EXPERIMENTAL STUDIES ON CONDENSED-PHASE INTERACTIONS OF
HYPERGOLIC PROPELLANTS

A Dissertation in
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by
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ABSTRACT

Current research is focused on the development of novel experimental techniques that can be used to obtain an understanding of the physical and chemical processes during the condensed-phase interaction of hypergolic pairs. A drop test setup, coupled with a high speed camera, was developed to conduct time-resolved studies on the pre-ignition, ignition and post-ignition events during the drop-on-pool impingement interactions of two hypergolic liquids. Thin-wire thermocouples were used to trace the temperatures of the liquid reactants as well as the gaseous products formed during the pre-ignition process which has a very short time scale. In addition, a confined interaction setup, coupled with rapid scan Fourier transform infrared (FTIR) spectroscopy, was developed to study the gaseous species evolved from the early reactions that occur upon the mixing of small quantity of liquid hypergols.

One major objective of this research is to develop an understanding of the pre-ignition reactions between the oxidizer nitric acid (HNO₃) and two target fuels: monomethylhydrazine (MMH), one of the most well-known hydrazine-based fuels, and N,N,N,N′-tetramethylethylenediamine (TMEDA), which may be one of the most promising alternative fuels. This is also a part of an effort to provide experimental support for the MMH-RFNA and TMEDA-RFNA mechanisms that are being developed by the Army Research Laboratory (ARL).

A three-stage hypergolic ignition process was revealed by both the temperature measurements in the drop tests and the pre-ignition products analysis in the confined
interaction experiments. In the first stage, condensed-phase reactions take place between MMH (or TMEDA) and HNO₃ upon their contact to form corresponding nitrate salts. The temperature at the interface between the two liquids increases rapidly to their boiling points due to the exothermic nitrate formation reactions. In the second stage, gas-phase reactions occur between the vapors of MMH (or TMEDA) and HNO₃ to form a particulate aerosol which is mainly composed of nitrates products. In the third stage, secondary reactions are activated when the temperature of the gaseous and aerosol species increases to a critical point. Rapid heat release from the secondary reactions leads to an ignition in the gas phase. The early species (or pre-ignition products) formed in the three stages were analyzed by rapid scan FTIR spectroscopy and possible reaction pathways were proposed in this work.

Two energetic nitrate compounds, MMH·2HNO₃ and TMEDA·8HNO₃, were synthesized from corresponding hypergolic pairs MMH/HNO₃ and TMEDA/HNO₃. Both of these two energetic nitrates have a stoichiometric F/O (fuel-to-oxidizer) ratio, thus can be treated as monopropellants. The combustion and thermal decomposition of these two compounds were studied in a strand burner and a confined rapid thermolysis (CRT)/FTIR setup, respectively. Combustion studies on these compounds provided first-hand burn-rate data for future use in premixed combustion modeling of the hypergolic pair MMH/HNO₃ and TMEDA/HNO₃. The decomposition reactions of these nitrates should also be considered as an important part in the MMH-RFNA and TMEDA-RFNA mechanisms.
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Chapter 1

Introduction

1.1 Background

A hypergolic bipropellant is a form of liquid propellant in which ignition occurs spontaneously upon contact between the oxidizer and fuel, thereby eliminating the need for a complex ignition system [1]. The reliable restart capability of these types of engines makes them ideal for spacecraft maneuvering systems. Compared to monopropellants, hypergolic propellants are also less likely to accumulate unburnt fuel and oxidizer in the combustion chamber to dangerous quantities, then detonate when starting. Such a potential catastrophic condition is known as a hard start [2].

The most commonly used hypergolic bipropellants are composed of hydrazine-based fuels and certain oxides of nitrogen such as nitrogen tetroxide (NTO, N₂O₄) and red fuming nitric acid (RFNA), which is a mixture of nitric acid and nitrogen tetroxide [3]. The most well-known hydrazine-based fuels include hydrazine (N₂H₄), monomethylhydrazine (MMH, CH₃NHNH₂), unsymmetrical dimethylhydrazine (UDMH, (CH₃)₂NNH₂), and their mixtures such as Aerozine 50 (50% hydrazine and 50% UDMH). They have been successfully deployed for decades in rocket engines such as the Russian Proton rocket, US Titan rocket, and Apollo spacecraft [3, 4]. Hydrazine-based hypergols have many advantages such as a short ignition delay, a high density impulse, and a low freezing point, etc. However, the disadvantage of these hypergols is that they are highly
toxic. Hydrazine and its derivatives have been shown to carcinogenic in animal testing, and it is expected that the use of these fuels could pose a potential health hazard to those personnel dealing with their handling. Therefore, researchers have always been looking for potential alternative fuels which are less toxic than hydrazines. Among a series of tertiary amines and azides which have been developed and tested as alternative fuels, \(N,N',N'\)-tetramethylethlenediamine (TMEDA), 2-dimethylaminoethylazide (DMAZ) and their mixtures are of special interest because they are not only less toxic than hydrazines, but also are quite comparable with hydrazines in terms of performance such as ignition delay and specific impulse [5-7].

In hypergolic propulsion systems, the liquid engines are known as impinging stream engines (ISEs) in which the liquid fuel and oxidizer are injected towards each other in the chamber to achieve hypergolic ignition and subsequent sustainable combustion. In conventional impinging stream engines, the fuel and oxidizer injectors point towards the chamber’s axial centerline. In recent years, the U.S. Army Aviation and Missile Research, Development, and Engineering Center (AMRDEC) has also developed a novel hypergolic engine concept which is referred to as the impinging stream vortex engine (ISVE) [8-11]. The fuel and oxidizer injectors are oriented tangential to the chamber wall in an ISVE engine. It is possible that such a modified design can reduce the size of the engine and improve the combustion efficiency. Researchers in AMRDEC are currently trying to develop a computational model to simulate the fluid and combustion dynamics in the ISVE [8-10]. To achieve such an attempt, they have developed reaction mechanisms for target fuel-oxidizer pairs, including MMH/RFNA, TMEDA/RFNA, DMAZ/RFNA and TMEDA-DMAZ mixture/RFNA [11, 12]. The MMH/RFNA
mechanism, for example, is composed of 81 species and 513 reactions which are mainly based on the research conducted by Catorie et al. [13, 14] on MMH/N₂O₄ and MMH/O₂ systems, Vanderhoff et al. [15] and Ilincic et al. [16] on nitramines and nitrate esters, as well as by Smith et al. [17] on natural gas combustion. In addition, these mechanisms have only covered gas-phase reactions. In order to use these mechanisms in the ISVE computational model, they have to assume that the liquid fuel and oxidizer were already vaporized at the moment of injection [10], which is of course not the case. In a hypergolic system, condensed-phase reactions will occur between the two liquid streams at the impinging point and among the liquid droplets at their interfaces. The vaporization of the liquids is in fact mainly due to the heat released from the condensed-phase reactions. Another concern is that this mechanism contains only a few reactions between the fuel molecules and HNO₃ (which is in fact the dominant ingredient of RFNA). For example, only a single MMH-HNO₃ complexation reaction is included in the MMH/RFNA mechanism to represent the reactions between MMH and HNO₃ [12]. Due to these concerns, further effort to improve these mechanisms is desired and is still ongoing.

1.2 Objectives

The overall objective of this work is to develop an understanding of the physical and chemical processes during the hypergolic interactions between various fuel-oxidizer pairs. In the first part, the focus is on examining the liquid-phase reactions between various fuels and nitric acid from room temperature to their boiling points. In the second part, this work is focused on the early steps (or pre-ignition reactions) between the fuel
and HNO₃ vapors at various elevated temperatures up to 300°C. These relevant species and reactions are of critical importance to accurately predicting the ignition delay. Another objective of this work is to understand the complex physical processes that occur during the hypergolic interaction between a fuel drop and an oxidizer pool beginning with the liquid-to-liquid contact to gas-phase ignition, which is usually achieved on a very short time scale. Measurement of important parameters, such as ignition delay and transient liquid- and gas-phase temperatures, can provide useful data for further development and validation of the chemical reaction mechanisms.

The target fuels in this work include both MMH, one of the most widely used today, and TMEDA, one of the most promising alternative fuels in the future. The target oxidizer is chosen as nitric acid (HNO₃) in this work.

1.3 References


Chapter 2

Literature Review

2.1 Literature Review on MMH

Monomethylhydrazine (MMH, CH$_3$NHNH$_2$) is a hydrazine derivative by replacing an H atom with a methyl group. MMH has a density of 0.875 g/cm$^3$, a boiling point of 91°C and a melting point of -52°C. An extensive literature search reveals that the previous studies on MMH were mainly focused on the following subjects: thermal decomposition of MMH (Section 2.1.1), interactions of MMH/NTO (Section 2.1.2), interactions of MMH/RFNA (Section 2.1.3), interactions of MMH/other oxidizers (Section 2.1.4), and studies on the nitrates of MMH (Section 2.1.5).

2.1.1 Thermal Decomposition of MMH

The understanding of a propellant’s thermal stability is critical for its storability. In addition, the decomposition reaction mechanism of a fuel is a very important part of the overall mechanism in a hypergolic system.

The thermal decomposition of MMH was first investigated by Kerr et al. [1], using a toluene-carrier technique. In the presence of toluene, the major products included H$_2$, CH$_4$, N$_2$, and NH$_3$. Eberstein and Glassman [2, 3] experimentally examined the decomposition of gas-phase MMH using an adiabatic flow reactor. The experiments were...
conducted under atmospheric pressure and at a temperature range between 750 and 1,000K. The mass spectrum analysis showed considerable amounts of H2, NH3 and HCN. They also developed a nine-step kinetic mechanism for the thermal decomposition of MMH, including global or semi-global reactions. Golden, et al. [4] studied the thermal decomposition of MMH between 850 and 1,100K at a very low pressure, also using a flow reactor. The main products reported were NH3, H2, CH2NH, and CH3NNH.

Martignoni et al. [5] studied the thermal decomposition of MMH at temperature higher than 500°C, using a heated quartz chamber directly preceding the entrance to a time-of-flight mass spectrometer. The major products were reported as N2, H2, NH3 and HCN.

Catoire et al. [6, 7] studied the thermal decomposition of gaseous MMH at 1,040-1,370 K, 140-455 kPa and in mixtures containing 97-99 mol% argon, using a shock-tube method. They also suggested a full kinetic model consisting of 99 elementary reactions and 39 species, and a reduced kinetic model consisting of 24 reactions for the decomposition of MMH. A more complete elementary reaction mechanism, consisting of 43 species and 160 reactions, was developed by Sun and Law [8], based on the quantum Rice-Ramsperger-Kassel (QRRK) theory. They also obtained the thermochemical properties of the species in MMH decomposition and the bond dissociation energies through ab initio calculations. The reactions with N-N and C-N bond scission were found to be the major reaction paths at atmospheric conditions.
2.1.2 Interactions between MMH and NTO

The minimum spontaneous ignition temperatures (S.I.T) of liquid MMH in NTO-air mixture atmosphere were examined by Perlee *et al.* [9]. They also examined the effects on minimum spontaneous ignition temperature caused by NTO concentration, initial liquid temperature, atmospheric pressure, and ambient oxygen. The minimum spontaneous pressures (S.I.P) of MMH/NTO at reduced pressures were examined by Corbelt *et al.* [10] with an unconfined impingement test setup. They also studied the flame stability of MMH in an NTO atmosphere at different vacuum levels. Mayer *et al.* [11] studied the pre-ignition behavior of condensed-phase MMH with gas-phase NTO at simulated high altitude conditions, low temperature (-11°C), and low NO₂ pressure range (to 110 mm Hg). No ignition occurred under these conditions. Instead, flameless reactions were observed at the surface of the MMH drop. They also examined the residue formation caused by the non-ignition reactions. The solid-phase reactions between MMH and NTO were examined by Christos *et al.* [12] by solidifying the reactants using liquid nitrogen. It was found that fast exothermic reactions took place at approximately -61°C. In addition, they examined the explosivity of liquid MMH in different atmospheric conditions using TNT equivalence (TE) concept. Rodriguez and Axworthy [13] measured the heat and gaseous species release rates for initial reactions of liquid phase MMH/NTO, using a free jet impingement technique with a quenching system. Daimon *et al.* [14] studied the condensed-phase hypergolic interaction between MMH and NTO using a drop test apparatus. Explosion-like reaction was captured by a high-speed camera, and the pressure spike was recorded by a pressure transducer. They found that increasing of
impact velocity and droplet size can reduce the ignition delay. The specific impulse ($I_{sp}$) and chamber temperature were predicted by Woodcock and Byers [15], at different pressures and different mixture ratios for MMH/NTO system. Their results showed that specific impulse and chamber temperature increased with increasing pressures. At a certain pressure, the specific impulse and chamber temperature would reach a maximum value at certain NTO/MMH ratio greater than 1. Catorie et al. [16] visualized the gas-phase reaction of MMH/NTO at room temperature using a high-speed camera. Fog formation caused by the pre-ignition reactions was observed. They also established a flammability diagram for MMH/NTO/He. Yuan et al. [17] simulated the spray phenomena of doublet and triplet impingements of NTO and MMH by using corresponding simulants (water-based and chloroform-based solutions). In a later study [18], they conducted the hot-fire impinging experiments for NTO/MMH, and compared the results such as temperature distribution obtained from the hot-fire experiments and predicted by the previous unreactive stimulants.

The gas-phase reaction of MMH/NTO at room temperature was examined by Seamans et al. [19], using a flow reactor. A viscous, clear-yellow liquid residue was observed. An elemental analysis showed the composition of this residue is: 14.6% C, H, 46.4% N, and 30.9% O. The IR spectrum suggested the presence of nitrate, amine, and N-N groups. They also found that this residue was thermally stable at temperatures lower than 135°C. The reaction between condensed-phase MMH and gas-phase NO₂, at room temperature and lower temperature (-11°C), was examined by Mayer et al. [11]. They suggested that the pre-ignition products, both residue and gaseous species, included methylhydrazinium nitrate (MMH·HNO₃), monomethylnitrosamine (CH₃NHNO),
nitromethane (H\textsubscript{3}CNO\textsubscript{2}), nitramide (H\textsubscript{2}NNO\textsubscript{2}), H\textsubscript{2}O, CO, CO\textsubscript{2}, NH\textsubscript{2}, NH\textsubscript{3}, NO, NO\textsubscript{2}, CH\textsubscript{2}. Saad \textit{et al.} [20] analyzed the products of condensed-phase MMH/NTO reactions under non-ignition conditions at -20°C in CCl\textsubscript{4} solution. Their results showed that the major pre-ignition products included methylhydrazinium nitrate (MMH\cdot HNO\textsubscript{3}), N-methylformamide (CH\textsubscript{3}NHCHO), CH\textsubscript{3}NH\textsubscript{2}, (CH\textsubscript{3})\textsubscript{2}NH, CH\textsubscript{3}OH, CH\textsubscript{3}NHNO, (CH\textsubscript{3})\textsubscript{2}NNO, H\textsubscript{2}O, N\textsubscript{2}, and oxides of carbon and nitrogen. Based on the product analysis, they proposed a condensed-phase pre-ignition reaction mechanism for MMH with NTO, which is summarized in Fig. 2.1. Catoire \textit{et al.} [7] calculated the gas-phase thermochemical properties of more than 50 C/H/N species expected to play a role in the chemistry of MMH. In a later study [21], they suggested a detailed kinetic model devoted to the gas-phase hypergolic ignition of MMH/NTO mixture below 298 K and their combustion above 1000 K, which consisted of 403 reactions among 82 species and included both pre-ignition reactions and combustion reactions. Frank \textit{et al.} [22] suggested a reaction mechanism for gas-phase redox reaction of MMH with NTO, based on Car-Parrinello Molecular Dynamics (CPMD) calculations. Reactions included the methyl diazene formation through HONO elimination, dimethyltetrazane isomers formation from an excess MMH, and the decomposition of dimethyltetrazane isomers in acid-base reactions, which are summarized in Fig. 2.2. McQuaid and Ishikawa [23, 24] examined the initial steps of MMH/NO\textsubscript{2} reaction, namely, H-atom abstraction from MMH by NO\textsubscript{2}, and the reaction of MMH radical with NO\textsubscript{2}, by an ab initio calculation. Researchers in the Army Research Laboratory developed a reaction mechanism for MMH and MON (a mixture of NTO and NO), consisting of 72 species and 495 reactions
[25]. This mechanism was used for modeling the impinging stream vortex engine, developed recently.

