Tools to Fight the Terrorist Threat

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TOOLS TO FIGHT THE TERRORIST THREAT

BY

MATTHEW MICHAEL PORTER

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
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DEAN OF THE GRADUATE SCHOOL

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ABSTRACT

Chemical, biological, radiological, nuclear, and explosives (CBRNE) terrorist threats put law enforcement and soldiers at risk both at home and abroad. Law enforcement and soldiers must be provided with tools and knowledge to stay ahead of the capabilities of terrorists. Hexamethylene Triperoxide Diamine (HMTD) is a homemade explosive easily synthesized from hexamine, citric acid, and hydrogen peroxide. Although HMTD is very sensitive and prone to stability problems, it has a history of terrorists use, such as in the London bombing of 2005. Because law enforcement personnel must handle this material with no guarantee of purity nor indication of additives, for the sake of safety, knowledge of the stability and reactivity of HMTD was expanded in order to make handling safer. Differential scanning calorimetry was utilized to screen the compatibility of HMTD with various additives. It was found that water and weak acids, such as citric acid, destabilize HMTD. Gas chromatography / mass spectrometry (GC/MS) was employed to characterize both headspace gases (e.g. trimethylamine and dimethylformamide) and condensed phase decomposition products. Monitoring the decomposition of HMTD at room temperature and with gentle heating (60 °C) under various levels of humidity proved that humidity plays a major role in the kinetics of HMTD decomposition. Liquid chromatography / mass spectrometry was helpful for identification of condensed phase decomposition products and monitoring isotopic labeling studies. Through a labeling study with equimolar $^{15}$N and $^{14}$N hexamine during the synthesis of HMTD, it was found that hexamine dissociates before the formation of HMTD.
There is currently a need for specialized pyrotechnic materials to combat the threat of biological weapons. Materials have been characterized and will be chosen based on their potential to produce heat and iodine to kill spore-forming bacteria (e.g. anthrax). One formulation, already proven to kill anthrax simulants, is diiodine pentoxide with aluminum; however, it suffers from poor stability and storage problems. The heat and iodine output from this mixture and candidate replacement mixtures were measured with bomb calorimetry and extraction and analysis of iodine by UV-Vis spectroscopy. Of the mixtures analyzed, calcium iodate and aluminum was found to be the highest producer of iodine gas. The heat output of this mixture and others can be increased by adding more fuel, with the cost of some iodine produced. Products of combustion were analyzed by thermal analysis, XPS, XRD, and LC/MS. Evidence was collected supporting the formation of metal iodides and metal oxides. One key reaction explaining the loss of iodine with increase in aluminum content is the reaction between aluminum and iodine, which forms aluminum triiodide.

As seen in multiple cases, including the Boston Marathon bombing, improvised explosives may be as simple as a fuel/oxidizer (FOX) mixture initiated by a hot wire. The knowledge of which materials or compositions are explosive is incomplete, and tests for explosivity are currently conducted at specific scales. For example, ammonium nitrate is classified as an oxidizer because it does not explode at the pound scale, but can become explosive at a larger scale or with a fuel added. Herein, a bomb calorimeter with a pressure transducer has been studied for its use as a small scale metric (2 g) for predicting whether fuel/oxidizer mixtures will be explosive at larger scales. These results have been compared with calculated and measured detonation velocities, and
measured air blast pressures. A positive correlation was observed between heat of burning and detonation velocity, and between heat of burning and air blast TNT equivalence.
ACKNOWLEDGMENTS

