox}} \text{N(NO}_2\text{)}_3^+(\text{21}) + e^- \xrightarrow{\text{NO}_2^+} \text{N(NO}_2\text{)}_3^-(\text{25}).
\]  

Secondly, the direct nitration of 1, by free nitronium (NO$_2^+$) ions,

\[
\text{N(NO}_2\text{)}_2^-(\text{I}) \xrightarrow{\text{NO}_2^+} \text{N(NO}_2\text{)}_3^-(\text{25}).
\]  

54
The second route was chosen, and synthesis of 25 was attempted by nitration of 1 using BF₄NO₂ in acetonitrile at -40 °C (Paper VIII). First detection of 25 was made by ¹⁴N-NMR (Figure 35). A peak at -65 ppm relative nitromethane was designated to the nitro groups of 25, a value that deviates only 2.7 ppm from our theoretical estimate of -62.3 ppm. Similar to the behavior of 1,[29,145,179] the signal of the central nitrogen of 25 appears to suffer from extensive line broadening due to quadrupolar relaxation[180] that prohibits its detection at low temperature. TNA was seen to decompose into HNO₃, N₂O₄, and N₂O when the temperature was increased towards room temperature, in agreement with the theoretical predictions.

The detection was strengthened by in situ IR measurements in which all theoretically predicted IR bands were observed. The bands were seen to disappear at higher temperatures, in agreement with the ¹⁴N-NMR observations and the theoretical predictions (Paper VIII).

TNA constitutes the largest all nitrogen-oxygen species known. After its synthesis from dinitramide salts have been developed further the compound might find applicability in cryogenic propulsion and in advanced energetic material research. TNA might also prove to be a useful reagent in hitherto unknown chemistry.
Figure 35. $^{14}$N-NMR of reaction mixtures at different temperatures. TNA is observed at -65.0 and -66.7 ppm when made from KDN and ADN, respectively. Nitromethane was used as an external reference.
5.5. Summary and Conclusions

A new generation of oxygen and nitrogen rich green energetic materials has been presented. Several conceptual compounds have been subjected to extensive theoretical studies, which focused on revealing physically relevant properties such as stability, density, means of detection and propellant performance. The dinitramide (1), trinitrogen dioxide (75), pentazole (77), oxopentazole (78), 1,3-dioxopentazole (79) and the 1-nitro-2-oxo-3-aminotriazene (76) anions all hold considerable promise in all these respects. Finally, the neutral trinitramide molecule (25), the largest all-nitrogen-oxygen compound known, was successfully synthesized and characterized by $^{14}$N-NMR and in situ IR spectroscopy. In conclusion, the presented work has demonstrated that physical understanding of conceptual compounds can be acquired through rigorous and careful theoretical studies, using the state-of-the-art in theoretical modeling.
This chapter covers the work done in synthesis, characterization and testing of polymeric materials for use with ADN. Important aspects and design criteria for propellant formulations are introduced first. A brief background and summary of the main results follow.

6.1. Design of a Rocket Propellant Formulation

A crucial part of a solid rocket propellant is the polymer matrix, which encloses the oxidizer (ADN), and the fuel (e.g. aluminium). The polymer matrix provides several mechanical properties needed during storage, and later during firing. An ideal polymer cure system exhibits very specific properties:

- It needs to be liquid when added to the other components to enable for cast curing.
- It needs to sustain very high loadings of solid components (up to 80 % by volume)
- After being mixed with ADN and fuel particles, chemical (or physical) cross-linking should transform the slurry into an elastomeric solid. The chemical cross-linking reaction needs to uphold several criteria:
  - It must be an addition reaction. Any volatile condensation products can cause bubbles, cracks and inhomogeneity in the final crosslinked matrix.
  - The cure kinetics needs to be sufficiently slow to allow for casting of the slurry, but not so slow as to allow for sedimentation of the oxidizer and fuel particles. This curing time, referred to as “pot-life”, should preferably be in the order of hours.
  - The curing temperature should be kept as low as possible, as to prevent mechanical stress in the finished case-bonded propellant. The melting point of ADN at 92 °C is the upper limit.
  - It should be close to thermoneutral, as to avoid heat gradients that could lead to mechanical loadings, cracks, or even autoignition of the propellant.
- The finished cross-linked network needs to adhere to the solid particles enough to give a propellant with good mechanical properties.
  - At firing, the propellant is subjected to intense mechanical stress, due to deformation of the exterior casing. To sustain this stress the propellant needs to be viscoelastic, and capable of stretching up to 50 %. As this property is provided by the relatively small quantity of polymer matrix, the viscoelasticity of the polymer without solid loading needs to exceed several hundred percent.
For practical reasons the viscoelastic behavior needs to be maintained during low temperatures, preferably as low as -40 or -50 °C. This requires the polymer matrix to have a very low glass-transition temperature ($T_g$), preferably -60 °C or lower.