\[
2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^- \\
\text{CH}_3\text{NNH}_2 + \text{NO}_2 \rightarrow \text{HN}^+\text{NH} + \text{HONO} \\
\text{HN}^+\text{NH} + \text{NO}_2 \rightarrow \text{NH}^-\text{NH} \rightarrow \text{CH}_3\text{NH}_2 + 2\text{NO} \\
\text{CH}_3\text{NH}_2 + \text{N}_2\text{O}_4 \rightarrow \text{CH}_3\text{NHNO} + [\text{CH}_3\text{N}^+\text{H}_3\text{]} \text{NO}_3^- \\
\text{CH}_3\text{NH}_2 + \text{HONO} \rightarrow \text{CH}_3\text{NHN} = \text{NH} + \text{H}_2\text{O} \\
\text{CH}_3\text{NHNO} \rightarrow \text{CH}_3\text{OH} + \text{N}_2 \\
\text{CH}_3\text{NNH}_2 + \text{NO}^+ \rightarrow \text{CH}_3\text{NHNHNO} + \text{H}^+ \\
\text{CH}_3\text{NNHNO} \rightarrow \text{CH}_3\text{NNH} = \text{NOH} \rightarrow \text{CH}_3\text{NH}_2 + \text{N}_2\text{O} \\
\text{CH}_3\text{NH}_2 + \text{NO}^+ \rightarrow \text{CH}_3\text{NHNO} + \text{H}^+ \\
\text{CH}_3\text{N}_3 + \text{N}_2\text{O}_4 \rightarrow \text{CH}_3\text{ONO}_2 + \text{NON}_3 \\
\text{CH}_3\text{N}_3 + \text{CH}_3\text{NHNO} \rightarrow \text{NON}_3 + (\text{CH}_3)_2\text{NH} \\
\text{NON}_3 \rightarrow \text{N}_2\text{O} + \text{N}_2 \\
\text{CH}_3\text{NNH}_2 + \text{H}^+ + \text{NO}_3^- \rightarrow \text{CH}_3\text{NHNH}_3^+ \text{NO}_3^- \\
\text{CH}_3\text{OH} + \text{NO}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{NO} \\
\text{CH}_2\text{O} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NHCH}_2\text{OH} \\
\text{CH}_2\text{O} + \text{NO}_2 \rightarrow \text{HCOOH} \\
\text{CH}_2\text{O} + \text{CH}_3\text{NNH}_2 \rightarrow \text{CH}_3\text{NHN} = \text{CH}_2 + \text{H}_2\text{O} \\
\text{CH}_3\text{NHCH}_2\text{OH} + \text{NO}_2 \rightarrow \text{CH}_3\text{NHCHO} + \text{H}_2\text{O} + \text{NO} \\
\text{HCOOH} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NO} \\
\text{HCOOH} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ \text{COO}^- \rightarrow \text{CH}_3\text{NHCHO} + \text{H}_2\text{O}
\]

Figure 2.1: Early reactions between MMH and NTO proposed by Saad et al.[20]
2.1.3 Interactions between MMH and HNO₃

For MMH, most research focused on the MMH/NTO combination since 1960s, as discussed in Sec. 2.1.2. However, NTO is not only extremely toxic but also very corrosive even on aerospace-grade materials. In most cases, it was found that the handling problems and safety risks outweighed the performance benefits. Therefore oxidizers with reduced toxicity and corrosiveness, such as some form of nitric acid (HNO₃), were of great interest. Several types of nitric acid mixtures can be used as oxidizers. White fuming nitric acid (WFNA) is concentrated nitric acid containing less than 2% water and impurities. Red fuming nitric acid (RFNA) consists of concentrated nitric acid with some dissolved nitrogen dioxide (NO₂).
Previous research on the MMH/HNO₃ combination is quite limited, and the RFNA is the most favorable oxidizer. Daimon et al. [14] studied the drop-pool interaction between MMH and RFNA using a drop test apparatus. It was found that the ignition delay of MMH/FNA was generally longer than that of MMH/NTO. Wang et al. [26] measured the ignition delay of MMH/IRFNA by both drop test and engine test. The ignition delay was reported to be 8 ms in the drop test and 0.1 ms in the engine test. Thompson [27] obtained the specific impulse and density pulse of MMH/IRFNA. At an oxidizer-to-fuel ratio of approximately 2.8, the specific impulse and density impulse reached their maximum value at 284 lbf sec/lbm and 13.36 lbf sec/cubic inch, respectively. Smith et al. [28-32] have extensively studied the hypergolic behavior between MMH and RFNA recently. They measured the chemical delay time (CDT) instead of ignition delay of MMH/RFNA, using a drop test apparatus with a laser-based diagnostic technique. They defined the CDT as the time from gas evolution after the contact until the appearance of a flame. Their experiments also showed that the MMH has a faster reaction rate (an average of 23% faster) with RFNA in air than in Argon, which led to a conclusion that the ambient oxygen plays a role by promoting the reaction of MMH/RFNA. They also measured the liquid-phase temperature during the drop test, and found that the temperature of the liquid pool is around 340K at the ignition point. This temperature matches the boiling point of CH₃NO₃, under which CH₃NO₃ may decompose rapidly.

No experimental studies were found in the literature on the chemical reaction aspect of MMH/HNO₃, such as product analysis, reaction mechanism studies, etc. It is generally believed that the chemical pathways for MMH/HNO₃ are similar as those for
MMH/NTO [25]. Based on the reaction mechanism for MMH/NTO, the ARL researchers have recently developed a full gas-phase reaction mechanism for MMH/HNO₃, consisting of 81 species and 518 reactions [33].

2.1.4 Interactions between MMH and other oxidizers

Some studies focused on the reactivity of MMH with environmental species such as oxygen, ozone (O₃), and NOₓ. These studies are important to evaluate the potential environmental pollution of MMH. In addition, results from these studies may aid the development of MMH/NTO or MMH/RFNA reaction mechanisms.

Allison and Faeth [34] studied the combustion characteristics of MMH in ambient oxygen. The effects of ambient oxygen mass fraction and MMH drop diameter on the drop burning rate were studied. Gray and Sherrington [35] studied the oxidation of gaseous MMH in oxygen atmosphere over a temperature range 370-510°C. The maximum spontaneous temperatures, pressures, and fuel-to-oxidizer ratios were measured. Tuazon et al. [36] studied the reactions of MMH with atmospheric species ozone (O₃) and NOx at varying reactant ratios. The FTIR spectrum showed the major products of the MMH + O₃ reaction were CH₃OOH, CH₃NNH, HCHO, CH₂N₂, and H₂O₂, with lower yields of CH₃OH, HCOOH, CO, NH₃, and N₂O. The major products of the MMH + NOₓ reactions were HONO, CH₃NNH, CH₃OOH, CH₃OH, N₂O, NH₃, HOONO₂, and MMH·HNO₃, together with two unidentified products that were probably formed in significant yields. Catoire et al. [37-40] conducted a series of studies on the hypergolic behaviors of MMH/O₂/Ar and MMH/H₂/O₂/Ar mixtures. They developed a
mechanism for the reactions between MMH and O₂, consisting of 70 species and 373 elementary reactions.

2.1.5 Studies on Nitrates of MMH

The reactions of MMH with NTO under ideal conditions and mixture ratios should yield CO₂, N₂ and H₂O. It has been found, however, that complete combustion is rarely, if ever, achieved in actual engine firings [41]. Incomplete combustion is particularly evident in pulse mode operation, where solid residues are accumulated during the start-restart cycle of the space maneuverable engine. These materials are deposited on the rocket chamber wall and nozzle surface, where they are subjected to reheating, oxidation, and hydrolysis. These condensed products may influence the optical performance of the exterior surfaces, i.e., sensors, solar panels or spacecraft instrumentation [42]. The major constituent of the combustion residues was believed to be methylhydrazinium nitrate (MMH·HNO₃) [11, 19, 20, 41, 42]. Therefore this salt was extensively studied.

MMH·HNO₃ can be prepared by mixing MMH with diluted nitric acid at low temperatures, and then dried under reduced pressure. It is generally believed that the methylhydrazinium ion has the extra hydrogen on the nitrogen next to the methyl group [43]. This salt has a density of 1.55 g/cm³ [43]. Its melting point is around 37°C [41,43]. It is extremely hygroscopic and thermally stable at temperature lower than 60°C [41]. It is insensitive towards shock, friction and electric charge up to about 20 kV [42]. It is toxic even when applied to the skin [44]. The infrared spectra of this salt are available in
these references [11, 22, 42, 43, 45]. The mass spectrum for this salt was provided by Lawton and Moran [43]. $^{14}\text{N}$ and $^1\text{H}$ NMR spectra were provided by Bonn [42] and Frank [22]. The differential thermogram of this salt is available by Lawton [43] and Takimoto [45]. The crystal structure of this salt was studied by Bonn [42]. The thermal decomposition of this salt was studied by Breisacher [41] and Bonn [42]. The products reported by Breisacher included $\text{CH}_3\text{NH}_2$, $\text{CH}_3\text{NO}_2$, $\text{CH}_3\text{N}_3$, $\text{CH}_4$, $\text{NH}_3$, $\text{NO}_2$, $\text{N}_2\text{O}$, $\text{NO}$, $\text{H}_2\text{O}$, $\text{N}_2$, $\text{O}_2$. The products reported by Bonn were in order of abundance $\text{NO}$, $\text{N}_2$, $\text{CO}$, $\text{CO}_2$, $\text{CH}_3\text{NH}_2$, $\text{NO}_2$, $\text{CH}_4$, $\text{NH}_3$, $\text{H}_2\text{O}$, $\text{CH}_3\text{N}_3$ and $\text{N}_2\text{O}$. Breisacher [41] also prepared and studied the methylhydrazinium dinitrate salt (MMH·$2\text{HNO}_3$). Its boiling point is approximately 74–78°C and the products of thermal decomposition were found similar to that of MMH·$\text{HNO}_3$.

2.2 Literature Review on TMEDA

$N,N,N',N'$-Tetramethylethylenediamine (TMEDA), with a chemical formula of $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, is a tertiary amine derived from ethylenediamine by replacement of the four N-H groups with four N-methyl groups. TMEDA has a density of 0.775 g/cm$^3$, a boiling point of 121°C and a melting point of -59°C. TMEDA is widely recognized as a bidentate ligand that forms stable complexes with many metal halides such as zinc chloride and copper iodide, giving complexes that are soluble inorganic solvents [46]. An extensive literature search reveals that very few studies have been conducted for TMEDA as a liquid fuel in hypergolic systems.
In the early-to-mid 1950’s, the potential of saturated, tertiary, alkyl multiamines (STAMs) for hypergolic propulsion was recognized and extensively examined by the Phillips Petroleum Co. (PPC) [47]. They have reported performance related properties for over 40 different multiamines, among which, \(N,N,N',N'-\text{tetramethylenediamine} \) (TMEDA) and \(N,N,N',N'-\text{tetramethyl-1,3-butanediamine} \) (TMB13DA) were considered to be most promising. Their short ignition delay and low freezing points separated their performance from all the other STAMs evaluated. They were, however, observed to have significantly longer ignition delays and lower specific impulse than hydrazine-based fuels. Therefore, these tertiary amines have never been deployed in rocket or spacecraft engines as replacement fuels for hydrazines.

Due to increasing interests in searching for less toxic fuels which could potentially replace MMH and UDMH in the future, researchers at the U. S. Army Aviation and Missile Research Development and Engineering Center (AMRDEC) have again focused their interests on a series of tertiary amines and azides [48-60], with special interests given to TMEDA and 2-dimethylaminoethylazide (DMAZ). In addition, Stevenson et al. [51] found that a mixture of TMEDA and DMAZ, with a mass ratio of approximately 2:1, has a shorter ignition delay compared to the ignition delay for either of the unmixed individual components. An additional benefit of this mixture is that it burned cleaner with fewer residues than when pure TMEDA was used as the fuel. Therefore, a special attention was also given to the mixtures of TMEDA and DMAZ. Some important properties and performance data of TMEDA, DMAZ and a mixture, containing 66.7% TMEDA and 33.3% DMAZ by weight, are given in Table 2.1. For comparison, corresponding data of MMH are also included.
### Table 2.1: Properties and performance data of several hypergolic propellants

<table>
<thead>
<tr>
<th>Structural Formula</th>
<th>MMH</th>
<th>DMAZ</th>
<th>TMEDA</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₃NHNH₂</td>
<td>(CH₃)₂NCH₂CH₂N₃</td>
<td>(CH₃)₂NCH₂CH₂(CH₃)₂</td>
<td>66.7% TMEDA 33.3% DMAZ</td>
</tr>
<tr>
<td>Density</td>
<td>0.87 g/cm³</td>
<td>0.99 g/cm³</td>
<td>0.78 g/cm³</td>
<td>-</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-52 °C</td>
<td>-69 °C</td>
<td>-55 °C</td>
<td>-</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>88 °C</td>
<td>135 °C</td>
<td>121 °C</td>
<td>-</td>
</tr>
<tr>
<td>Ignition delay</td>
<td>Unit: ms</td>
<td></td>
<td></td>
<td>Refs: [26, 51]</td>
</tr>
<tr>
<td>Drop Test*</td>
<td>8</td>
<td>26</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>Engine Test*</td>
<td>0.1</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Specific impulse*</td>
<td>Unit: lbf·sec/lbm</td>
<td></td>
<td></td>
<td>Refs: [27, 49]</td>
</tr>
<tr>
<td></td>
<td>284</td>
<td>287</td>
<td>281</td>
<td>283**</td>
</tr>
</tbody>
</table>

* Data were acquired when IRFNA was used as the oxidizer;  
** Specific impulse of this mixture is estimated based on the ratio of DMAZ and TMEDA.

In an effort to develop a computational model for the impinging stream vortex engine (ISVE), the U.S. Army Research Laboratory (ARL) has developed chemical kinetics mechanisms for TMEDA/RFNA, DMAZ/RFNA and TMEDA-DMAZ/RFNA, respectively [48]. The TMEDA/RFNA mechanism is comprised of ~1400 reactions and involving over 400 species. They suggested that the initiation step involves the H-atom abstraction from TMEDA by NO₂ to form a radical (CH₃)₂NCH*CH₂N(CH₃)₂ which can be further oxidized by NO₂ through pathways suggested in Fig. 2.3. Since there is a lack of experimental data for validating these mechanisms, further effort is required to improve these mechanisms. Due to this reason, details regarding these mechanisms are still not available in the open literature.
2.3 References


Chapter 3

Experimental Setup

In this work, several experimental setups are developed to study the physical phenomena as well as chemical reactions between various pairs of hypergolic fuel and oxidizer. Specifically, a drop test setup is developed to investigate the physical phenomena that occur when a drop of fuel impinges on a liquid oxidizer pool; a confined interaction setup is developed to study the condensed-phase reactions between small amounts of liquid fuels and liquid oxidizers (i.e., HNO₃); and a rapid thermolysis setup is used to study the thermal decomposition of the nitrates which are synthesized from the hypergolic pairs. The chemical species are analyzed by interfacing the above mentioned setups with a Fourier transform infrared spectrometer (FTIR) and a time-of-flight mass spectrometer (ToF-MS). Detailed introductions of these setups and instruments are discussed as below.

3.1 Drop Test Setup

A schematic diagram of the drop test setup is presented in Fig. 3.1. In general, this apparatus allows a drop of fuel to fall on a nitric acid pool. The hypergolic ignition event, as well as the pre- and post-ignition processes, is recorded by a Phantom V710 high-speed camera. In addition, the temporal evolutions of gas- and liquid-phase temperatures,
luminous and sonic signals are captured by corresponding sensors such as thermocouples, photodiodes and microphones. The procedures of a typical experiment are introduced next.

Figure 3.1: Schematic diagram of the drop test setup

An excess amount of the oxidizer (i.e., nitric acid) of approximately 80 µL is placed at the bottom of a 10×10 mm², 50 mm tall glass cuvette. A section of the cuvette is removed to facilitate the placement of thermocouples for measurement of gas-phase temperatures. Three Al₂O₃-coated K-type thermocouples, 0.002 inch in diameter, are mounted on individual Teflon plates stacked vertically. Teflon plates are used because it is an excellent corrosion-resistant material to nitric acid. The first thermocouple is ½ inch above the cuvette bottom, and the spacing between two nearby thermocouples is ½ inch.
Liquid fuel (i.e., MMH) is loaded in a syringe which is inserted into a fixed perpendicular steel holder. A drop of fuel with a volume of approximately 7 µL is produced by releasing the plunger on the syringe, and the drop falls toward the center of oxidizer pool which is 50 mm below. The thermocouples are slightly off-centered to avoid interference with motion of the fuel drop. A He-Ne laser, and a corresponding photodiode, placed underneath the syringe and above the thermocouple assembly, triggers the data acquisition system through a reduction in the photodiode signal as the drop of fuel descends across the laser beam. In a series of separate tests, a second laser and photodiode pair placed just above the surface of the oxidizer pool were used to identify the starting point of the measurement of ignition delays. The time of impact was repeatedly found to be 64 ms after the drop crossed the first laser beam. The flash of luminosity from ignition is detected by a series of photodiodes placed along the wall of the cuvette. The ignition delay here is defined as the time needed to release luminosity observable to the photodiode after the drop-pool contact. In addition, a microphone is placed near the cuvette to capture the sonic signal in the drop tests. The thermocouple traces at different heights above the reaction surface are routed through a differential-based amplifier and recorded by a Nicolet multipro data acquisition system. The thermocouples were found to be coated with combustion products after each test, and hence were discarded in favor of new thermocouples at the beginning of each successive test. Additionally, to measure the liquid-phase temperature, the position of the horizontally stretched thermocouple wire was determined using two thin glass slides. These two glass slides were placed in vertical grooves machined in the test rig, which allowed the two ends of the glass slides to be positioned within the liquid near opposite
side walls of the cuvette. By placing the respective lead of the wire in the narrow space between each side wall of the cuvette and the glass slide, the vertical position of the thermocouple was fixed and the wire itself could be carefully stretched horizontally within and across the liquid pool.

To investigate the pressure effect on ignition delays of hypergolic pairs, a modified setup which allows the drop-on-pool impingement experiment to be conducted in closed chamber that can be either operated at elevated or reduced pressures. The modified drop test setup is shown in Fig. 3.2. The general procedures are the same as described above. The drop of fuel is produced by a syringe and the nitric acid pool is placed right beneath the syringe. The syringe is kept in a closed holder and is driven by a
pneumatic actuator. The chamber is first purged by N₂ and is then either pressurized by compressed gas from a gas cylinder or reduced in pressure by a vacuumed by a vacuum pump. The purge gas flow is evenly distributed across the chamber by running though many tiny holes punched on a round plastic piece. The high speed camera is also triggered by a laser-photodiode device as shown in the figure. In this setup, ignition delays are measured by counting the video frames between the contact of two liquids and the occurrence of luminosity. The high speed videos were acquired at a frame rate of 5000 fps. Therefore the temporal resolution of ignition delay measurement is 0.2 ms.