Thank you Dr. Jimmie Oxley and Dr. Jim Smith for all of the incredible opportunities you have provided which have furthered my education and experience as a scientist. Thank you for welcoming me into such a unique research group, and helping me on path in pursuing my passion for pyrotechnics and explosives. Thank you to my high school and college chemistry teachers David See and Jack Hayes for seeing my potential and encouraging me to be a scientist, when I had no idea what that meant. A big thank you to all of my lab mates. I accredit much of my success to having good help. I’ve learned that being a successful scientist means surrounding yourself with those you trust to help you reach your goals, while at the same time trying to help those around you reach their goals. Thank you to my wife, Ashley, son, Ethan, and daughter, Josephine. I love all of you so much. You give me the greatest motivation to work and provide as a husband and father. Thank you Mom and Dad for encouraging me to pursue a career that brings me joy. Most importantly, I would not be who I am without God, and His help. For man is born for trouble, as sparks fly upward. But as for me, I would seek God, and I would place my cause before God; Who does great and unsearchable things, wonders without number (Job 5:7-9). The fear of the Lord leads to life so that one may sleep satisfied, untouched by evil (Proverbs 19:23). In this you greatly rejoice, even though now for a little while, if necessary, you have been distressed by various trials so that the proof of your faith, being more precious than gold which is perishable, even though tested by fire, may be found to result in praise and glory and honor at the revelation of Jesus Christ (1 Peter 1:6-7).
PREFACE

This dissertation has been prepared in manuscript format in accordance with the guidelines of the Graduate School of the University of Rhode Island. The research contained herein is separated into three manuscripts. The first manuscript, “Synthesis and Degradation of Hexamethylene Triperoxide Diamine (HMTD),” has been published in the journal *Propellants, Explosives, Pyrotechnics*. The second manuscript, “Potential Biocides: Iodine-Producing Pyrotechnics,” has been submitted for publication in the journal *Propellants, Explosives, Pyrotechnics*. The third manuscript, “Correlation of Explosive Properties of Fuel/Oxidizer Mixtures,” is being prepared for submission to the journal *Propellants, Explosives, Pyrotechnics*. 
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LIST OF ABBREVIATIONS

ACN - Acetonitrile
BHMP - bis(hydroxymethyl) peroxide
BMAP - bis(methylamine) peroxide
C4 – Military Explosive Composition 4
ESD – Electrostatic Discharge
EN - Ethylenimine
DFT - Density Functional Theory
DMF - Dimethylformamide
DSC - Differential Scanning Calorimetry
EA - Ethyl Acetate
FOX – Fuel/Oxidizer Mixture
FM - Formamide
GC/MS - Gas Chromatography / Mass Spectrometry
HMTD - Hexamethylene Triperoxide Diamine
IR – Infrared Spectroscopy
LC/MS - Liquid Chromatography / Mass Spectrometry
MFM - Methyl formamide
NMR - Nuclear Magnetic Resonance Spectroscopy
PETN – Pentaerythritol Tetranitrate
PVC – Polyvinyl Chloride
RDX - 2,4,6-cyclotrimethylene-1,3,5-trinitramine
RH - Relative Humidity
SDT - Simultaneous Differential Scanning Calorimetry Thermogravimetric Analysis

SPME - Solid Phase Microextraction

TIL – Threshold Initiation Level

TMA - Trimethylamine

TMDD - Tetramethylene Dioxide Diamine

TMDDD - Tetramethylene Dioxide Diamine Dialdehyde

UV-Vis – Ultraviolet-Visible Spectroscopy

XPS – X-Ray Photoelectron Spectroscopy

XRD - Powder X-Ray Diffraction
MANUSCRIPT 1

SYNTHESIS AND DEGRADATION OF HEXAMETHYLENE TRIPEROXIDE DIAMINE (HMTD)

by

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Abstract

The synthesis and decomposition of hexamethylene triperoxide diamine (HMTD) were studied. Mechanisms were proposed based on isotopic labeling and mass spectral interpretation of both condensed phase products and head-space products. Formation of HMTD from hexamine appeared to proceed from dissociated hexamine as evident from scrambling of the $^{15}$N label when synthesis was carried out with equal molar labeled/unlabeled hexamine. Decomposition of HMTD was considered with additives and in the presence and absence of moisture. In addition to mass spectral interpretation, density functional theory (DFT) was used to calculate energy differences of transition states and the entropies of intermediates along different possible decomposition pathways. HMTD is destabilized by water and citric acid making purification following initial synthesis essential in order to avoid unanticipated violent reaction.