Finally, all components of the propellant formulation needs to be chemically compatible with one another. This has proven very difficult to achieve with ADN, using conventional polymer matrices.

The polymer of choice in most state-of-the-art AP-based propellants is hydroxyl-terminated polybutadiene (HTPB, $T_g \approx -70$ °C). This polymer is commonly cured (cross-linked) by reacting di- and tri-functional isocyanates (-N=C=O) with the terminal hydroxyl groups of HTPB, creating thermally stable urethane (-NH-COO-) bonds. There are reports of ADN-based propellants prepared in similar manners.[36,181,182] However, as isocyanates are toxic to humans, as well as incompatible with ADN,[183] the use of such conventional cure chemistry is far from ideal.

This thesis deals partly with the development of a new cycloaddition-based cure system for ADN, free of isocyanates and designed to meet the above criteria. One key component in these efforts is the 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) monomer.

### 6.2. poly-3-ethyl-3-(hydroxymethyl)oxetane (poly-TMPO)

The polymerization of different hydroxyl-functionalized oxetanes is well known.[184,185] The linear polymer of TMPO has been reported to be a highly crystalline material with a melting point of 163 °C.[186] The polymerization mechanism, synthesis and physical properties of the hyperbranched TMPO homopolymer (Figure 36) have been reported.[187-192] Hyperbranched poly-TMPO, obtained through cationic ring-opening polymerization, is an amorphous material with a reported $T_g$ of 54 °C.[190] Polymerization is known to occur both through the ACE and AM mechanisms.[188] Termination of chain-growth happens almost exclusively through intramolecular chain transfer, resulting in macrocyclic fragments.[188]

The monomer conversion is important for the DB in poly-TMPO.[191] Below a conversion of 30 %, the polymer is almost exclusively linear, whereas at higher conversion more dendritic units are formed.[191] Temperature is also important in governing the structure, with low temperatures favoring linear segments and high temperatures leading to dendritic units.[193] The DB in poly-3-methyl-3-(hydroxymethyl)oxetane has also been reported to increase with increasing catalyst-to-monomer ratio.[194] Recent studies have shown that materials derived from the TMPO monomer holds promise in a variety of applications and processes, such as surface modification,[195,196] anion recognition,[197] protein separation,[198] organic electronics,[199,200] and catalysis[201] to name a few.

During the initial HFC compatibility study (section 4.7) it was realized that poly-TMPO is very stable together with ADN. The good compatibility is believed to be a consequence of the high degree of surface-active hydroxyl groups on the globular macromolecule, which act stabilizing at an ADN-polymer interface. This is in accord
with the quantum chemical analysis on ADN (section 4.9), which argues for the importance of surface stabilization.

![Hyperbranched Poly-TMPO](image)

**Figure 36.** Schematic representation of hyperbranched poly-TMPO.

### 6.3. Tri-block copolymers of poly-TMPO and PEG

Paper IX deals with the synthesis of a set of materials, in which TMPO monomers were gradually polymerized onto the terminal hydroxyl groups of 2000 g/mol poly(ethylene glycol) (PEG) chains. The initial aim of this study was to develop a material with tunable thermal properties. On the basis of comparison with polystyrene-block-polybutadiene copolymers, it was argued that triblocks of flexible PEG-segments and stiff poly-TMPO segments might exhibit thermoplastic behavior. As the HFC study (Section 4.7) had revealed a promising compatibility with diethylene glycol dimethyl ether (40) and ADN, it was believed that also the ether functionality of PEG would be compatible.

The TMPO monomers were added drop wise, as to maximize the likelihood of reaction with the terminal hydroxyl groups of PEG, in contrast to TMPO homopolymerization. The catalyst concentration and the temperature were kept high to promote the AM mechanism, which favors the formation of hyperbranched segments (Figure 37).
Figure 37. Polyether tri-block-copolymers consisting of linear PEG and hyperbranched TMPO were realized through maintaining high instantaneous monomer conversion, catalyst concentration and temperature.