3.2 Confined Interaction Setup

Figure 3.3: a) Overall view of the confined interaction setup, and b) top view and dimensions in inches of the interaction zone machined in block I.

A confined interaction setup, interfaced with a Bruker IFS 66/S Fourier transform infrared spectrometer, is used to analyze the gaseous and aerosol species produced largely from the condensed-phase interactions between liquid fuels and nitric acid. Figure
3.3a shows the assembly of the confined interaction setup. Liquid fuel and oxidizer are loaded in two Hamilton 7100-series syringes, respectively, and therefore the volatile reactants can be kept for a relative long time without any significant loss due to evaporation. The syringes are placed in two rectangular slots on a polycarbonate plate. The two needles of the syringes are inserted into two small channels (0.024 in. diameter) machined on two Al₂O₃-coated stainless steel blocks (block I and II). The channels and contact interface between block I and II are sealed by a perfluoroalkoxy (PFA) polymer or aluminum film to minimize capillary effects. Shown as a partial top view of block I in Fig. 3.3b, the two reactants meet and react in an approximately flat channel (0.08 in. long, 0.04 in. wide and 0.015 in. deep), which is partially occupied by the needle tip. Gases flow into a flat channel that is 0.012 in. deep, which insures high convective heat transfer. The evolved gases from the flat channel are confined in N₂ purged channel (0.3 in. diameter and 7 in. long) and detected by the modulated beam of the FTIR spectrometer. A ZnSe window is mounted at each end of the channel to provide optical access by the modulated beam of the FTIR spectrometer. A cartridge heater is mounted in block I so that the reaction zone can be heated to any desired temperature up to 300 °C. All the tests were conducted under ambient pressure. The channel is purged by N₂ before each test and the purging valve is shut off during the test. The spectra of gaseous products are obtained in near real-time with a spectral resolution of 2 cm⁻¹ and a temporal resolution of 50 ms. In each test, 150 spectra are collected, requiring a sample time of 7.5 s. The syringes and reaction zone are cleaned after each test, and the sealing films are replaced.
3.3 Confined Rapid Thermolysis Setup

The technique utilized to study the products formed under rapid decomposition of a material is referred to as confined rapid thermolysis (CRT) setup. Using this technique, the thermal decomposition is limited to a volume confined between two heated, parallel surfaces. By using a small sample size compared to the volume, it is possible to study liquids that may otherwise largely boil off rather than decompose. The setup is composed of a constant pressure chamber, a Bruker IFS 66/S FTIR spectrometer and a commercially available time-of-flight mass spectrometer (ToFMS). A three-dimensional view of the chamber, including a cut that exposes the sample holder, is shown in Fig. 3.4a. The sample holder is designed to be lifted by the bottom heater to enclose the
sample between the two heaters. Two ports are provided on the chamber, one serves as an inlet to the purge gas and the other exhausts decomposition products and the purge gas stream. The constant pressure chamber, resting on a rigid frame, has a height of 27.5 cm and an inner diameter of 5 cm approximately. The CRT/FTIR technique has been described in detail in previous works [1, 2].

The rapid thermolysis is achieved by using two heaters: a stationary top heater and a mobile bottom heater. In both heaters, isothermal conditions are established by using high-watt density cartridge heaters (Omega CIR-1014/120V) and controlled by proportional-integral-derivative (PID) controllers (Omega CN8500). Both heaters are sheathed in copper rods, 53 mm in height and 15.6 mm in diameter. There are two auxiliary systems, a pneumatic piston-cylinder (Motion Controls) for lifting the bottom heater and a purge gas system. The purging system using an inert gas serves a dual purpose. One, it purges the chamber of the decomposition products and prevents recirculation of products into the path of the modulated FTIR beam, and two, it prevents oxidation of the copper rods at elevated temperatures. The temperature of the cartridge heaters is monitored and controlled by two 75 μm K-type thermocouples embedded in the copper sheaths of the heaters. To achieve rapid thermolysis, defined as an event that occurs within 5 seconds, high temperatures are used. The experimental procedure is as follows: the heaters are brought up to the pre-set temperature. Approximately 0.5 mg of the ionic liquid is placed on the sample holder. As shown in Fig. 3.4a, the sample holder is a hollow cylindrical ring with a thin foil attached on top. Though it is possible to utilize different types of foils, an 11 μm thick aluminum foil is used to minimize conductive heat transfer resistance. The sample holder is then placed over the guiding tube for the bottom
heater and the bottom heater is raised by the pneumatic piston-cylinder. The sample holder is brought in contact with the ring retaining an aluminum foil over the top heater. This ring also defines and seals a gap of approximately 300 μm between the two heaters. The final position of the sample holder and the two heaters is shown in Fig. 3.4b. A rectangular slit, 8.25 mm by 300 μm, is left open in the gap for gases generated during decomposition of the sample to gain access to the FTIR beam or to the orifice port on the vacuum chamber.

3.4 Strand Burner

A schematic diagram of the strand burner used for studying the combustion of MMH nitrates is shown in Fig. 3.5. The strand burner is composed of a combustion chamber (bottom portion) and an exhaust chamber (top portion). The strands of monopropellants are placed in the bottom chamber which is purged and pressurized by N₂. A nichrome wire (Φ = 0.1 mm), which is mounted on two copper poles and buried straight along the top surface of strand, is used to ignite the monopropellants. A constant electric current of 1 A, which is slightly lower than the maximum allowable current (1.27 A) above which the nichrome wire will melt and break apart, is provided by a DC power supply through a high pressure feedthrough. The purging flow is kept running through the chamber from the bottom inlet to the top outlet during the test so that the exhaust gases can be carried out of the chamber rapidly to avoid a sudden chamber pressure increase. Meanwhile, the soot of carbon particles (smoke) from incomplete combustion can also be rapidly blown out of the chamber to maintain a clear optical access to the liquid strand
and the flame. The purge gas flow is evenly distributed across the chamber by running through many tiny holes punched on a round plastic piece. The ignition and combustion processes were recorded by a Phantom V710 high-speed camera, though an optical access glass window with a thickness of 1 inch. A piece of paper with a printed ruler is placed just behind the strand to record the instantaneous position of the burning surface, which allows the calculation of the regression rates.

![Schematic diagram of strand burner](image)

**Figure 3.5: Schematic diagram of strand burner**

### 3.5 FTIR Spectrometer

The gaseous products evolve into the FTIR beam passing through two ZnSe (or KRS-5) windows, which are offset by 0.313 inches from the center of the chamber,
offering a spectral coverage of 500-10,000 cm$^{-1}$. This wide range is truncated using a germanium coated KBr beamsplitter and a mercury-cadmium-telluride detector to the mid-IR range of 600-5,000 cm$^{-1}$. The gases evolved during the thermolysis are detected, identified and quantified using FTIR transmission spectroscopy. The spectra are acquired with a spectral resolution of 2 cm$^{-1}$ and a temporal resolution of 50 ms.

3.6 Data Reduction in FTIR Spectroscopy

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

3.7 References


Chapter 4

Interactions between MMH and Nitric Acid

The hypergolic interactions between monomethylhydrazine (MMH, CH₃NHNH₂) and various forms of nitric acid are studied by the drop test setup and the confined interaction setup which are introduced in Sects. 3.1 and 3.2, respectively. In the drop test experiments, high-speed videos are acquired to visualize the pre-ignition, ignition and post-ignition events when a MMH droplet impinges on a pool of nitric acid. Meanwhile, temperatures at various locations are recorded by Al₂O₃-coated thermocouples placed in both the liquid-phase and gas-phase regions. In the confined interaction experiments, gaseous species which are evolved from reactions between small amounts of MMH and nitric acid are analyzed by time-resolved FTIR spectroscopy. The major early reactions between MMH and HNO₃ are discussed.

4.1 Drop Tests

A detailed introduction of the experimental setup is available in Sect. 3.1. In this work, the drop-on-pool impingement interactions between MMH and three different nitric acid solutions are studied. The three nitric solutions are: (1) 90%HNO₃ that contains 10% of H₂O; (2) white fuming nitric acid (WFNA) that contains less than 0.5% of impurities; and (3) red fuming nitric acid (RFNA) that contains about 12-24% N₂O₄ by
weight. In this work, all the chemicals were purchased from Sigma-Aldrich and used without further purification.

### 4.1.1 MMH/90%HNO₃

![Figure 4.1](image)

Figure 4.1: a) Selected images from a drop test of MMH (drop) / 90%HNO₃ (pool); and b) signals acquired by photodiode (PD) and microphone (MIC) in the same test of (a).

High speed videos were acquired by a Phantom V710 camera at a frame rate of 2000 fps in order to resolve the pre-ignition and ignition events that occurred on an extremely short time scale. Figure 4.1a shows a few selected images from a typical drop...
test in which a MMH drop falls into a 90% HNO₃ pool. In all drop tests, the MMH drop generated by the syringe has a volume of 7 μL (about 2.38 mm in diameter) and the nitric acid pool has a size of 80 μL. The glass cuvette has a 9×9 mm² square interior cross-section, resulting in an average depth of the pool of about 1 mm. However, the nitric acid layer in the center is noticeably thinner than that at the edge due to surface tension. In all drop tests, time t = 0 corresponds to the instant when the drop hits the liquid pool. Ignition is defined to occur when emission from luminosity is indicated by a rapid increase in voltage output signal from the photodiode.

As shown in Fig. 4.1a, when the MMH droplet traveled vertically down in the cuvette, an aerosol trace was formed from reactions with HNO₃ vapor which was initially filled in the cuvette. Liquid-phase reactions occurred rapidly upon contact between the two liquids, and a large amount of products accumulated above the liquid surface to form a particulate aerosol cloud. The formation of this aerosol cloud is most probably due to the vaporization of reactants and subsequent salt formation/complexation reactions. As shown in the images at t = 2, 20, and 75 ms, the aerosol cloud kept growing in the gas phase until at t = 77 ms, it vanished rapidly and a faint luminous flame was observed. Therefore, the ignition delay of this test is about 77 ms. The same ignition delay was determined by the photodiode and microphone signals shown in Fig. 4.1b. Microphone signals are commonly used in drop test studies to record some of the key events, such as droplet impact, droplet explosion and ignition [1]. In this work, a total of 20 tests were conducted by releasing an MMH droplet into 80 μL of 90% HNO₃, with ignition delays varying from 70 to 100 ms.
In a series of separate tests, temperatures at several locations in both liquid- and gas-phase regions were measured by Al$_2$O$_3$-coated K type thermocouples (0.001 inch in diameter). Details regarding the coating and mounting techniques, as well as the positions of thermocouples, were introduced in Sect. 3.1.

Figure 4.2: Liquid-phase temperature trace (a) and gas-phase temperature traces (b) in a drop test of MMH (drop) / 90%HNO$_3$ (pool)

Figure 4.2a shows the liquid-phase temperature trace obtained in a typical drop test of MMH/90%HNO$_3$. The temperature of the liquid close to the fuel/oxidizer interface
was traced by placing a thermocouple beneath the liquid surface. The liquid temperatures increased from room temperature to about 100°C within a few milliseconds. Temperatures then fluctuated between 80 and 100°C (the boiling point is 87°C for MMH and 102°C for 90%HNO₃ [2]). Since the thermocouple was buried in the liquid, it did not sense the rapid temperature rise at about t = 100 ms due to gas-phase ignition as detected by the photodiode.

Figure 4.2b shows the gas-phase temperature traces obtained in a typical drop test of MMH/90%HNO₃. Temperature of the gaseous and aerosol species was traced by two thermocouples placed at different locations as indicated in the figure. After each test, the thermocouples were destroyed due to the high temperatures and flow caused by expansion from gas-phase reactions, although the flame was sustained for only a few milliseconds. However, the thermocouples were found to work properly during the pre-ignition stage, which is the focus of this study. In all tests, the gas-phase temperatures show three distinct stages, as described next:

Stage 1: Temperatures increased from ambient values to around 100°C, which is close to the boiling point of 90% HNO₃. This temperature rise was most likely due to gas flow of reactants evaporated from the liquid pool after the liquid temperature reached its boiling point. The bottom thermocouple sensed this temperature rise much faster than the top thermocouple because it is much closer to the liquid pool.

Stage 2: Gas-phase temperatures gradually increased from 100 to about 280°C due to the exothermic gas-phase reactions.

Stage 3: At t = 95 ms, temperatures increased rapidly from 280°C to a flame temperature of about 1350°C. This temperature rise was due to the gas-phase ignition and
was sensed by both thermocouples almost simultaneously. The lower thermocouple was destroyed at about $t = 110$ ms. The photodiode also sensed a weak luminous signal at $t = 95$ ms. Therefore, the ignition delay in this test was about 95 ms. It should be noted that ignition delays shown in Fig. 4.2, in which a pre-cut cuvette with a height of 0.2 inch was used to allow the access of thermocouples, were slightly longer than that from Fig. 4.1, in which the original cuvette with a height of 1.78 inch was used.

Several drop tests were also conducted by releasing a 90% HNO$_3$ drop into 80 $\mu$L of MMH. Although a similar particulate cloud was formed after the impact, the extent of heat release was limited and gas-phase ignition was not achieved.

### 4.1.2 MMH/WFNA and MMH/RFNA

Twenty tests were conducted by releasing an MMH droplet into 80 $\mu$L of WFNA, with ignition delays varying from 19 to 22 ms. Although all tests were conducted by carefully following the same procedure, two different types of interaction phenomena, shown in Figs. 4.3 and 4.4, respectively, were observed. In both cases, a columnar aerosol trace was observed prior to the droplet impact, and an aerosol cloud was formed near the pool surface after the droplet impact.

In case I (Fig. 4.3), the MMH droplet exploded at $t = 10$ ms, and the cuvette was quickly filled with a well-mixed mist. At $t = 22$ ms, the mist suddenly turned into a luminous flame. As shown in Fig. 4.3b, the luminosity from a likely pre-mixed flame lasted only a very short time, and simultaneously, a very loud sound was recorded by the microphone.
In case II (Fig. 4.4), the MMH droplet was ejected from the WFNA pool at $t = 22$ ms. The aerosol cloud around the droplet vanished rapidly and a luminous flame was formed between the droplet and the pool. From $t = 22$ to 216 ms, the MMH droplet was smoothly floating on and rolling along the surface of the WFNA pool. A force balance was established between the droplet due to gravity and the repelling force at the interface due to gas flow. At $t = 218$ ms, the gas flow increased and the drop was pushed further away from the pool, as shown at $t = 250$ ms. Subsequently, the gas flow decreased causing the droplet to impact the pool again ($t = 330$ ms) and repelled again ($t = 350$ ms). This impacting-repelling type of interaction continued until finally the drop disintegrated.
During the entire process, the diffusion flame was self-sustained due to continuous gasification of MMH from the droplet and vaporization of nitric acid from the pool. Figure 4.4b shows the photodiode and microphone signals from the same test. The photodiode sensed a weak but long-lasting (compared to case I in Fig. 4.3b) luminous signal starting at $t = 22$ ms and the microphone detected a series of pressure waves corresponding to the multiple impacting-repelling interactions between the droplet and the pool.

A total of 5 tests were also conducted by releasing a WFNA droplet into 80 $\mu$L of MMH. The tests were quite repeatable with ignition delays of around 20-25 ms. Some selected high speed images from a typical test are shown in Fig. 4.5. When a drop of
WFNA plunged into a MMH pool, it was surrounded by MMH and a cone-shape diffusion flame (candle-like) sustained for about 350 ms. Unlike the MMH droplet, the WFNA droplet was not elevated by the gas flow from the pool and droplet vaporization, since its mass is about twice the mass compared to the MMH droplet with the same size.

A total of 20 videos were acquired for the interaction between a drop of MMH and RFNA pool. Quite similar to that discussed in the MMH-WFNA section, the MMH droplet may be ejected from the pool or simply exploded after the impact. Figure 4.6 shows a test in which droplet-ejection occurred. A columnar particulate trace was formed due to the reactions with pre-occupied HNO₃ vapor (as shown at t = -20 ms). However, this particulate trace vanished as the droplet approached closer to the RFNA pool, and an oval-shape luminous flame was observed, as shown at t = -5 ms. This pre-contact ignition was observed only when RFNA was used, which means it is most likely caused by reactions with gaseous NO₂. The droplet then plunged into and was ejected from the pool, surrounded with a diffusion flame. At t = 106 ms, the droplet exploded on its second
contact with the pool. In some other tests, the droplet exploded immediately upon its first contact with the pool. Since a pre-contact ignition was observed, the ignition delay for MMH-RFNA liquid-liquid interaction can not be evaluated in such a test. However, in a series of drop tests involving a drop of RFNA and a MMH pool (80μL), pre-contact ignition was not observed. The ignition delays were all within 4 to 5 ms for a total of 6 tests. Additionally, attempts were made to probe the gas-phase temperatures in the drop tests involving MMH with fuming nitric acid (WFNA and RFNA), but repeatable measurements were not achieved.

![Figure 4.6: Selected images from a drop test of MMH (drop) / RFNA (80 μL)](image)

4.2 Confined Interaction Experiments

As shown in the high-speed videos, the major observation prior to ignition was the formation and accumulation of an aerosol cloud. This cloud contained products from the liquid-phase and subsequent gas-phase reactions. In order to identify the pre-ignition species formed at different temperature levels, confined-interaction/FTIR experiments were conducted at a series of preset temperatures (20, 50, 100, 150, 200 and 250°C). At
20 and 50°C, which are lower than the boiling points of reactants, the products were mainly formed from liquid-phase reactions; at 100, 150, 200 and 250°C, the reactants quickly evaporated; therefore, the products were mainly formed by gas-phase reactions. The products from liquid- and gas-phase reactions are discussed in Sec. 4.2.1 and 4.2.2, respectively.