1 Introduction

HMTD is synthesized from the reaction of hexamine with hydrogen peroxide. The oxidation is catalyzed by acid, usually citric acid. It was discovered in 1885 by Legler using formaldehyde, ammonium sulfate, and hydrogen peroxide [1]. The structure was proposed in 1900 by Baeyer and Villiger [2]. Von Girsewald was the first to use hexamine, citric acid, and hydrogen peroxide [3]. X-ray diffraction showed exactly planar 3-fold coordination about the two bridgehead nitrogen atoms rather than pyramidal structure [4,5]. This ring strain in HMTD may account for its low thermal stability and high sensitivity to friction [6,7]. Because there have been several unexpected violent reactions involving HMTD where counterterrorism personnel have
been injured, we launched a study to better understand its chemistry and, for the purposes of detection, to identify its signature under a variety of conditions.

2 Experimental Section

2.1. Synthesis of HMTD with citric acid

When HMTD was synthesized simply from ice-cooled hydrogen peroxide (9.60 g, 50 wt%, 141.18 mmol) with the slow addition of hexamine (2.43 g, 17.37 mmol) and later addition of anhydrous citric acid (3.66g, 19.03mmol), the reaction was warmed to room temperature, by allowing the ice bath to melt. Under these conditions the reaction mixture stirred 5 to 6 hours before HMTD precipitation was observed [5]. Crude HMTD, vacuum filtered, washed with excess distilled water (~200 mL) to remove acid and HPLC grade methanol (~200 mL) to aid drying was gently stirred and left to dry several hours on the vacuum filter. The yield of crude HMTD was ~50 %, assuming 1:1 molar ratio hexamine:HMTD. Recrystallization was conducted with 70/30 v/v mix of ethyl acetate (EA) /acetonitrile (ACN). Solvent was difficult to remove even after drying under high vacuum for 24 hours. The evidence collected to support that HMTD was synthesized with these conditions included GC/MS (see section 2.12), DSC (see section 2.10), melting point (by Mel-Temp apparatus), LC/MS (see section 2.14), NMR (Bruker 300 MHz, \(^1\)H NMR [CDCl\(_3\)]: δ4.80), and IR (Thermo Nicolet 6700 FTIR). The evidence gathered to support that HMTD was synthesized under any of the alternate conditions listed below (including labeling studies) included GC/MS, melting point, and LC/MS. **Note:** HMTD is an extremely sensitive primary explosive; no fritted glass, metal spatulas nor excess force or friction should be applied.
2.2. Synthesis of HMTD with other acids or no acid

Using same amounts of hexamine and hydrogen peroxide as above, but no acid added, precipitation of HMTD was not observed for 7 days at room temperature. After 9 days of stirring, 261 mg HMTD was recovered, ~7% yield assuming 1:1 molar ratio hexamine:HMTD. Other diprotic and triprotic acids used, in place of citric acid, included sulfuric acid, phosphoric acid, and oxalic acid; like citric acid, they were added in 1.1 to 1 molar ratios hexamine:acid. Monoprotic acids gave poor yields (Table 5) if added in 1.1 to 1 molar ratios. If these (acetic acid, trifluoroacetic acid, formic acid, and nitric acid) were added in a 2.2 to 1 molar ratio hexamine:acid, yields were comparable to those achieved with citric acid.

2.3. Synthesis of HMTD with formaldehyde (\(^{13}\text{C} \text{ or }^{12}\text{C}\))

Formaldehyde, up to 6 moles per mole hexamine, appeared to accelerate the reaction and increased the yield to over 100% based 1 to 1 hexamine:HMTD. For example, HMTD was synthesized by adding hexamine (0.4499 g, 3.22 mmol) to a solution of \(^{13}\text{C} \text{ formaldehyde in water (2.0153 g of solution, 20 wt\%, 13.43mmol) in an ice bath. Hydrogen peroxide was then slowly added (1.7871 g of solution, 50 wt\%, 26.28 mmol) and later, anhydrous citric acid (0.6817 g, 3.55 mmol). HMTD started to precipitate within 2 hours, in contrast to the 5 to 6 hours required without formaldehyde. The reaction was allowed to continue overnight as the ice bath warmed up. Aliquots of the reaction mix were taken every 0.5 hour for 4 hours after the addition of the acid, and the final aliquot was taken 27 hours later. The crude HMTD was vacuum-filtered, washed with distilled water (~200 mL) to remove acid and then HPLC grade methanol (~200 mL) to aid drying (dried several hours by vacuum filtration).
2.4. Synthesis of HMTD with $^{15}$N Ammonium Sulfate