The synthesis scheme succeeded and five materials with varying amounts of TMPO attached to PEG were constructed (86-90, Table 3). Size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectroscopy (Figure 38) was used to show that the molecular weights grew with the addition of TMPO on a naked PEG. The existence of predominantly di- and tri-block copolymers was further proven by $^{13}$C/$^{1}$H-NMR, and precipitation experiments.

Table 3. Some characteristics of the triblock materials

<table>
<thead>
<tr>
<th>TMPO: PEG ratio</th>
<th>$M_w$ ($M_n$) (g/mol)</th>
<th>($M_w/M_n$)</th>
<th>DB</th>
<th>$T_m$ ($^{0}T_m$) (°C)</th>
<th>Crystallinity$^{[a]}$ (%)</th>
<th>Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>linear PEG</td>
<td>2000 (1900)</td>
<td>1.06</td>
<td>0.0</td>
<td>54</td>
<td>76</td>
</tr>
<tr>
<td>86</td>
<td>2.4 (2.0):1$^{[b]}$</td>
<td>1900 (1600)</td>
<td>1.20</td>
<td>0.67</td>
<td>49</td>
<td>56</td>
</tr>
<tr>
<td>87</td>
<td>4.8 (3.9):1$^{[b]}$</td>
<td>2200 (1900)</td>
<td>1.17</td>
<td>0.53</td>
<td>42</td>
<td>37</td>
</tr>
<tr>
<td>88</td>
<td>8.7 (7.7):1$^{[b]}$</td>
<td>2500 (2000)</td>
<td>1.3</td>
<td>0.50</td>
<td>38</td>
<td>28</td>
</tr>
<tr>
<td>89</td>
<td>12.9 (11.7):1$^{[b]}$</td>
<td>2700 (2000)</td>
<td>1.4</td>
<td>0.48</td>
<td>35</td>
<td>18</td>
</tr>
<tr>
<td>90</td>
<td>16.0 (14.0):1$^{[b]}$</td>
<td>3300 (2400)</td>
<td>1.4</td>
<td>0.47</td>
<td>35</td>
<td>12</td>
</tr>
<tr>
<td>91</td>
<td>poly-TMPO</td>
<td>4200 (1800)</td>
<td>2.3</td>
<td>0.42 ($^{a}$34)</td>
<td>0</td>
<td>93</td>
</tr>
</tbody>
</table>

[a] Determined with SEC, conventional calibration with linear polystyrene standards in THF. [b] Relative 100% crystalline PEG ($M_w$ = 4000 g/mol), as given by reference [203] [c] Exact amount of added TMPO is calculated from crude $^{1}$H-NMR using the CH$_2$ group of poly-TMPO (1.27 ppm) relative the CH$_3$ group in PEG (3.51 ppm). The added and weighted amounts are inaccurate due to partial polymerization of TMPO in the drop funnel. Amounts of TMPO in final products are given within parenthesis.

The crystallinity of the materials and the melting temperature correlated well with the amount of included TMPO per macromolecule. Unfortunately the materials did not show elastomeric behavior; neither did they prove compatible with ADN. The incompatibility could later be attributed to the PEG-core. Despite this setback, the materials demonstrated a straightforward one-pot synthetic strategy to dumbbell shaped ether triblocks, a molecular architecture that typically requires several synthetic steps [202]. Explicit control of crystallinity and melting point are also important attributes desirable in many materials.
Figure 38. MALDI-TOF was used to prove copolymerization of TMPO and PEG. Copolymer 88 is shown.

6.4. Copolymers of TMPO and THF and the curing of GAP

One possible alternative to isocyanate-based cure chemistry is the 1,3-dipolar cycloaddition reaction between azide groups (-N₃) and activated carbon-carbon double or triple bonds. Very recently this approach has been applied to ADN, together with the energetic glycidyl azide polymer (GAP, H-(O-CH(CH₃)₃CH₂)ₙ-OH, Tₘ ≈ -48 °C). Aside from an unfortunate high thermal sensitivity, and an early tendency to deflagration, these formulations are reported to be comparable to similar AP-formulations.

To utilize the ADN-compatible poly-TMPO in a related fashion, the hyperbranched material was partly functionalized by alkynes, using DMAP-catalyzed esterification. Similar to the previous work, electron-poor alkynes situated on propargyl ester functionalities were used, as they are known to enable fast reaction rates at moderate temperatures (Figure 39).