4.2.1 Liquid-liquid Interaction (20 and 50°C)

Figure 4.7: a) Average IR spectrum from confined interaction between MMH and 70%HNO₃ at 20°C and 1 atm N₂; b) IR spectrum obtained by subtracting the IR bands of H₂O from a); and c) a reference IR spectrum of MMH at 20°C (ν - stretching vibration; δ – deformation vibration).

The nitric acid solutions have complex compositions (i.e., HNO₃, H₂O, HNO₃·H₂O, HNO₃·3H₂O, NO₃⁻, H₃O⁺, NO₂⁺, etc.) which are highly dependent on their
concentrations as well as temperatures [3, 4]. Therefore, the liquid-phase reactivity (i.e., acidity and oxidizability) of nitric acid solutions is highly related to their concentrations. In the liquid phase, MMH was neutralized to monomethylhydrazinium nitrate when 70%HNO₃ was used. However, when a stronger oxidizer (90%HNO₃ or WFNA) was used, MMH was partially neutralized to form the nitrate salt and partially oxidized to form methyl nitrate (CH₃ONO₂), methyl azide (CH₃N₃), N₂O, H₂O and N₂.

Figure 4.7a shows an averaged IR spectrum of species from a confined interaction experiment at 20ºC, using 0.5 μL of MMH and 0.5μL of 70%HNO₃. Averaging of spectra reduces the random noise in the spectrum. Figure 4.7b is obtained by subtracting the IR bands of H₂O from Fig. 4.7a. Spectral subtraction is an important method to simplify the product spectrum thus helps to identify the remaining bands [5]. The IR bands in Fig. 4.7b agree with the spectrum of monomethylhydrazinium nitrate reported elsewhere [6-8]. This nitrate product was also reported as an important pre-ignition product in the MMH/N₂O₄ system [6, 8-10]. The IR absorption bands in Fig. 4.7b are mostly due to the nitrate anion (NO₃⁻), and the cation groups -NH₃⁺ and -NH₂⁺ [11-15]. Since MMH contains two electrophilic nitrogen atoms, theoretically three inorganic nitrates can be formed: [CH₃NHNH₃]⁺NO₃⁻, [CH₃NH₂NH₂]⁺NO₃⁻ and [CH₃NH₂NH₃]²⁺[NO₃]₂. Therefore, the spectrum in Fig. 4.7b may represent a mixture of several nitrate salts. Breisacher et al. [16] prepared and studied both MMH·HNO₃ and MMH·2HNO₃. For comparison, an IR spectrum of gaseous MMH at 20ºC is also included in Fig. 4.7c. The major vibrational modes of MMH were assigned based on a detailed analysis by Durig et al. [17].
Figure 4.8: a) Average IR spectrum of the first 30 spectra obtained from confined interaction between MMH and 90%HNO$_3$ at 20ºC and 1 atm N$_2$; b) average IR spectrum of the last 30 spectra obtained from the same test; and c) Time-resolved IR absorption of species evolved from the same test (maximum absorption of all species were normalized to 1).

Figure 4.8 shows the IR spectra of species evolved from the confined interaction between 0.5 µL of MMH and 0.5 µL of 90%HNO$_3$ at 20ºC. The spectra in Figs. 4.8a and 8b were obtained by averaging the first 30 and last 30 spectra out of a total of 150 spectra obtained in the same test. The major products include monomethylhydrazinium nitrate, methyl nitrate (CH$_3$ONO$_2$), methyl azide (CH$_3$N$_3$), N$_2$O and H$_2$O. The IR-inactive species N$_2$ was also detected in the mass spectrum. The IR bands of CH$_3$N$_3$ and CH$_3$ONO$_2$ in Fig.
4.8b match exactly with results from Khlifi et al. [18] and Brand and Cawthon [19]. Figure 4.8c shows the time-resolved profiles of major species from the same test discussed above. The IR absorption intensity of each species was normalized to 1. Liquid-phase reactions occurred very fast and all the species evolved almost simultaneously. MMH nitrate then gradually disappeared from IR the spectra. It is most likely that this nitrate salt has extremely low volatility at these temperatures and condensed out on the chamber walls. It is also possible that this salt was further converted to the other species, whose concentrations increased slowly. The rapid decrease of H2O in Fig. 4.8c is probably due to the hygroscopic nature of MMH nitrate [16].

The species evolved from confined interaction between MMH and WFNA are the same as those evolved from the interaction between MMH and 90%HNO3, namely monomethylhydrazinium nitrate, methyl nitrate, methyl azide, N2O, H2O and N2. In addition, the results from confined interaction experiments at 50°C were similar to those of 20ºC, thus are not presented here.

4.2.2 Vapor-Vapor Interaction (100-250°C)

When the interaction zone was preheated to temperatures above the boiling points of reactants, a major portion of the reactants was gasified prior to their liquid-liquid contact. Thus, the reactions mainly occurred in the gas phase. As discussed in the previous section, the concentrations of nitric acid solutions may substantially affect their reactivity (especially oxidizability). However, in the gas phase, MMH reacted with all three forms of nitric acid quite similarly. At temperatures below 250°C, the vapors of
MMH and HNO₃ reacted to form an aerosol cloud which was mainly composed of monomethylhydrazinium nitrate. This type of gas-phase acid-base reactions are usually called ‘gas-to-particle’ or ‘gas-to-aerosol’ reactions and widely studied by atmospheric chemists [20-23]. Monomethylhydrazinium nitrate has extremely low volatility at these temperatures [6], and complexes tend to condense out to form an aerosol cloud. At temperatures above 250°C, the formation of such an aerosol cloud was not favored and many other species were detected.

Figure 4.9: Average IR spectrum from a confined interaction between MMH and WFNA at 200°C and 1 atm N₂.

Figure 4.9 shows the averaged IR spectrum of products evolved from a confined interaction experiment at 200°C, using 0.1 μL of MMH and 0.1 μL of WFNA. The dominant product was monomethylhydrazinium nitrate, and minor products were oxidation products CH₃ONO₂, CH₃N₃, N₂O, NO and H₂O. It should be noted that liquid-liquid contact and liquid-phase reactions between MMH and WFNA may still occur for a very short period of time, although the two liquids are believed to be gasified rapidly as soon as they were pushed out from the syringes. Therefore, it is uncertain whether these small amounts of oxidation products were from liquid-phase or gas-phase reactions.
Figure 4.10: a) Average IR spectra from confined interaction between MMH and WFNA at 250ºC and 1 atm N\textsubscript{2}; b) IR spectrum obtained by subtracting H\textsubscript{2}O from (a); and c) IR spectrum obtained by subtracting HONO, CH\textsubscript{3}ONO\textsubscript{3}, N\textsubscript{2}O, CO\textsubscript{2}, and CH\textsubscript{4} from b).

Figure 4.10a shows the averaged IR spectrum of products evolved from a confined interaction experiment at 250ºC, using 0.1 \textmu L of MMH and 0.1 \textmu L of WFNA. The spectra in Fig. 4.10b and 4.10c were obtained by spectral subtraction on the original spectrum in Fig. 4.10a. At 250ºC, the formation of monomethylhydrazinium nitrate was not favored. Instead, large amounts of H\textsubscript{2}O and HONO were produced. Other IR-active products include CH\textsubscript{3}ONO\textsubscript{2}, CH\textsubscript{3}ONO, CH\textsubscript{3}N\textsubscript{3}, CH\textsubscript{3}OH, CH\textsubscript{3}NH\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, NO, and small amounts of HNCO, NH\textsubscript{3}, HCN and CO\textsubscript{2}. IR-inactive species N\textsubscript{2} was also
identified in the mass spectrum. The IR bands of each species and corresponding references are listed in Table 4.1.

Table 4.1: IR frequencies of species in Fig. 4.10 (vs=very strong, s=strong, m=medium)

<table>
<thead>
<tr>
<th>Species</th>
<th>Major IR bands observed in this work (cm⁻¹)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃, H₂O, NO₂, NO, N₂O, CO₂, CH₄, HCN, CH₃OH and NH₃ See HITRAN data base</td>
<td>[24]</td>
<td></td>
</tr>
<tr>
<td>MMH</td>
<td>3261(s), 2960(vs), 2852(vs), 2785(vs), 1595(m), 1480(s), 1451(s), 1293(m), 1119(s), 968(s), 888(vs), 771(vs)</td>
<td>[17]</td>
</tr>
<tr>
<td>MMH Nitrate</td>
<td>3322(s), 3080(s), 2796(m, br), 2495(m), 1617(s), 1460(s), 1383(vs), 1215(m), 1106(m), 1000(m), 882(m), 827(m)</td>
<td>[7]</td>
</tr>
<tr>
<td>trans-HONO</td>
<td>3590(m), 1699(s), 1264(s), 791(s)</td>
<td>[25]</td>
</tr>
<tr>
<td>cis-HONO</td>
<td>1640(s), 853(s)</td>
<td>[25]</td>
</tr>
<tr>
<td>HNCO</td>
<td>2269</td>
<td>[26]</td>
</tr>
<tr>
<td>CH₃N₃</td>
<td>2190(m), 2107(s), 1276(m)</td>
<td>[18]</td>
</tr>
<tr>
<td>CH₃ONO₂</td>
<td>2965(m), 1666(vs), 1435(m), 1290(vs), 1017(s), 855(s), 759(m)</td>
<td>[19]</td>
</tr>
<tr>
<td>CH₃ONO</td>
<td>1678(s), 1620(vs), 991(s), 811(vs)</td>
<td>[27]</td>
</tr>
<tr>
<td>CH₃NH₂</td>
<td>2955(s), 1621(m), 1046(m), 782(s)</td>
<td>[28]</td>
</tr>
</tbody>
</table>

4.3 Early Reactions between MMH and HNO₃

4.3.1 Liquid-phase Reactions

The present work shows that in the liquid phase, the reactions between MMH and nitric acid are similar to those between hydrazine (N₂H₄) and nitric acid, which have been well studied [29-34]. In nitric acid solution, hydrazine was first neutralized by nitric acid
to form hydrazinium nitrate ($N_2H_5NO_3$), which was then oxidized by excess nitric acid to form ammonium nitrate ($NH_4NO_3$), hydrazoic acid ($HN_3$), $N_2$, $N_2O$, and $H_2O$. The reaction pathways of $N_2H_4/HNO_3$ were discussed in Karraker’s work [30]. Similarly, MMH was first neutralized by nitric acid to form monomethylhydrazinium nitrate ($MMH\cdot HNO_3$), which was then oxidized by excess nitric acid to form methyl nitrate ($CH_3ONO_2$), methyl azide ($CH_3N_3$), $N_2O$, $N_2$, and $H_2O$. The possible liquid-phase reactions (R1-R14) of MMH/HNO_3 are suggested in Fig. 4.11 and a short description of these reactions is given as follows:

MMH contains two electrophilic nitrogen atoms, and as such, it can be mono-protonated (R1) and diprotonated (R2) by nitric acid. The monomethylhydrazinium salt can be further oxidized by excess nitric acid through pathways R3-R14. The initial step of the oxidation of hydrazinium ion in nitric acid solution is believed to be the formation of nitrous acid, $H_2O$ and a diazene intermediate [30], based on which, reactions R3 and R4 are proposed. In this process, an N-nitrohydrazinium compound $[CH_3NH^+(NO_2)NH_2]$, which is unstable in acidic solution [35], is suggested as an intermediate species. Similarly, the methyl diazenium cation ($CH_3NH^+=NH$) from reaction R4 can react with nitric acid to form an N-nitrodiazenium intermediate $[CH_3N^+(NO_2)=NH]$ (R5), which can convert into a methyldiazonium ion ($CH_3N_2^+$) through an HONO elimination step (R6). A well-known reaction of diazonium ion is called ‘replacement of nitrogen’ [36], in which the nitrogen is lost as $N_2$. For example, methyldiazonium ion can react with $H_2O$ to form $CH_3OH$, $N_2$ and $H^+$ [37]. In nitric acid solution, methyldiazonium cation may react with $NO_3^-$ to form methyl nitrate and $N_2$ (R7). In addition, monomethylhydrazinium ion can also react with nitrous acid from reactions R4 and R6 to form methyl azide ($CH_3N_3$).
and H$_2$O (R8-R9). MMH was reported to be oxidized by nitrous acid to form methyl azide [38]. Studies on the reactions between hydrazine and nitrous acid indicated that nitrous acid or nitrite can be scavenged by hydrazine rapidly, proceeding at almost the encounter rate [29, 39-41]. The possible reaction pathways between hydrazine and nitrous acid were studied by Perrott et al. [39] and Doherty et al. [41], based on which, reactions R8 and R9 are proposed. In this process, an unstable N-nitrosohydrazinium compound [CH$_3$NH$^+$NO$^-$NH$_2$] is suggested as an intermediate species (R8). An N-nitrosohydrazinium compound can decompose through two parallel routes, to an azide and H$_2$O at high acidities and to an amine and N$_2$O at low acidities [39]. In nitric acid solution, the N-nitrosohydrazinium compound from reaction R8 will decompose through rearrangement and dehydration to form methyl azide and H$_2$O (R9) [16]. It should be noted that reaction R9 is a global reaction with the possible elementary steps discussed by Smith [42]. Methyl azide from reaction R9 may further react with nitric acid (R10) or nitrous acid (R11) through the displacement of azido group by hydroxyl group, which is a well-known reaction of alkyl azides in acidic medium [43]. Based on the studies conducted by Stedman [44] and Doyle et al. [45], two intrinsically unstable oxides of nitrogen, nitryl azide (N$_3$NO$_2$) and nitrosyl azide (N$_3$NO), were proposed as the intermediate species. Nitryl azide and nitrosyl azide can only been prepared at very low temperatures [45, 46], and can easily decompose to 2N$_2$O (R12) and N$_2$ + N$_2$O (R13), respectively [47]. Reaction R12 is a global reaction with the possible elementary steps discussed by Zeng et al. [48]. The methanol from reactions R10 and R11 can further react with nitric acid to form methyl nitrate and H$_2$O (R14).
It is important to note that the nitronium ion (NO$_2^+$) might be the de facto oxidizing agent in concentrated nitric acid [4, 29, 31, 32]. NO$_2^+$ exists in concentrated...
nitric acid solutions at ambient temperatures due to the self-ionization equilibrium [49] given by

\[
\text{HNO}_3 + \text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^- \rightleftharpoons \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}
\]

4.3.2 Gas-phase Reactions

Figure 4.12 shows some gas-phase reactions (R15-R40) suggested for MMH/HNO₃ based on the product analysis in section 4.2.2. At temperatures below 250ºC, the ‘gas-to-aerosol’ type of reactions are favored between the vapors of MMH and HNO₃, and it is generally believed that the first step of this type of reactions is the formation of a hydrogen-bonded complex (R15). Proton transfer from the acid to the base forms an ion pair as the complex grows (R16) [20-23]. Ab initio studies indicated that although the gas-phase proton transfer process is thermally unfavorable, it can be achieved with proper perturbing agents such as electrons [22] or ambient water molecules [23]. In the present study, proton transfer during the growth of the MMH-HNO₃ complex might be due to the perturbation by the nearby molecules, such as HNO₃ or MMH.

At temperatures above 250ºC, the major products did not include monomethylhydrazinium nitrate, and the aerosol cloud was not observed. One possible explanation is that the gas-phase salt formation reactions are not favored and replaced by a more favorable gas-phase oxidation mechanism at these temperatures. Another reasonable explanation is that the monomethylhydrazinium nitrate salt becomes very unstable at these temperatures and can decompose rapidly. Studies on the decomposition of nitrates of many amines showed that the first step was to form HNO₃ and the
corresponding amines [50, 51]. It is very likely that monomethylhydrazinium nitrate decomposes in a similar way, namely, to form MMH and HNO₃ vapors first. Since HNO₃ vapor is thermally unstable and can decompose rapidly at temperatures above 250°C [52-54], it may react with MMH through an oxidation mechanism suggested in Fig. 4.12 (R17-R40) other than the salt formation reactions (R15-R16). A short description of these reactions is given next.

In the gas phase, the first step of HNO₃ decomposition is the HO-NO₂ bond breaking, which forms OH and NO₂ radicals (R17) [52]. The activation energy of this reaction is about 40 kcal/mol, much lower than the other potential pathways, H + ONO₂ (100 kcal/mol) and HONO + O (80 kcal/mol) [52]. The OH and NO₂ radicals can react with MMH through H-atom abstraction steps (R18-R22) to form H₂O and HONO, respectively. These reactions were studied by McQuaid and Ishikawa using ab initio techniques [55, 56]. In this process, an N-nitro compound is proposed as an intermediate (R19, R21), which can decompose into methyl diazene (CH₃N=NH) through a HONO elimination step (R20, R22). HONO is a very reactive species, and it can generate NO (R23). The NO then reacts with the MMH radical to form an N-nitroso intermediate (R24, R28). N-nitroso compound (I) may decompose through an HNO elimination reaction (R25) to form methyl diazene, or through rearrangement and dehydration steps (R26) to form methyl azide. Reaction (R26) is well-known [16, 38], and the possible elementary steps are described by Smith [42]. N-nitroso compound (II) can decompose through rearrangement (R29) and N₂O elimination (R30) steps to form methylamine (CH₃NH₂) [9, 39]. N-nitroso compound (I) can also transform to (II) when heated (R27) [43]. Nitroxyl (HNO) from reaction R25 can form a dimer (R31) which then decomposes
into N2O and H2O (R32) [57]. Methyl diazene (CH3N=NH) intermediate can further react with the OH or NO2 radicals to form methyl diazene radical (CH3N=N·) through H2O elimination (R33) or HONO elimination (R34). The methyl diazene radical may with other radicals to form methanol or methyl nitrite (CH3ONO) through an N2 elimination reaction (R35-R38). Methanol can further react with HNO3 or HONO to form CH3ONO2 or CH3ONO through an H2O elimination reaction (R39-R40).

\[ \text{(T < 250\degree C)} \]
\[
\begin{align*}
\text{CH}_3\text{NHNH}_2 + \text{HNO}_3 & \rightarrow \text{CH}_3\text{NHNH}_2 - \text{HNO}_3 \rightarrow [\text{CH}_3\text{NHNH}_3]^+ \text{NO}_3^- \\
\text{(vapors)} & \text{(hydrogen bonded complex)} (\text{particulate aerosol})
\end{align*}
\]

\[ \text{(T > 250\degree C)} \]
\[
\begin{align*}
\text{HNO}_3 & \rightarrow \text{HO}^* + \cdot \text{NO}_2 \\
\text{CH}_3\text{NHNH}_2 + \text{HO}^* & \rightarrow \text{H}_2\text{O} + \text{H}_2\text{N}-\text{N}-\text{CH}_3 \text{ or } \text{HN}-\text{NH}-\text{CH}_3 \\
\text{H}_2\text{N}=\text{N}-\text{CH}_3 + \cdot \text{NO}_2 & \rightarrow \text{H}_2\text{N}-\cdot\text{N}-\text{CH}_3 \rightarrow \text{CH}_3\text{N}=\text{NH} + \text{HONO} \\
\text{HONO} & \rightarrow \text{HO}^* + \cdot \text{NO} \\
\text{H}_2\text{N}-\text{N}-\text{CH}_3 + \cdot \text{NO} & \rightarrow \text{H}_2\text{N}-\cdot\text{N}-\text{CH}_3 (\text{I}) \rightarrow \text{CH}_3\text{N}=\text{NH} + \text{HNO} \\
\text{HN}-\text{NH} + \cdot \text{NO} & \rightarrow \text{HN}-\text{NH}_{\text{CH}_3} (\text{II}) \rightarrow \text{N}-\text{NH}_{\text{CH}_3} \rightarrow \text{CH}_3\text{NH}_2 + \text{N}_2\text{O} \\
\text{CH}_3\text{N}=\text{NH} + \text{HO} & \rightarrow \text{CH}_3\text{N}=\text{N} + \text{H}_2\text{O} \\
\text{CH}_3\text{N}=\text{NH} + \cdot \text{NO}_2 & \rightarrow \text{CH}_3\text{N}=\text{N} + \text{HONO} \\
\text{CH}_3\text{N}=\text{N} + \cdot \text{NO}_2 & \rightarrow \text{CH}_3\text{N}=\text{N} = \text{NO}_2 \rightarrow \text{CH}_3\text{ONO} + \text{N}_2 \\
\text{CH}_3\text{N}=\text{N} + \text{HO} & \rightarrow \text{CH}_3\text{N}=\text{NOH} \rightarrow \text{CH}_3\text{OH} + \text{N}_2 \\
\text{CH}_3\text{OH} + \text{HNO}_3 & \rightarrow \text{CH}_3\text{ONO}_2 + \text{H}_2\text{O}
\end{align*}
\]

Figure 4.12: Gas-phase reactions between MMH and HNO3
It should be noted that the proposed reactions R17-R40 are based on the product analysis from the tests at 250°C. The major detected species, such as H₂O, HONO, CH₃OH, CH₃ONO₂, CH₃ONO, CH₃N₃, CH₃NH₂, N₂ and N₂O, are all included in these proposed reactions. The minor species, such as CH₄, NH₃, HCN, HNCO and CO₂, can be formed by many reactions included in the MMH/RFNA mechanism by Anderson et al. [58], thus are not discussed in this study. In addition, with increasing the temperatures, additional gas-phase reactions may play an important role in the pre-ignition stage. For example, the thermal decomposition of CH₃ONO₂, CH₃ONO and CH₃N₃ could be very important [59-66]. Due to the limitation of the current confined interaction setup, reactions between MMH and HNO₃ at preset temperatures higher than 250°C were not attempted.

4.4 Conclusions

In this work, we experimentally studied the physical interactions in drop tests as well as the chemical interactions in confined interaction experiments between MMH and three nitric acid solutions. We observed two critical temperatures which approximately divide the successive hypergolic ignition process in a drop test into three stages each with distinct chemical mechanisms. These three stages and corresponding products are summarized in Fig. 4.13. The first stage involved liquid-phase reactions which formed products listed in box I. The liquid-phase reactions also released a significant amount of heat to cause the temperature of the liquid reactants to rise from ambient levels to the boiling point (first critical temperature). The second stage involved gas-phase reactions
between MMH and HNO₃ vapors released from the liquid phase. The products from these gas-phase reactions formed an aerosol cloud composed mainly of MMH nitrates. The gas-phase temperature rose from the boiling point to 280°C (second critical temperature) due to the exothermicity of proton transfer or complex formation reactions or both. The third stage involved reactions at temperatures above 280°C, including the thermal decomposition of the particulate nitrate cloud. These reactions were very fast and exothermic. Therefore, the temperature rose rapidly from 280°C to levels where burn out of thermocouple occurred. The major pre-ignition products formed in the third stage are listed in box II. The liquid- and gas-phase reactions in these three stages are also proposed.

Figure 4.13: Hypergolic ignition processes of MMH/HNO₃ in a drop test
This work provides important experimental data for formulating and validating gas-phase reaction mechanisms between MMH and HNO$_3$ [58]. Among the species identified in this work, CH$_3$N$_3$ and CH$_3$NH$_2$ are not included in the mechanism. Species such as CH$_3$ONO$_2$ and CH$_3$ONO are included in the mechanism, but they cannot be formed early in the reaction sequence. Therefore, one potential improvement of this mechanism is to add the early reactions proposed in the present work related to the formation of these species. It is also very important to include decomposition as well as oxidation and reduction reactions of these species, which are in part available in the literature [59-66]. In addition, a single reversible MMH-HNO$_3$ complexation reaction might be insufficient to describe the formation of the aerosol and the important heat release associated with the formation of an ion pair. Furthermore, the hypergolic system studied in this work involved liquids, vapors as well as solid nitrate particles, therefore, interfacial reactions may also be important.

4.5 References


Chapter 5
Interactions between TMEDA and Nitric Acid

The hypergolic interaction between TMEDA and nitric acid was studied by the drop test setup and confined interaction setup which were introduced in Sects. 3.1 and 3.2, respectively. The gaseous species from condensed- and gas-phase reactions between TMEDA and HNO₃ were analyzed by a confined interaction setup, coupled with a Fourier transform infrared (FTIR) spectrometer. The solid residue from the condensed-phase reactions between TMEDA and HNO₃ was studied by using a confined rapid thermolysis (CRT) setup coupled with FTIR spectroscopy and time-of-flight mass spectrometry. Based on the product analysis, the pre-ignition reactions between TMEDA and nitric acid are discussed. In addition, high-speed videos were acquired to resolve the pre-ignition, ignition and post-ignition events in a drop test when a fuel drop impinged on a pool of nitric acid. Temperature profiles were also obtained in gas and condensed phases using coated fine-wire thermocouples.

5.1 Confined Interaction Experiments

The confined interaction experiments of the hypergolic pair TMEDA/90%HNO₃ were conducted by following the procedures described in the Sect. 3.2. IR spectra were acquired at a series of pre-set temperatures 25, 50, 100, 150, 200 and 250°C to identify
species formed during the condensed-phase and gas-phase interaction between TMEDA and 90% HNO₃. An IR spectrum was acquired for gaseous TMEDA for reference, since none could be found in the open literature. Figure 5.1 shows a spectrum of gaseous TMEDA at 200°C, and an analysis of the corresponding functional groups based on the infrared characteristic group frequencies [1]. The TMEDA IR spectrum has strong bands at 2979, 2953, 2821, 2775, 1463 and 1040 cm⁻¹; medium bands at 2867, 1273 and 1147 cm⁻¹; weak bands at 1363, 1099, 946, 940, 834, 829 and 789 cm⁻¹.

Figure 5.1: IR spectrum of gaseous TMEDA at 200°C and 1 atm N₂.

Figure 5.2: IR spectrum of TMEDADN in KBr pellet at room temperature and 1 atm N₂.
It is well-known that a Lewis-type acid-base reaction with the formation of a salt occurs in amine-HNO₃ systems [2-4]. With two tertiary amine groups, TMEDA can be both monoprotonated (pKₐ = 8.97) and diprotonated (pKₐ = 5.85) [5]. With excess nitric acid, TMEDA is more likely to be diprotonated to a dinitrate, TMEDADN. An IR spectrum of solid TMEDADN was also acquired for reference, as shown in Fig. 5.2. The sample was prepared by mixing diluted TMEDA with diluted nitric acid at a mole ratio of 1:2. TMEDA and nitric acid was diluted to a concentration of 10 wt% HNO₃ by distilled water to reduce the rate of the exothermic reactions. TMEDADN was then separated in a vacuum dryer for 24 hours to remove the excess water and other impurities, such as unreacted TMEDA or HNO₃. An SEM/EDS (Scanning Electron Microscopy / Energy Disperse Spectroscopy) analysis on this sample showed that the C/O ratio of this sample was about 1:1, strongly indicating that this powder was mainly TMEDADN. The solid-phase FTIR spectrum of TMEDADN was acquired using the standard KBr pellet pressing technique. In this technique, a mixture of 0.15 mg TMEDADN and 150 mg KBr was pressed to a pellet with a diameter of 8 mm and thickness of 1 mm. As shown in Fig. 5.4, the TMEDADN IR spectrum in the solid phase has very strong bands at 1486, 1388, 1362 and 1303 cm⁻¹; medium bands at 3047, 3020, 2642, 2466, 1416, 1276, 1239, 1416, 1041, 1001, 982 and 826 cm⁻¹; weak bands at 2907, 2780 (broad), 1758, 1744, 1156, 1132, 786 and 719 cm⁻¹. The suggested vibrational modes were assigned to each band in Fig. 5.2. Generally, the nitrate ion (NO₃⁻) shows three characteristic bands in the IR spectrum: ν₂ (out-of-plane deformation, 800-860 cm⁻¹), ν₃ (doubly degenerate stretch, 1350-1410 cm⁻¹) and ν₄ (doubly degenerate in-plane bending, 710-730 cm⁻¹) [6, 7]. For TMEDADN, these bands are 826, 1388 and 719 cm⁻¹, respectively. Compared to
TMEDA, the stretching vibration of methyl group in TMEDADN shifts about 68 cm\(^{-1}\) to higher frequencies due to the protonation of its nearby N atom. A similar shift (by 64 cm\(^{-1}\)) has also been observed between trimethylamine and trimethylammonium cation [8].

Figure 5.3 shows a selected spectrum of species evolved from the interaction between 0.5 µL TMEDA and 1 µL 90% HNO\(_3\) at 25°C. A separate thermocouple measurement showed that the temperature of the gases in the confined interaction region increased to about 80°C due to the exothermic reactions. As shown in Fig. 5.3, the only product formed between TMEDA and 90% HNO\(_3\) at room temperature is TMEDADN. Small amounts of HNO\(_3\), H\(_2\)O and TMEDA are also detected in the spectrum. The reactants are mainly consumed by condensed-phase reaction which forms a white residue accumulating in the reaction zone. In addition, TMEDA and HNO\(_3\) are partially evaporated and reactions occur in the vapors to form TMEDADN in the gas phase, which is detected in the IR spectrum. The formation of this cloud is most probably due to the condensation of TMEDADN in the gas phase, producing a slope in the baseline of the
spectral transmittance. The work by Kravets et al. contains an excellent discussion on the effects of small particles on the spectral transmittance [9].

When the initial temperature of the confinement is increased to 50°C, the species observed in the spectrum are the same as those observed when the initial temperature is 25°C; thus, only a nitrate salt is formed. However, many more IR-active species evolve when the initial temperature of the confinement is increased to 100, 150 and 200°C. Figure 5.4 shows selected IR spectra of species evolved from the interaction between 0.2 µL TMEDA and 0.2 µL 90% HNO₃ at an initial temperature of 100 and 200°C, respectively. As shown in Fig. 5.4, TMEDADN is still the dominant product detected at these temperatures. Other IR-active species include H₂O, NO₂, NO, CO₂, N₂O, CH₂O, HONO.

![Figure 5.4: Selected IR spectrum of species evolved from confined interaction between TMEDA and 90% HNO₃ at 100 and 200°C, 1 atm N₂.](image)

Figure 5.4: Selected IR spectrum of species evolved from confined interaction between TMEDA and 90% HNO₃ at 100 and 200°C, 1 atm N₂.
Figure 5.5: IR spectrum of species evolved from confined interaction between TMEDA and 90% HNO₃ at 250°C and 1 atm N₂; (A – original spectrum; B – spectrum after subtraction of H₂O, NO₂ and CO₂ from the original spectrum; C – spectrum after subtraction of H₂O, NO₂, CO₂, N₂O, NO, CH₂O and (CH₃)₂NNO from the original spectrum.)

Figure 5.5 shows a selected IR spectrum of species evolved from the interaction between 0.2 µL TMEDA and 0.2 µL 90% HNO₃ at an initial temperature of 250°C. In Fig. 5.5, part A is the original spectrum; part B is the spectrum after subtracting H₂O, NO₂ and CO₂; part C is the spectrum after further subtracting N₂O, NO, CH₂O and (CH₃)₂NNO. Spectral subtraction is an important method to simply the product spectrum [10]. The IR spectra of (CH₃)₂NNO and (CH₃)₂NCHO were obtained separately on the same setup and at the same temperature for comparison with the product IR spectrum.
Most bands from the product IR spectrum are identified. Table 5.1 lists the species identified from Fig. 5.5 and their corresponding IR absorption bands.

Table 5.1. Species identified in Fig. 5.5 and their corresponding frequencies

<table>
<thead>
<tr>
<th>Major Species</th>
<th>Frequencies (cm(^{-1}))</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O, NO(_2), CO(_2), NO, N(_2)O, CO, CH(_2)O</td>
<td>See HITRAN data base</td>
<td>[11]</td>
</tr>
<tr>
<td>(CH(_3))(_2)NNO</td>
<td>2961, 1488, 1292, 1015</td>
<td>Acquired *</td>
</tr>
<tr>
<td>(CH(_3))(_2)NCHO</td>
<td>2940, 2847, 1714, 1383, 1082</td>
<td>Acquired *</td>
</tr>
<tr>
<td>trans-HONO</td>
<td>3590, 1699, 1264, 791</td>
<td>[12]</td>
</tr>
<tr>
<td>cis-HONO</td>
<td>1640, 853</td>
<td>[12]</td>
</tr>
</tbody>
</table>

The following species may also exist in small amounts

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>glyoxal, (CHO)(_2)</td>
<td>2843, 2834, 1745, 1733, 1338, 1312, 1064, 1049</td>
</tr>
<tr>
<td>-N=C=O</td>
<td>2250-2300</td>
</tr>
<tr>
<td>CH(_2)=NCH(_3)</td>
<td>3024, 2974, 2962, 1662, 1475, 1444, 1220, 1026</td>
</tr>
<tr>
<td>Unassigned bands</td>
<td>A strong band at around 1680 cm(^{-1}); several sharp bands in the region 1500-1600 cm(^{-1}) (1575, 1558, 1540 and 1506) and several sharp bands in the region 1750-1900 cm(^{-1}) (1843, 1830 and 1771).</td>
</tr>
</tbody>
</table>

* Note: individual reference spectra of (CH\(_3\))\(_2\)NNO and (CH\(_3\))\(_2\)NCHO were obtained separately for comparison with spectra obtained from the hypergolic tests.

### 5.2 Thermolysis of TMEDADN

A confined rapid thermolysis of TMEDA dinitrate (TMEDADN), which is the dominant early product in the TMEDA/HNO\(_3\) interaction, was conducted at a series of pre-set temperatures by using the CRT/FTIR/ToFMS setup described in Sect. 3.3. A detailed introduction on the time-of-flight mass spectrometer (ToFMS) is available in early studies [15, 16]. At a heating rate of 2000 K/s, TMEDADN started to rapidly
decompose at approximately 290°C. Selected IR and mass spectra of the gaseous species evolved from thermolysis of TMEDADN at 330°C are shown in Figs. 5.6 and 5.7, respectively. The mass spectrum analysis in Fig. 5.7 is based on NIST mass spectra database [17]. The species evolved from the thermolysis of TMEDADN are similar to those evolved from the direct interaction between TMEDA and 90% HNO₃ at 250°C. In addition, TMEDA is also detected as a major product from the thermolysis of TMEDADN. Based on this observation, the first step of TMEDADN decomposition is to form TMEDA and HNO₃. At these temperatures, HNO₃ could decompose to form NO₂, H₂O and O₂ [18]. However, it is more likely that HNO₃ is rapidly consumed by reactions with TMEDA, which is fuel-rich, to form NO, HONO, and N₂O. At these temperatures, NO₂ may also readily react with TMEDA forming HONO and a TMEDA radical.

Figure 5.6: IR spectrum of gaseous species from rapid thermolysis of TMEDADN at 330°C and 1 atm N₂.
5.3 Early Reactions between TMEDA and HNO₃

Based on the product analysis from the interaction of TMEDA/90% HNO₃ as well as rapid thermolysis of TMEDADN, some major pre-ignition reactions in the condensed and gas phases are proposed. For a hypergolic liquid bipropellant, the reactions will first take place in the condensed phase where the two liquids come into contact. Reactions will then extend to the gas phase among the evaporated reactants and products from condensed-phase reactions, which finally lead to a gas-phase ignition.