Contrary to earlier cycloaddition-based attempts, in which polymer matrices were prepared from GAP using more conventional low molecular weight curing agents, the use of alkyne functionalized macromolecules as curing agents constitutes a novel approach to cure chemistry. The relatively low viscosity of hyperbranched structures provides good processability, while a large number of functional groups enable efficient tailoring of multiple properties, such as compatibility, elasticity, and reactivity.

The regioselective cupper(I)-catalyzed 1,3-dipolar cycloaddition reaction has successfully been marketed within the field of “click chemistry”, as it provides straightforward and atom efficient synthetic steps. However, since Cu(I) forms a highly sensitive explosive together with the dinitramide anion, and as regioselectivity is not necessary in this application, all curing reactions were performed cupper-free at elevated temperature (75 °C).
It was argued that poly-TMPO should retain overall compatibility despite that necessary alkyne groups were embedded among the stabilizing hydroxyl groups of the material. This could be assumed as long as similar physical interactions were maintained between solid ADN and the surrounding polymer. Encouragingly this appeared to be a valid assumption, and 92 showed excellent compatibility when evaluated with ADN using HFC. Unfortunately, and despite promising reactivity testing with a low molecular weight model compound containing azides, 92 proved unable to cure GAP at 75 °C. The reason is likely the low mobility of the poly-TMPO core.

To make a new set of TMPO-based hyperbranched materials with increased mobility (lower Tg) the copolymerization of TMPO and THF was attempted. Copolymerization of oxetanes with THF is well established,[220,221] and copolymers of THF and energetic monomers such as bis azido methyl oxetane (BAMO) have also been reported.[222] The resulting materials, which were made through BF3OEt2-catalyzed cationic ring-opening polymerization, are shown as 94 through 98 in Table 4.

### Table 4. Some characteristics of the TMPO-THF-based materials

<table>
<thead>
<tr>
<th>Rxn.</th>
<th>Mw (Mn) g/mol</th>
<th>Mw/Mn</th>
<th>DF (%)</th>
<th>TMPO:THF (%)</th>
<th>Tg (°C)</th>
<th>TMPO wt%</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>92</td>
<td>7400 (3000)</td>
<td>2.5</td>
<td>22</td>
<td>1.0</td>
<td>-5</td>
<td>79</td>
<td>96</td>
</tr>
<tr>
<td>93</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20:3</td>
<td>+13</td>
<td>92</td>
<td>91</td>
</tr>
<tr>
<td>94</td>
<td>14800 (2600)</td>
<td>5.7</td>
<td>-</td>
<td>8:3</td>
<td>-1</td>
<td>81</td>
<td>78</td>
</tr>
<tr>
<td>95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7:3</td>
<td>-10</td>
<td>79</td>
<td>88</td>
</tr>
<tr>
<td>96</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100:3</td>
<td>+32</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td>97</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20:3</td>
<td>+15</td>
<td>91</td>
<td>93</td>
</tr>
<tr>
<td>98</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3:2</td>
<td>-20</td>
<td>71</td>
<td>100[e]</td>
</tr>
<tr>
<td>99</td>
<td>9500 (5000)</td>
<td>1.9</td>
<td>18</td>
<td>16:3</td>
<td>-7</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td>100</td>
<td>7700 (4400)</td>
<td>1.7</td>
<td>22</td>
<td>3:2</td>
<td>-29</td>
<td>60</td>
<td>65</td>
</tr>
</tbody>
</table>

[a] See experimental section of Paper IX for experimental details. [b] Determined with SEC, conventional calibration with linear polystyrene standards in THF. [c] Calculated from 1H-NMR. [d] Yield defined as the amount of TMPO recovered in the final product, and calculated from 1H-NMR and the weights of the final polymers. [e] Used directly for preparing 100[f] purified by dialysis in EtOH. Contains <1 wt% EtOH.