The initiation reaction between TMEDA and HNO₃ is an exothermic salt formation reaction with the formation of TMEDADN. This Lewis-type acid-base reaction is well-known in many amine-HNO₃ systems [2-4]. The global reaction is written as follows:

\[ \text{TMEDA} + 2\text{HNO}_3 \rightarrow \text{TMEDADN} \quad (1) \]
In the condensed phase (solution or solid), TMEDADN is most likely a nitrate salt or zwitter ion, \([(\text{CH}_3\text{)}_2\text{NHCH}_2\text{CH}_2\text{NH(\text{CH}_3\text{)}_2}][\text{NO}_3^-]\); in the gas phase, TMEDADN is most likely a complex TMEDA·2HNO\text{3}. The heat of reaction predicted by Gaussian03 (B3LYP/6-31G(d,p)) [19], using a method suggested by Osmont et al. [20] is approximately -30 kcal/mol. This acid-base type of reaction normally has a low activation energy and thus is very rapid. Therefore, the salt formation is the dominant reaction between TMEDA and nitric acid until TMEDADN starts to rapidly decompose at temperatures above approximately 290°C.

At elevated temperatures, liquid HNO\text{3} starts to decompose through a self-acceleration process, which produces NO\text{2}, O\text{2} and H\text{2}O as the final products [18]. The global reaction can be written as follows:

\[4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \quad (2)\]

As shown in Figs. 5.4 and 5.5, NO\text{2} and H\text{2}O were largely produced at elevated temperatures. O\text{2} is not an IR-active species thus can not be detected. Reaction (2) may mainly occur in the condensed phase. In the gas phase, the decomposition of nitric acid vapor is extremely slow at temperatures below 250°C [18].

At elevated temperatures, TMEDA may react with NO\text{2} which may be produced from reaction (2). The first step is abstraction of a hydrogen atom from TMEDA by NO\text{2}, which forms a TMEDA radical and HONO. The radical then reacts with NO\text{2} to give a nitro compound or nitrite. This mechanism is well-known in alkane nitration [21]. An unstable alkyl nitrite derivative may rearrange to give a nitrosamine and elimination of a carbonyl compound [22]. Based on the experimental observations from this work as well
as a theoretical study conducted by Chen et al. [23], reactions (3)-(5) are suggested for TMEDA and NO₂.

\[
(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2 + \text{NO}_2 \rightarrow (\text{CH}_3)_2\text{NCHCH}_2\text{N}(\text{CH}_3)_2 + \text{HONO} \quad (3)
\]

\[
(\text{CH}_3)_2\text{NCHCH}_2\text{N}(\text{CH}_3)_2 + \text{NO}_2 \rightarrow (\text{CH}_3)_2\text{NCH(ONO)CH}_2\text{N}(\text{CH}_3)_2 \quad (4)
\]

\[
(\text{CH}_3)_2\text{NCH(ONO)CH}_2\text{N}(\text{CH}_3)_2 \rightarrow (\text{CH}_3)_2\text{NNO} + (\text{CH}_3)_2\text{NCH}_2\text{CHO} \quad (5)
\]

As shown in Fig. 5.5, dimethylnitrosamine \((\text{CH}_3)_2\text{NNO}\) and HONO are major products observed in the pre-ignition stage. Without a reference IR spectrum, it is difficult to identify \((\text{CH}_3)_2\text{NCH}_2\text{CHO}\) in the product spectra. However, a mass at \(m/z = 87\) in Fig. 5.7 and an unidentified aldehyde \(\text{CH=O}\) stretching frequency around 1680 cm\(^{-1}\) in Fig. 5.5 suggest the possible presence of \((\text{CH}_3)_2\text{NCH}_2\text{CHO}\). In addition, since \((\text{CH}_3)_2\text{NCH}_2\text{CHO}\) has a \(-\text{CH}_2-\) group, it may further react with NO₂ through pathways similar to reactions (3)-(5).

\[
(\text{CH}_3)_2\text{NCH}_2\text{CHO} + \text{NO}_2 \rightarrow (\text{CH}_3)_2\text{NCHCHO} + \text{HONO} \quad (6)
\]

\[
(\text{CH}_3)_2\text{NCHCHO} + \text{NO}_2 \rightarrow (\text{CH}_3)_2\text{NCH(ONO)CHO} \quad (7)
\]

\[
(\text{CH}_3)_2\text{NCH(ONO)CHO} \rightarrow (\text{CH}_3)_2\text{NNO} + (\text{CHO})_2 \quad (8)
\]

\[
(\text{CH}_3)_2\text{NCH(ONO)CHO} \rightarrow (\text{CH}_3)_2\text{NCHO} + \text{NO} \quad (9)
\]

HONO, \((\text{CH}_3)_2\text{NNO}\), \((\text{CHO})_2\) and \((\text{CH}_3)_2\text{NCHO}\) are observed in the IR spectrum shown in Fig. 5.5. A mass at \(m/z = 132\) in Fig. 5.7 may be from the intermediate nitrite compound in reaction (7), or its nitro isomer \((\text{CH}_3)_2\text{NCH(NO}_2\text{)CHO}\) which is stable for detection [21]. The \(C\)-nitroso compound in reaction (9) may be unstable and can readily
isomerize to the corresponding oxime compound [24, 25]. This type of reaction is the principal synthetic method used to generate C=N structures [26].

\[
\begin{align*}
\text{O}_2\text{C}_\text{H} & \rightarrow \text{O}_2\text{C}^\text{NOH} \\
\end{align*}
\]

The –NCO stretching vibration at around 2300 cm\(^{-1}\) in Fig. 5.5 and a mass at m/z = 59 in Fig. 5.7 suggest possible presence of hydroxyl isocyanate HONCO. The above steps (3) – (10) can be written in two global reactions:

\[
\begin{align*}
\text{TMEDA} + 4\text{NO}_2 \rightarrow 2(\text{CH}_3\text{NNO}) + (\text{CHO})_2 + 2\text{HONO} & \quad (11) \\
(\text{CH}_3\text{NNO}) + (\text{CH}_3\text{NCHO}) + \text{HONCO} + 2\text{HONO} & \quad (12)
\end{align*}
\]

\(\text{NO}_2\) may also abstract a hydrogen atom from the –CH\(_3\) group to form CH\(_2\)O and a nitroso compound. At elevated temperatures, highly exothermic reactions will occur between CH\(_2\)O and NO\(_2\), which have been well studied in the decomposition and combustion of many energetic compounds such as RDX [27, 28]. Here, reactions between CH\(_2\)O and NO\(_2\) (or HONO) may in large part be responsible for producing the luminous flame zone in the hypergolic interaction between TMEDA and nitric acid. Formation of CH\(_2\)O may arise from hydrogen abstraction reactions written globally as:

\[
\begin{align*}
\text{H}_3\text{C}\text{N}_\text{R} + 2\text{NO}_2 \rightarrow \text{ON} \quad & \text{N}_\text{R} + \text{CH}_2\text{O} + \text{HONO} \\
\end{align*}
\]

With a considerable generation of HONO in this system, a well-known tertiary amine nitrosation mechanism may also occur between TMEDA and HONO [29]. The global reaction can be written as follows:
\[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N(CH}_3)_2 + 4\text{HONO} \rightarrow 2(\text{CH}_3)_2\text{NNO} + (\text{CHO})_2 + \text{N}_2\text{O} + 3\text{H}_2\text{O}\] (14)

Reaction (14) is generally believed to occur in acidic solutions with a hydrolysis step. In this system, however, HONO formed through various gas-phase reactions (11)-(13) may mainly stay in the gas phase. Therefore, reaction (14) may be less important compared to the gas-phase reactions (11)-(13).

5.4 Drop Tests and Temperature Measurements

Figure 5.8: Selected frames from a high-speed video for TMEDA (drop) and 90% HNO₃ (pool), \(t = -5, 0, 10, 30, 45, 60, 75, 90, 110, 130\) ms, respectively.

The drop-on-pool impingement interaction between TMEDA and 90%HNO₃ were studied by the drop test setup described in Sect. 3.1. The TMEDA droplet produced by the Hamilton syringe has a diameter around 2.4 mm, which corresponds to a volume of about 7 µL. Approximately 80 µL of 90% HNO₃ is loaded at the base of the glass cuvette. The velocity of the droplet at the moment of impact was estimated to be 1.1 m/s,
assuming free fall from a height of 50 mm. Figure 5.8 shows a series of selected frames from the drop test of TMEDA and 90\% HNO\textsubscript{3} as the event progresses from the free fall of the droplet to ignition and self-sustained combustion. Time \( t = 0 \) corresponds to the instant when the drop hits the pool. Observations are discussed by dividing the entire process into six distinct stages (I-VI):

Stage I (prior to droplet impact): The TMEDA droplet leaves the syringe and travels toward the pool of HNO\textsubscript{3} at the base of the cuvette. A ‘tail-like’ particulate cloud is observed behind the droplet when it approaches the nitric acid surface, where the nitric acid vapor has accumulated due to evaporation. The appearance of the cloud suggests that the TMEDA vapor reacts with nitric acid vapor above the pool to form a condensed-phase product, which is believed to be particulates of TMEDADN.

Stage II (0 – 10 ms): The TMEDA droplet impacts on and plunges into the nitric acid pool. The impact of the droplet initiates a series of waves that spread across the surface of liquid pool. Condensed-phase TMEDA dinitrate is formed along the wave front where the two liquids come into contact. Meanwhile, the TMEDA droplet reaches the bottom of the cuvette and mixes with the nitric acid. This is a mass transfer (mixing) dominated process, and is similar to the drop-pool interaction between two nonreactive fluids involving a vortex ring generation and propagation [30]. The exothermic neutralization reaction occurs at the drop-pool interface, where TMEDADN accumulates, causing evaporation of the reactants.

Stage III (10 – 60 ms): The white particulate cloud above the liquid surface is growing continuously. The white cloud is largely formed from agglomeration of the product from gas-phase reactions between the evaporated TMEDA and nitric acid. In the
liquid pool, a large amount of nitrate salt is also generated by condensed-phase reactions and dissolved in or further reacted with the excess nitric acid. With the increasing liquid temperature, the excess liquid nitric acid starts to decompose to form NO₂, which enters into the gas phase above the liquid. As a result, the white nitrate salt cloud changes to a slight brown color, attributed to the presence of NO₂. The NO₂ may also dimerize to form N₂O₄, which is an exothermic process, but N₂O₄ is a clear gas.

Stage IV (60 – 90 ms): In this stage, much faster reactions occur due to the increasing temperature and species concentrations. In the gas phase, a rapid expansion of gaseous species is observed; meanwhile, the white cloud disappears gradually due to the thermal decomposition of TMEDADN.

Stage V (90 – 120 ms): At t = 90 ms, ignition, which is defined as the emergence of a visible luminous kernel, is observed in the gas phase above the liquid surface. Therefore, the ignition delay of TMEDA / 90% HNO₃ pair is about 90 ms in a drop test under these conditions (droplet size, nitric acid pool size, droplet impact-speed, atmosphere temperature and pressure, etc.). The ignition delay for a hypergolic pair is defined as the time delay between the contact of the two liquids and the occurrence of luminosity. The flame then moves quickly towards other parts where gaseous pre-ignition species (i.e., dimethylnitrosamine and various aldehydes) and vapors of reactants (TMEDA and HNO₃) have accumulated. At the end of this stage, the luminous flame retreats to a position near the liquid surface, where reactions from the vaporized liquid species sustain the flame.

Stage VI (after 120 ms): In this stage, a self-sustained luminous flame is maintained above the surface of the liquid pool. Specifically, the flame stays above the
center region of the pool where the drop of TMEDA initially plunged into the pool. The unreacted TMEDA, which is mainly confined in the region where it entered the acid pool, is gasified. The vapors of TMEDA and nitric acid then sustain the flame above the liquid surface until the unreacted TMEDA is fully consumed. It is also likely that the nitrate salt dissolved in the excess nitric acid also participates in the chemical reactions to release gaseous species, which also contribute to sustain the flame.

The liquid-phase and gas-phase temperatures in the drop tests were recorded by using Al₂O₃ coated fine-wire thermocouples, as described in Sect. 3.1. Figure 5.9 shows typical transient temperature traces in the gas phase along the cuvette center. The temperatures were measured at three different positions in each test. Position 1 is ¼ inch above the bottom of the cuvette (0.15~0.2 inches above the surface of the pool). Positions 2 and 3 are ¼ and ½ inch above position 1, respectively. K-type thermocouples with a diameter of 0.002 inch were used in this test. In Fig. 5.9, time \( t = 0 \) corresponds to the instant when the drop comes in contact with the liquid HNO₃ surface in the cuvette. The transient temperature traces of a drop test show three distinct stages (A, B and C):

Stage A (0 – 63 ms): This stage coincides with stage II and III in the high-speed video analysis. In this stage, all three thermocouples do not show any appreciable increase of temperature, although the temperature in the liquid is believed to increase by heat generation from the salt formation reaction. Stage B (63 – 94 ms): This stage corresponds to stage IV in the video analysis. In this stage, the bottom and middle thermocouples show a rapid temperature rise from room temperature to around 105°C, which is slightly higher than the boiling point of 90% HNO₃. This temperature increase is mostly probably due to the rapid gasification of nitric acid or a rapid release of gaseous
species from condensed-phase reactions. The middle thermocouple senses the temperature rise about 10 ms later than the bottom thermocouple because the gases reach the bottom thermocouple first. The gas-phase temperature then slowly increases to around 130°C, which is most probably due to the exothermic reactions between the gaseous species. The top-most thermocouple did not sense the temperature increase in this stage, because it is too far from the pool’s surface. Stage C (94 ms – 125 ms): This stage includes the stage V in the video analysis. In this stage, all there thermocouples sense a rapid temperature increase due to the combustion of gaseous species in the cuvette. The maximum temperatures at position 1, 2 and 3 are 960, 650 and 260°C, respectively.

Figure 5.9: Temperature traces above the liquid pool in a drop test involving 80 µL of 90% HNO₃ and a 7 µL drop of TMEDA.
Figure 5.10 shows the transient temperature traces at three different locations within the liquid pool. Location 1 is at the center of the liquid pool. Location 1 is the center of the cuvette where the droplet plunged into the nitric acid; locations 2 and 3 are, respectively, 2 mm and 4 mm away from the center. Since both location 1 and 2 are within the impact area covered by the spherical fuel droplet, the liquid temperature increases quickly to a temperature around 100°C (the boiling points of 90% HNO₃ and TMEDA are 95 and 120°C, respectively). Location 3 is far away from the interaction zone so that it shows a much slower temperature increase. Since the thermocouples are covered by liquid nitric acid, they are insensitive to the ignition event which occurs in the gas phase.

Figure 5.10: Temperature traces of the liquid pool in a drop test involving 80 µL of 90% HNO₃ and a 7 µL drop of TMEDA.
5.5 Conclusions

The hypergolic interactions between TMEDA and 90% HNO₃ are studied by a drop test setup and a confined interaction setup. The formation and subsequent decomposition of a nitrate salt (TMEDADN) plays an important role in the pre-ignition reaction between TMEDA and nitric acid, both in the condensed phase and gas phase. In the condensed phase, the exothermic salt formation reaction is the initiation step which offers the heat needed for evaporating the reactants, decomposition of HNO₃ and further reactions between TMEDA and HNO₃ (or NO₂). In the gas phase, the vapors of TMEDA and nitric acid react immediately to form either an ion pair or a complex which condenses to a solid particulate cloud at low temperatures and start to decompose rapidly when heated to approximately 300°C. With excess nitric acid, the decomposition temperature of the salt is substantially decreased to around 150°C due to an acid-catalyzed effect. Dimethylnitrosamine, several aldehydes, various nitrogen oxides, CO₂ and H₂O were identified as the major species from the interactions between TMEDA and HNO₃ as well as the rapid thermal decomposition of TMEDADN. The ignition delay is about 90 ms in a drop test and can be roughly divided into two stages. The first 60 ms delay is mainly due to the mixing of reactants and condensed-phase reactions. The subsequent 30 ms delay is mainly due to the gas-phase reactions among the evaporated reactants and the gaseous species evolved from condensed-phase reactions.
5.6 References


Chapter 6

MMH·2HNO₃ and TMEDA·8HNO₃

6.1 Preparation of MMH·2HNO₃ and TMEDA·8HNO₃

Hypergolic fuels MMH and TMEDA will ignite spontaneously upon contact with nitric acid. The hypergolic ignition is initiated by exothermic nitrate salt formation reactions which generate enough heat to activate the secondary reactions which have been discussed in Chapters 4 and 5. If the heat from the salt formation reactions is removed quickly enough in order to prevent the secondary reactions from occurring, the reactions between the hypergolic pair will end with the nitrate salt formation.

In this work, two nitrate salts, MMH·2HNO₃ and TMEDA·2HNO₃, are synthesized by following two steps: 1) slowly mix the aqueous solutions of MMH (or TMEDA) and HNO₃ in an ice bath with a mole ratio of 1:2 to obtain an aqueous solution of MMH·2HNO₃ or TMEDA·2HNO₃; 2) remove the water by keep the solutions in a vacuum dryer (< 1 torr) for 24 hours. As shown in Fig. 6.1a and 6.1b, the collected MMH·2HNO₃ and TMEDA·2HNO₃ are white powder with a density of 1.55 and 1.67 g/cm³, respectively. MMH·2HNO₃ is slightly hygroscopic and has a melting point of 74°C. It has a stoichiometric F/O (fuel-to-oxidizer) ratio, and the overall combustion reaction can be written as follows:

\[ \text{CH}_3\text{NHNH}_2\cdot2\text{HNO}_3 \rightarrow \text{CO}_2 + 4\text{H}_2\text{O} + 2\text{N}_2 \]
However, TMEDA·2HNO₃, which can also be written as C₆H₁₈O₆N₄, is extremely oxidizer lean, and therefore this nitrate itself cannot be considered as a monopropellant. A liquid compound with a stoichiometric F/O ratio, which can be written as TMEDA·8HNO₃ or C₆H₂₄O₂₄N₁₀, was synthesized by adding 6 moles of HNO₃ to 1 mole of TMEDA·2HNO₃. As shown in Fig. 6.1c, TMEDA·8HNO₃ is a viscous yellow liquid with a density of 1.49 g/ml which is almost the same as that of WFNA. Complete combustion of TMEDA·8HNO₃ can be written as follows:

\[
\text{C}_6\text{H}_{24}\text{O}_{24}\text{N}_{10} \rightarrow 6 \text{ CO}_2 + 12 \text{ H}_2\text{O} + 5 \text{ N}_2
\]

![Figure 6.1](image)

Figure 6.1: a) MMH·2HNO₃; b) TMEDA·2HNO₃; and c) TMEDA·8HNO₃

It is important to note that TMEDA·8HNO₃ is a thermally unstable liquid and will decompose rapidly after about 6-7 hours even when it is stored at room temperature. The self-accelerating decomposition process of this liquid was recorded by a camera and selected images are shown in Fig. 6.2. During the first 5 hours, this liquid propellant was stable and no noticeable changes were observed. After about 6.5 hours, gas bubbles started to emerge from the liquid due to decomposition reactions. After about 7 hours, the
decomposition reactions became very violent and the release of gas bubbles becomes rapid. Such self-accelerating decomposition phenomena have also been reported for hydroxylammonium nitrate (HAN)/nitric acid solutions [1]. Therefore, one should not store TMEDA·8HNO₃ in capped vessels in order to avoid potential explosive hazards due to the pressure buildup.

![Figure 6.2: Self-accelerating decomposition of TMEDA·8HNO₃ at room temperature: a) 0-5 hours; b) after 6.5 hours; and c) after 7 hours.](image)

In this work, the thermal decomposition and combustion of MMH·2HNO₃ and TMEDA·8HNO₃ were studied. One objective is to understand the decomposition pathways of these ionic compounds which are important early products in the hypergolic mechanisms of MMH/HNO₃ and TMEDA/HNO₃, respectively. These decomposition reactions have not been discussed in literature and are not included in the current ARL mechanisms [2, 3]. Another objective is to provide burn rate data for future use in premixed combustion modeling of the hypergolic pair MMH/HNO₃ and TMEDA/HNO₃.
6.2 Combustion of TMEDA·8HNO₃

A detailed description of the strand burner, which is used to study the burn rate of monopropellants, is given in Sect. 3.4. Liquid strands of TMEDA·8HNO₃, with a diameter of 8 mm and a height of 1 cm, were ignited and burned in the strand burner at various pressures ranging from atmospheric pressure to 1000 psig (gauge pressure). Figure 6.3 contains images from combustion tests at several gauge pressures, showing the typical gas- and liquid-phase processes and flame structures during the combustion and regression of the liquid strands.

![Figure 6.3: Combustion of TMEDA·8HNO₃ at various gauge pressures (unit: psig)](image)

At one atmosphere (0 psig), the liquid strand begins to decompose when its surface is heated by the hot nichrome wire, but it failed ignite. A bubbling zone is formed above the liquid surface due to the release of gases. The thermal decomposition and secondary reactions of TMEDA·8HNO₃ are exothermic and a self-sustained regression of the liquid strand, with a rate of approximately 0.3 mm/s, is observed. Self-sustained
decomposition (SSD), in which a locally initiated decomposition will spread throughout the mass of material, is a well-known hazard of ammonium nitrate (AN) based fertilizers [4]. At 100 and 200 psig, a similar non-luminous self-sustained liquid strand regression was observed. At 300 psig and higher pressures, the liquid strands were ignited by the hot nichrome wire and a bright luminous flame was observed above the liquid surface. At 300 psig, the flame positions itself quite far away from the liquid surface, with a foam layer (approximately 6 mm) and a dark zone (approximately 1 mm) sitting between the flame and the liquid. The foam layer is a two-phase region that is composed of liquid and gas bubbles which are formed by decomposition and evaporation. The dark zone is a gas-phase region where relatively slow reactions occur, usually involving NO, N₂O and HCN [5, 6]. The temperature increases from the liquid’s boiling point (or decomposition temperature) to its adiabatic flame temperature in this transition zone (foam layer and dark zone). At this pressure, the flame is not quite stable. It moves up and down frequently with respect to the bubbling surface of the foam layer. When the pressure is increased to 400 psig, the foam layer and dark zone are substantially reduced. A stable flame stays close to and regresses with the liquid surface at an almost constant rate. It should be noted that the regression rate increases slightly with time because the liquid strand becomes preheated by the glass wall, which is heated by the foam layer and hot combustion gases. At higher pressures, such as 600-1,000 psig, the foam layer is further reduced in size and the flame is almost in contact with the liquid surface. At these pressures, dark zone is almost undetectable. The glass strand holder cracked after each test due to the heat transfer from the very hot combustion products.
The burn rates of TMEDA·8HNO₃ strands from 400 to 1,000 psig are plotted in Fig. 6.4. The data represent average values of three tests at each pressure and the error bars indicate that the burn-rate measurements are quite repeatable. At these pressures, the burn rate increases with pressure almost linearly. The burn rate of TMEDA·8HNO₃ is slower than that of hydroxylammonium nitrate based liquid propellants [7].

![Figure 6.4: Burn rate of TMEDA·8HNO₃](image)

6.3 Decomposition of TMEDA·8HNO₃

The decomposition of TMEDA·8HNO₃ was investigated by conducting confined rapid thermolysis experiments at various temperatures from room temperature to 120°C with a step of 10°C. A detailed introduction of the confined rapid thermolysis CRT/FTIR setup is given in Sect. 3.3. In each test, only a very small amount of TMEDA·8HNO₃ (5 µL) was used so that it can be heated to the preset temperature rapidly. Figure 6.5 shows the infrared spectra of gaseous IR-active species evolved from the decomposition of
TMEDA·8HNO₃ at three selected temperatures (40, 80 and 120°C). The spectrum in each plot is an average of 150 spectra from one test.

Figure 6.5: IR spectra of gaseous species evolved from rapid thermolysis of TMEDA·8HNO₃ at various temperatures: a) 40°C; b) 80°C; ad c) 120°C.

At 40°C and lower temperatures, the dominant species is nitric acid vapor (HNO₃) which is due to the evaporation of nitric acid, which is a major constituent of this liquid propellant. Small amounts of NO₂ and H₂O, which are typical products from the decomposition of nitric acid [8], were also detected, as shown in Fig. 6.5a. At 50-80°C, the major IR-active species evolved from the condensed-phase decomposition include
NO₂, H₂O, HNO₃, HCOOH, CO₂ and glyoxylic acid (HOCCOOH) which has infrared absorption bands at 1798 and 1748 cm⁻¹ due to the carbonyl and carboxylic groups [9], as shown in Fig. 6.5b. The formation of carbon containing species indicates that TMEDA cation, (CH₃)₂NH⁺CH₂CH₂NH⁺(CH₃)₂, is involved in the reactions and decomposes at these temperatures. At 90-120°C, additional species such as CH₂O, N₂O, NO and a small amount of dimethylnitrosamine (CH₃)₂NNO (1015, 1292 and 1488 cm⁻¹) are also detected, as shown in Fig. 6.5c. TMEDA·8HNO₃ decomposes at much lower temperatures than TMEDA dinitrate (TMEDA·2HNO₃) which requires quite high temperatures (around 290°C) to overcome the lattice energy to form TMEDA and HNO₃, TMEDA·2HNO₃ → TMEDA + 2HNO₃. Decomposition and reaction of TMEDA·8HNO₃, however, is much easier because the TMEDA cation can be directly oxidized by the existing HNO₃ in this liquid.

![Figure 6.6: Temporal evolution of species from rapid thermolysis of TMEDA8HNO₃ at 80°C and 1 atm N₂.](image-url)
The temporal evolution of IR-active gaseous species at 80°C is shown in Fig. 6.6. The species concentrations of various species, such as H₂O, HNO₃, NO₂, CO₂ and HCOOH are extracted by a non-linear, least-squares method by comparison with theoretical transmittance. The radiative properties, such as partition function, half-width of spectral lines, and its temperature exponent, are determined from HITRAN database [10]. A more detailed introduction of this data reduction technique is available in an earlier work. It should be note that glyoxylic acid (HOCCOOH) has not been quantified due to the lack of its theoretical transmittance in the HITRAN database. As indicated by the temporal species profiles in Fig. 6.6, HNO₃ and NO₂ evolve rapidly as soon as TMEDA·8HNO₃ is heated (t = 0). Meanwhile, H₂O and glyoxylic acid evolve slowly due to slow decomposition in the condensed phase. The rapid decrease of concentrations of species in this plot is caused by the purge-gas flow of N₂. At t = 1.7 s, rapid condensed-phase decomposition release large amounts of NO₂ and H₂O. Glyoxylic acid, formic acid and CO₂ also evolve rapidly. Compared to other species, HNO₃ only increases slightly at t = 1.7 s because it rapidly reacts to form other species. The evolution of large amounts of NO₂ and H₂O indicates the condensed-phase decomposition of nitric acid is of great importance in the decomposition mechanism. Nitric acid and its aqueous solutions decompose to form NO₂, O₂ and H₂O as the final products. The global reaction can be written as follows [8]:

\[ 4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \]

The formation of HCOOH and glyoxylic acid has been reported in the oxidation of many aliphatic alkylamines [11].
The oxidation paths of TMEDA cation \((\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}^+(\text{CH}_3)_2\) by nitric acid are proposed in Fig. 6.7. Oxidation of alkyl groups generally follows two steps: 1) oxidation of alkyl groups to carbonyl groups such as aldehydes \((-\text{CHO})\); and 2) further oxidation of carbonyl groups to carboxylic groups \((-\text{COOH})\). Reactions R1-R4 show the paths through which the TMEDA cation is oxidized by HNO_3 to form aldehyde intermediates such as \((\text{CH}_3)_2\text{NHCH}_2\text{CHO}\) and HOC-CHO, involving the elimination of H_2O and the formation of an unstable nitrite \((-\text{ONO})\) intermediate. The remaining part is converted to dimethylnitrosamine \((\text{CH}_3)_2\text{NNO}\) which has a relative high boiling point \((153^\circ\text{C})\) and tends to stay in the condensed phase, and therefore only a very small amount of \((\text{CH}_3)_2\text{NNO}\) was detected at these temperatures. Reactions R5 and R6 involve the further oxidation of glyoxal (HOC-CHO) to glyoxylic acid (HOC-COOH) which was observed in the experiments. Reactions R7 and R8 represent the further oxidation of glyoxylic acid (HOC-COOH) to oxalic acid (HOOC-COOH), through the same paths as R5-R6, involving the formation of a nitrite intermediate and ONONO_2 which is the isomer of dinitrogen tetroxide \((\text{N}_2\text{O}_4)\). ONONO_2 will decompose to NO_2 through the equilibrium reactions R9 and R10 \([12]\). Reaction R11 is the decomposition of oxalic acid, which was reported \([13, 14]\) to form formic acid HCOOH and CO_2 which were observed in the experiments. Reaction R12 is the decomposition of glyoxylic acid to form formaldehyde CH_2O and CO_2 \([15]\). These reactions \((\text{R1-R12})\) are exothermic from a global reaction point of view, and can cause a self-sustained regression of the liquid strand at atmosphere conditions as discussed in Figs. 6.2 and 6.3.
Figure 6.7: Oxidation of TMEDA cation by HNO₃
6.4 Combustion of MMH-2HNO₃

Strands of MMH-2HNO₃ were prepared by pressing the nitrates powder into a glass vial (Φ 8 mm) with a length of 2 cm. To be cautious, a small amount of these nitrates was initially tested (grinding and pressing) to check their sensitivity to shock and friction. No detonation or any sensible changes were observed. It was also reported in literature that MMH nitrates showed poor sensitivity to drop hammer test [16]. The average density of the strand is about 1.3 g/cm³, which is estimated by (mass of filled nitrates / volume of glass via). The density of the strand is smaller than that of the nitrate (1.55 g/cm³).

Figure 6.8: Combustion of MMH-2HNO₃ at gauge pressure 400 (a) and 1000 psig (b)

Figure 6.8a and 6.8b show selected images from typical combustion tests of MMH-2HNO₃ at a gauge pressure of 400 and 1,000 psig, respectively. In each test, an average burn rate was estimated by: height of strand (mm) / total time consumed (s). For example, at 400 psig (Fig. 6.8a), it takes about 2 s to burn a strand with a height of 12 mm. Therefore, the estimated burn rate in this test is about 6 mm/s. At 1,000 psig (Fig.
6.5 Decomposition of MMH·2HNO$_3$

The thermal decomposition of MMH·2HNO$_3$ was examined by the CRT/FTIR setup at various temperatures up to 300°C. In this rapid thermolysis setup, MMH·2HNO$_3$
starts to decompose at about 120°C, and the identified IR-active species include HNO₃, CH₃ONO₂, CH₃N₃, HN₃, H₂O, N₂O, NO, NO₂, CH₄ and CO₂. It should be noted that IR-inactive species (i.e., N₂) may also exist. Figure 6.10a shows an IR spectrum obtained by averaging a total 150 spectra obtained in a test at 160°C. Figure 6.10b is the remaining spectrum after subtracting the IR bands of H₂O and HNO₃ from Fig. 6.10a. Spectral subtraction can help to separate and identify the species whose major IR bands overlap with those of HNO₃, such as CH₃ONO₂ in this case.

A large amount of HNO₃ was released from the decomposition of MMH nitrates and only a very small amount of NO₂ is detected. This observation does not agree with the work of Breisacher et al. [17], in which NO₂ rather than HNO₃ was believed to be a
major product based on data from mass spectrometry. This observation is likely caused by their use of electron-impact ionization which will dissociate HNO₃ to produce lower molecular-weight species, such as NO₂⁺ and NO⁺ [18]. Therefore, the mass spectrometric analysis of Breisacher et al. was unable to differentiate HNO₃ from NO₂. For the same reason, they were unable to identify methyl nitrate CH₃ONO₂ which will also dissociate upon electron impact [19].

\[
\begin{align*}
[\text{CH}_3\text{NH}_2\text{NH}_3]^+ + 2\text{NO}_3^- & \rightarrow \begin{cases} 
[\text{CH}_3\text{NH}_2\text{NH}_3]^+ \text{NO}_3^- \\
[\text{CH}_3\text{NHNH}_3]^+ \text{NO}_3^- 
\end{cases} + \text{HONO}_2 \\
\text{H}_2\text{N}^-\text{NH}_2^+ + \text{HONO}_2 & \rightarrow \text{NO}_2^- + \text{H}_2\text{N}^-\text{NH}_2^+ + \text{H}_2\text{O} \\
\text{H}_2\text{N}^-\text{NH}_2^+ + \text{HONO} & \rightarrow \text{NO}_2^- + \text{H}_2\text{N}^-\text{NH}_2^+ + \text{H}_2\text{O} \\
\text{CH}_3\text{N}^-\text{NH}^+ + \text{HONO} & \rightarrow \text{NO}_2^- + \text{CH}_3\text{N}^-\text{NH}^+ + \text{H}_2\text{O} \\
\text{HN}^-\text{NH}^+ + \text{HONO}_2 & \rightarrow \text{NO}_2^- + \text{HN}^-\text{NH}^+ + \text{H}_2\text{O} \\
\text{N}^-\text{NH}_3^+ \text{NO}_3^- & \rightarrow \text{CH}_3\text{ONO}_2 + \text{N}_2 \\
\text{CH}_3\text{N}_3 + \text{HONO}_2 & \rightarrow \text{HN}_3 + \text{CH}_3\text{ONO}_2
\end{align*}
\]

Figure 6.11: Proposed MMH·2HNO₃ decomposition reactions
The suggested pathways for MMH·2HNO₃ decomposition are provided in Fig. 6.11. In reaction (1), the nitrate decomposes to release HNO₃, which is identified as a major early product in the IR spectra. In reaction (2), the monomethylhydrazinium cation reacts with nitric acid to form an unstable nitro intermediate which decomposes to methyldiazenium cation through a HONO elimination step (reaction 3). In reaction (4) and (6), monomethylhydrazinium cation reacts with HONO to form N-nitrosohydrazinium intermediates which can decompose to form methyl azide through H₂O elimination step (reaction 5) or to form methyl ammonium cation through the N₂O elimination step (reaction 7) [20]. In reaction (8), methyldiazenium cation reacts with nitric acid to form a nitro intermediate which decomposes to a methyldiazonium cation through a HONO elimination step (reaction 9). In reaction (10), the methyldiazonium nitrate decomposes to methyl nitrate through a step which is well-known as ‘replacement of nitrogen’ [21], in which the nitrogen is lost as N₂. Methyl azide may also react with nitric acid to form hydrazoic acid and methyl nitrate [22] both of which are detected in the IR spectra. The minor species, such as CH₄, NO and CO₂, can be formed by many reactions included in the MMH/RFNA mechanism by Anderson et al. [2], thus are not discussed in this study.

6.6 Conclusions

Two nitrates compounds, MMH·2HNO₃ (solid) and TMEDA·8HNO₃ (liquid) were synthesized from the hypergolic pair MMH/HNO₃ and TMEDA/HNO₃, respectively. Both nitrate compounds have a stoichiometric F/O (fuel-to-oxidizer) ratio and can burn in nitrogen purged chamber. Burn rate of MMH·2HNO₃ increases almost
linearly from 0.56 mm/s at 1 atm to 14 mm/s at a gauge pressure of 800 psig. At 1,000 psig, its burn rate is about 400 mm/s. MMH-2HNO₃ starts to decompose at about 120°C. The nitrates first decompose to form abundant HNO₃ which then reacts with the MMH cation to form several important early species such as CH₃ONO₂, CH₃N₃, HN₃, H₂O, N₂O, and small amounts of NO, NO₂, CH₄ and CO₂.