1H-NMR analysis revealed what appear to be very specific relative ratios of TMPO and THF in all copolymers, e.g. 8:3, 16:3 and 20:3 (Table 4). The exact ratios correlated with the relative ratios of TMPO and THF monomers present during the polymerization (see Paper X for experimental details). For instance, if smaller proportions of TMPO were present during polymerization (e.g. in 94, 95 and 98), larger amounts of THF were incorporated, in different exact ratios, respectively. Lower catalyst concentration (e.g. in 93), and reaction temperature (e.g. in 94) also appears to affect the ratio in favor of TMPO. This strongly suggests a kinetically controlled build up of non-random copolymers. The exact ratios are likely a consequence of the trigonal structure of dendritic poly-TMPO (Figure 40).
As was expected the inclusion of THF reduced the $T_g$ of the materials significantly. Most of the copolymers also showed a good compatibility towards ADN. However, if more than 20 wt% of THF was present in the materials the compatibility worsened past the allowed threshold (see Paper X).

As a consequence of the type of polymerization, and the hyperbranched nature of the materials, the polydispersities ($M_w/M_n$) were high. A full characterization of the weight distribution of all materials proved cumbersome due to their inherent “stickiness”, which caused problem in the separation column in the SEC, and hampered measurement using MALDI-TOF. Fortunately exact control of polydispersity is not required for the intended application as a polymer matrix.

After the successful syntheses of ADN-compatible polymers with enhanced flexibility compared to pure poly-TMPO, the alkyne functionalization and the curing of GAP was reattempted (99 and 100, Table 4, Figure 41). The new materials showed a lowered compatibility with ADN. The increased thermal outputs in these cases seem to be a cumulative effect of both propargyl ester groups and THF. Luckily the reactivity was not very high, and it can be argued that a cured system, which is more rigid and where the alkyne-groups are transformed into more thermally stable triazole-linkages, will be ADN-compatible.

The reactivity of the materials with respect to GAP was tested with a rheometer, using both 10 and 25 wt% of the curing agents. Material 99 enabled rapid curing of GAP at 75 °C (Figure 42). The short curing times, which were on the order of a few hours, are promising as they limit incompatibility issues, while providing a desirable pot life.
Figure 41. Schematic curing of GAP using a macromolecular curing agent (e.g. 99).

Figure 42. Rapid curing of GAP was observed at 75 °C using 25 wt% of material 99.

6.5. Summary and Conclusions

The development of a feasible ADN-compatible polymer matrix has remained a challenge for researchers during the last two decades. For practical reasons most attempts have included more conventional cure chemistry, such as isocyanate cross-linkers. This chapter has presented two novel approaches, both based on the hyperbranched and ADN-compatible polyether poly-TMPO.

First, dumbbell-shaped poly-TMPO-PEG-poly-TMPO tri-blocks were synthesized in a one-pot procedure by cationic ring-opening polymerization. Explicit control of the composition, melting point and the crystallinity was demonstrated. Unfortunately the materials proved incompatible with ADN.

Compared to pure poly-TMPO the copolymerization of TMPO and THF allows for the construction of macromolecules with significantly lower glass transition temperatures. The monomers were shown to polymerize in very exact ratios, and most of the resulting materials showed good compatibility with ADN. Partial alkyne functionalization enabled macromolecules that could act as curing agents with the ADN-compatible GAP polymer, through the 1,3-dipolar cycloaddition reaction. Rapid curing of GAP was demonstrated at 75 °C.

In conclusion, a novel way of producing isocyanate-free polymer matrices for ADN-based propellants has been demonstrated. The procedure constitutes a proof-of-concept and future studies are needed to work out the full potential and limitations of the proposed system.
Modern quantum chemical and spectroscopic methods have proven a powerful combination for acquiring knowledge into complicated chemical systems. The long sought questions regarding dinitramide stability, reactivity and solid-state behavior have to a large extent been answered.

Theoretical research into as-of-yet unknown compounds has similarly, by reference to existing compounds as well as later synthesis, been shown able to predict numerous chemical, physical and spectroscopic properties at a high level of accuracy. Caution is advised however, as theoretical treatment of such systems require careful consideration into the complexities of the corresponding potential energy surfaces. In other words, it is easy to miss something.

By using spectroscopic measurements and quantum chemical treatments as a guide, successful novel materials (polymers) have been developed in parallel. The advantages of such interdisciplinary chemical research, as compared to more conventional trial-and-error-like approaches, are stressed. Future advanced material research will rely increasingly on the intertwined use of experimental and theoretical chemistry. This is especially obvious in the field of high energy density materials.

It is concluded that for solid ADN-based propellants to become a viable option in operational systems, additional experimental testing and development are necessary. It is the sincere hope of the author that the work presented in this thesis will be used to facilitate such efforts.
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References