TMEDA-8HNO₃ can be ignited and burned at pressures above 300 psig, and the burn rate increases with pressure linearly from 2 mm/s at 400 psig to 4.6 mm/s at 1,000 psig. At pressures below 300 psig, the liquid strands decomposed and regressed without a luminous flame. The regression rate is about 0.3 mm/s at 0 psig (1 atm). TMEDA-8HNO₃ is thermally unstable and can only be kept for a short period of time under atmospheric conditions; if kept longer, it will decompose through a self-accelerating decomposition process. The major reaction pathways from the decomposition of TMEDA-8HNO₃ include: 1) decomposition of nitric acid to form NO₂ and H₂O; 2) the oxidation of TMEDA cation by nitric acid to form carboxylic acids HOC-COOH and HCOOH; and 3) further oxidation of these carboxylic acids to form CO₂.

The combustion studies on these two compounds provided first-hand burn rate data for future use in premixed combustion modeling of the hypergolic pair MMH/HNO₃ and TMEDA/HNO₃. The reaction mechanisms of thermal decomposition of the two nitrates can be added to the MMH-RFNA or TMEDA-RFNA mechanisms.
6.7 References


Chapter 7

Pressure Effect on Ignition Delay

The pressure effect on the ignition delay of several hypergolic pairs was studied by the drop test setup described in Fig. 3.2 in Chapter 3. White fuming nitric acid (WFNA) was used as the oxidizer and four different fuels, monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH), tetramethylethylenediamine (TMEDA) and 2-dimethylaminoethylazide (DMAZ), were tested. The two hydrazines are well-known fuels which have been deployed for decades in rocket engines and spacecraft [1]. TMEDA and DMAZ are less toxic than hydrazines and are considered as potential alternative fuels for MMH [2-4]. In addition, a mixture of DMAZ and TMEDA, with a mass ratio of 2:1, was claimed to have both a density impulse and ignition delay that are comparable to MMH [5]. Therefore, the pressure effect on the ignition delay of this mixture was also examined in this work.

7.1 MMH and UDMH with WFNA

The drop-on-pool impingement interactions and ignition delays of MMH and UDMH with WFNA were studied at various pressures from -40 kPa to 400 kPa (gauge pressure). The pressurization gas is N₂. For MMH/WFNA, two different types of drop-pool interactions were observed. At pressures below 0 kPa (gauge), the droplet stays in the nitric acid pool after the impact (type I), while at elevated pressures the droplet is
ejected from the oxidizer pool and then suspended above the pool surface (type II). Typical physical observations from the two types of interaction are illustrated in Fig. 7.1a and 7.1b, which show selected images from a test at -20 kPa (gauge) and a test at 50 kPa (gauge), respectively.

![Image of drop tests](image)

Figure 7.1: Drop tests: a) MMH/WFNA at -20 kPa; b) MMH/WFNA at 50 kPa; 3) UDMH/WFNA at 0 kPa (gauge pressure)

Type I: as shown in Fig. 7.1a, the droplet impinges on the nitric acid pool at t = 0. An aerosol cloud, which is believed to be MMH nitrates, is formed along the path of the falling droplet through the reactions between the fuel droplet and the nitric acid vapor that is confined in the glass vial. Upon impact, liquid-phase reactions will occur at the contact surface which forms nitrates, generate abundant heat, and produce plenty of
gases. It is generally believed that a gas layer (or vapor layer) will be formed between the droplet and pool surface [6]. In this case, the gas flow is not strong enough to eject the droplet from the pool. Meanwhile, the vapors of the two reactants react above the pool to form a nitrate cloud as shown at t = 80 ms. When the temperature rises to a certain level, the accumulated nitrate cloud decomposes rapidly followed by a gas-phase ignition which occurs at t = 87 ms. A stable cone-shape diffusion flame sustained for about 350 ms.

Type II: as shown in Fig. 7.1b, the reactions between the droplet and pool surface generate a gas flow that is strong enough to eject the fuel droplet from the nitric acid pool at t = 8 ms. Luminosity is observed at the moment of ejection, and a diffusion flame is formed between the droplet and the pool. With the establishment of a force balance between the droplet gravity and the repelling force from the gas flow, the MMH droplet is floating on and rolling along the WFNA pool surface smoothly for about 200 ms followed by rapid disintegration into many smaller droplets.

The relation between the gravity (G) of droplet and the repelling force (F) from the gas flow determines whether the droplet will be ejected or not. If F > G, the droplet will be ejected. Gravity (G) is a constant in all tests if one assumes that applied chamber pressure has negligible effect on size of droplet, which is reasonable because surface tension is usually not sensitive to pressure. Therefore, the gas flow, which generates the repelling force, should increase with pressure to explain the above observations. The gas flow may come from two paths: 1) the gases generated by the liquid-phase reactions, which should be independent of pressure because the density change is negligible; and 2) the gases formed by the gas-phase reactions in the vapor layer, which should increase
with pressure because the vapor concentrations should increase with pressure. The existence of a very thin vapor layer between the droplet and pool surface is claimed by Daimon et al. [6] who visualized the layer using a special technique.

Theoretically, there should be a critical pressure $P_c$, at which the repelling force ($F_c$) is equal to gravity ($G$). A small perturbation may lead to totally different drop-on-pool interactions and cause huge difference on ignition delays. It is interesting to note that this critical pressure is around 0 kPa (gauge) for both interaction types I and II, with an ignition delay of 80 and 14 ms, respectively. All tests at sub-atmospheric pressures of -20 and -40 kPa (gauge) follows type I, whereas all tests at elevated pressures of 50, 100, 200, 300 and 400 kPa (gauge) follows type II interaction. The ignition delays of MMH/WFNA at these pressures are plotted in Fig. 7.2. It should be noted the ignition delays measured in this work have a resolution of 0.2 ms since a frame rate of 5000 fps is used. The data in the dashed frame in Fig. 7.2 indicate that the ignition delay is shorter than 0.2 ms.
Figure 7.2: Ignition delay of MMH/WFNA and UDMH/WFNA

A gas-phase ignition is usually achieved through the gasification of reactants and subsequent gas-phase reactions, therefore the chamber pressure can affect ignition delay through two competing mechanisms. On one hand, gasification of reactants requires more heat at higher chamber pressures since boiling point increases with pressure. The delay in gasification with increasing pressure may thus cause a delay in ignition. On the other hand, increased pressure may have a positive effect on gas-phase reactions through increasing the concentrations of gaseous reactants. In the case of MMH/WFNA, the second mechanism controls the ignition delay, and therefore it decreases with increasing pressure.

As mentioned earlier, interaction type I has a much longer ignition delay than type II even at the same pressure; a plausible explanation is not available. The speculation is made that when the droplet stays in the pool, a layer of nitrate salts may form between the two liquid reactants, which prevents or reduces the rates of the reactions and lead to a longer ignition delay. However, small variations in the experimental conditions, such as slightly different droplet size or concentration of reactants in the vial, may affect the thickness of the nitrate layer and contribute to the uncertainty in the type of the observed interaction.

Ignition delay of UDMH/WFNA at pressures ranging from -40 kPa to 400 kPa (gauge) is also studied. Figure 7.1c shows selected images from a drop-on-pool impingement test at 1 atm. UDMH reacts with WFNA more violently and has a shorter ignition delay compared to MMH/WFNA. The droplet is ejected from the pool and breaks into many smaller droplets. The repelling force from the gas flow is larger than the
gravity of droplet (F > G) even at a reduced pressure of -40 kPa (gauge), therefore only one type of interaction (droplet ejection) was observed in all tests. It is not clear whether a critical pressure will also exist at even further reduced pressures. Similar to MMH/WFNA, the ignition delay of UDMH/WFNA decreases with increasing pressure, as shown in Fig. 7.2.

### 7.2 TMEDA, DMAZ and their mixture with WFNA

![Images of drop tests at 500 kPa (gauge): a) DMAZ/WFNA, b) TMEDA/WFNA, and c) Mixture (66.7% TMEDA + 33.3% DMAZ) /WFNA](image)

Figure 7.3: Drop tests at 500 kPa (gauge): a) DMAZ/WFNA, b) TMEDA/WFNA, and c) Mixture (66.7% TMEDA + 33.3% DMAZ) /WFNA
The drop-on-pool impingement interactions and the ignition delays of a tertiary amine TMEDA, and an azide DMAZ and a mixture of 66.7% TMEDA with 33.3% DMAZ were studied at various reduced and elevated pressures. Figures 7.3a, b and c show selected images from drop tests of DMAZ/WFNA, TMEDA/WFNA, and mixture/WFNA at 500 kPa, respectively. H-abstraction from C-H has a much higher barrier (13.4 kcal/mol) [7] than that from N-H (8.3 kcal/mol) [8], therefore a gas flow from the rapid gas-phase reactions, which is strong enough to eject the fuel droplet, was not formed. Instead, the early reactions between TMEDA (or DMAZ) vapor and nitric acid vapor form a dense nitrate cloud, as shown Fig. 7.3a and b. The accumulation of heat from nitrates formation finally leads to the decomposition of nitrates and a gas-phase ignition. The ignition delays of TMEDA, DMAZ, and their mixture at pressures from -40 to 600 kPa (g) were measured and plotted in Fig. 7.4. In general, the ignition delay increases with increasing pressure. As discussed earlier, the pressure shows an opposite effect on ignition delays of hydrazines, for which the controlling factor on ignition delays is gas-phase reactions, such as H abstraction from amino groups. However, in the case of TMEDA and DMAZ, H abstraction from methyl groups is relatively slow at pre-ignition temperatures. Instead, the controlling factor on ignition delay is the temperature rise from nitrate-salt formation reactions in the liquid phase, which takes a longer time at higher pressures due to higher boiling points. This may also explain why TMEDA has a shorter ignition delay than DMAZ. More heat is released by TMEDA nitrate formation compared to DMAZ nitrate formation, because one mole of TMEDA can react with two moles of HNO₃ to form a dinitrate. It should be noted that the evolved gas-phase reactants,
including HNO₃ and the fuels, are rapidly consumed to form a particulate cloud of ionic nitrates, and these reactions are also exothermic.

![Figure 7.4: Ignition delay of TMEDA, DMAZ and their mixture with WFNA](image)

The mixture of TMEDA and DMAZ has a shorter ignition delay than pure TMEDA and DMAZ, as shown in Fig. 7.4. Compared to pure DMAZ, the addition of TMEDA to DMAZ increases the heat release from salt formation reactions, thus reduces the ignition delay. Compared to pure TMEDA, the addition of DMAZ brings in an azide group which may react at relatively lower temperatures than the temperature required to decompose TMEDA salts or other secondary reactions such as H abstraction from a methyl group. A combination of these two factors leads to a shorter ignition delay. In addition, the ignition delay of this mixture shows little dependence on pressure. The ignition delay is around 10 ms which is close to the value (9 ms) obtained in Stevenson’s
work [5]. It is should be noted that for DMAZ/WFNA, the ignition delay of DMAZ/WFNA increases with decreasing pressure at reduced pressures, as shown in Fig. 7.4. A minimum ignition delay is observed at about 0 kPa (gauge).

7.3 Conclusions

The pressure effect on ignition delays of several fuels with nitric acid was examined. Pressure may affect the ignition delay through two different mechanisms. 1) Increasing pressure can reduce ignition delay if secondary gas-phase reactions, such as H abstraction reactions, are important and are the controlling factors of ignition delay. Typical examples are MMH and UDMH. 2) Increasing pressure can delay the gasification of reactants due to an increased boiling point, and therefore, it can cause a longer ignition delay if the ignition is mainly determined by the heat release from salt formation reactions in the liquid phase. Typical examples are TMEDA and DMAZ, since their secondary reactions (i.e., H abstraction from C-H) are very slow at pre-ignition temperatures. In addition to the pressure effect, a change of physical interaction type between droplet and pool can cause a huge difference on ignition delay. An example is MMH/WFNA at 0 kPa (gauge), which has an ignition delay of about 14 ms if the droplet is ejected and 80 ms if the droplet stays in the pool. Another interesting finding in this work is that a mixture of TMEDA and DMAZ has a shorter ignition delay than both pure TMEDA and DMAZ. The ignition delay of this mixture shows little dependence on pressure, and thus controlled by liquid-phase reactions whose rates are unaffected by the applied pressure.
7.4 References


Chapter 8

Summary of Work

The current work has developed several novel experimental techniques to study the physical and chemical processes during the condensed-phase interactions between hypergolic pairs. A drop test setup is developed to investigate the physical phenomena that occur when a drop of fuel impinges on a liquid oxidizer pool. With this novel drop test setup, the pre-ignition, ignition and post-ignition events, which usually occur on a very fast time scale, can be studied by acquiring high speed images at a high frame rate up to 5000 fps. In addition, temporal profiles of temperatures at various locations can be acquired by Al$_2$O$_3$-coated thermocouples placed in both the liquid-phase and gas-phase regions. A confined interaction setup is developed to study the early chemical reactions that occur when mixing small amounts of liquid fuels and liquid oxidizers. The chemical species are analyzed by interfacing the confined interaction setup with a Fourier transform infrared spectrometer (FTIR).

The hypergolic interaction between two target fuels, MMH and TMEDA, with several nitric acid solutions was studied by the novel experimental techniques. A three-stage hypergolic ignition process was identified for both fuels MMH and TMEDA with the oxidizer HNO$_3$. The three distinct stages can be interpreted by temperature profiles as well as chemical species and reactions.
For MMH/HNO₃, the temperature rose rapidly from ambient levels to the boiling point in the first stage, from the boiling point to 280°C relatively slowly in the second stage and from 280°C to a flame temperature very rapidly in the third stage. The first stage involved liquid-phase reactions which mainly formed the monomethylhydrazinium nitrates, as well as oxidation products methyl nitrate (CH₃ONO₂), methyl azide (CH₃N₃), N₂O, H₂O and N₂. The second stage involved vapor-vapor reactions with the formation of an aerosol cloud which was mainly composed of monomethylhydrazinium nitrate. The third stage involved secondary gas-phase reactions leading to ignition. These third-stage reactions were initiated by the thermal decomposition of nitric acid, and the identified species in this stage include H₂O, HONO, CH₃ONO₂, CH₃ONO, CH₃N₃, CH₃OH, CH₃NH₂, CH₄, N₂O, NO, and small amounts of HNCO, NH₃, HCN and CO₂.

For TMEDA/HNO₃, the temperature rose rapidly from ambient levels to the boiling point in the first stage, from the boiling point to 130°C relatively slowly in the second stage and from 130°C to a flame temperature very rapidly in the third stage. The first stage involved liquid-phase reactions which formed the salt TMEDA dinitrate (TMEDADN). The second stage involved vapor-vapor reactions with the formation of an aerosol cloud which was mainly composed of TMEDADN. The third stage involved secondary gas-phase reactions with the formation of dimethylnitrosamine (CH₃)₂NNO, dimethylformamide (CH₃)₂NCHO, CH₂O, H₂O, NO₂, HONO, NO, CO₂, N₂O and CO.

Two nitrates compounds, MMH·2HNO₃ (solid) and TMEDA·8HNO₃ (liquid) were synthesized from the hypergolic pair MMH/HNO₃ and TMEDA/HNO₃, respectively. Both nitrate compounds have a stoichiometric F/O (fuel-to-oxidizer) ratio and can be treated as pre-mixed MMH-HNO₃ system and pre-mixed TMEDA-HNO₃.
system. The burn rates of these two nitrates were measured in a strand burner. Burn rate of MMH·2HNO₃ increases almost linearly from 0.56 mm/s at 1 atm to 14 mm/s at a gauge pressure of 800 psig. At 1,000 psig, the burn rate of MMH·2HNO₃ is about 400 mm/s. TMEDA·8HNO₃ can be ignited and burned at pressures above 300 psig, and the burn rate increases with pressure linearly from 2 mm/s at 400 psig to 4.6 mm/s at 1,000 psig. At pressures below 300 psig, the liquid strands decomposed and regressed without a luminous flame. The regression rate is about 0.3 mm/s at 0 psig (1 atm).

Thermal decomposition of these two nitrates was studied by a confined rapid thermolysis (CRT) setup. MMH·2HNO₃ starts to decompose at about 120°C. The major IR active species from the decomposition of MMH·2HNO₃ include HNO₃, H₂O, CH₃ONO₂, CH₃N₃, HN₃, N₂O, and small amounts of NO, NO₂, CH₄ and CO₂. TMEDA·8HNO₃ is thermally unstable and can only be kept for a short period of time under atmospheric conditions; if kept longer, it will decompose through a self-accelerating decomposition process. In this ionic solution, the TMEDA cation can be oxidized by nitric acid to form carboxylic acids HOC-COOH and HCOOH. And these carboxylic acids can be further oxidized to form CO₂.

In addition, the pressure effect on ignition delays of several hypergolic fuels with WFNA was examined by a drop test setup. The ressure may affect the ignition delay through two different mechanisms. 1) Increasing pressure can reduce ignition delay if secondary gas-phase reactions, such as H abstraction reactions, are important and are the controlling factors of ignition delay. Typical examples are MMH and UDMH. 2) Increasing pressure can delay the gasification of reactants due to an increased boiling point, and therefore, it can cause a longer ignition delay if the ignition is mainly
determined by the heat release from salt formation reactions in the liquid phase. Typical examples are TMEDA and DMAZ, since their secondary reactions (i.e., H abstraction from C-H) are very slow at pre-ignition temperatures.
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