HMTD was synthesized from ice-cooled hydrogen peroxide (2.4082 g, 50 wt%, 35.42 mmol) with the slow addition of hexamine (0.6061 g, 4.33 mmol) and later addition of anhydrous citric acid (0.9146 g, 4.76 mmol). After the citric acid dissolved, $^{15}$N ammonium sulfate was added (0.2874 g, 2.17 mmol). After 4 to 5 hours, HMTD began to precipitate from the cold solution. The reaction warmed to room temperature overnight, and crude HMTD was vacuum filtered, washed by gentle agitation with distilled water (~200 mL) to remove acid then HPLC grade methanol (~200 mL) to aid drying. It was then left to dry several hours on the vacuum filter. The crude HMTD yield was about 60 % (assuming 1:1 molar ratio hexamine:HMTD).

2.5. Synthesis of $^{15}$N Hexamine and HMTD Decomposition Products

Pure $^{15}$N hexamine was synthesized by adding formaldehyde (1.7463 g solution, 37 wt%, 21.54 mmol) to $^{15}$N ammonium hydroxide (2.3117 g solution, 10.4 wt%, 13.36 mmol) at 40 °C, using a procedure from Nielsen [8]. The reaction mixture was stirred for 2 hours, 2 mL of methanol was added, and the water/methanol solution was removed by evaporation at 40 °C. The crude hexamine was purified by sublimation at 185-200 °C; a water aspirator was used to maintain the vacuum. The purified hexamine (397.6 mg, 2.76 mmol) had a melting /sublimation point at 265-275 °C (by Mel-Temp apparatus). GC/MS (gas chromatography with mass spectrometric detection) (144 m/z), infrared spectroscopy (IR), and $^1$H NMR (CDCl$_3$): δ4.73, showed good purity. Stirring formaldehyde and formamide at ambient conditions for a day yielded N-(hydroxymethyl)formamide (m/z 75, table 3.2) along with hexamine [9]. The synthesis of 1,3,5-triformylhexahydro-s-triazine (m/z 171, table 3.11) was accomplished by
adding acetic-formic anhydride to hexamethylenetetramine at room temperature, using the method of Gilbert [10]. Tetramethylene diperoxide diamine dialdehyde (TMDDDD) was synthesized by the route of Wierzbicki [5]. N,N'-methylenebisformamide (m/z 102, table 3.5) was purchased from Aldrich.

2.6. Synthesis Conditions of HMTD with a 1-to-1 mix of $^{14}$N and $^{15}$N hexamine

HMTD was synthesized by adding $^{14}$N hexamine (304.0 mg, 2.17 mmol) and $^{15}$N hexamine (304.0 mg, 2.11 mmol) to hydrogen peroxide (2.4077 g of solution, 50 wt%, 35.41 mmol). Anhydrous citric acid was added (0.9154 g, 4.76 mmol), and the reaction mixture was allowed to stir overnight as the ice bath warmed up. Aliquots were taken every hour until the HMTD precipitated after 6 hrs. The final aliquot of the reaction mix was taken after 19hrs. The crude HMTD was vacuum-filtered, washed with excess distilled water (~200 mL) to remove acid then HPLC grade methanol (~200 mL) to aid drying and left to dry several hours on the vacuum filter.

2.7. Isothermal Decomposition

HMTD was aged neat and with additives of interest. Typically samples, about 20 mg total, were heated at 60 °C or 80 °C in an oven for varying lengths of time. For testing the compatibility of HMTD with common reagents, liquids (200 μL) were added to some samples and solids (~3.5 mg, i.e. 15 wt%) were added to other samples. Most samples were stored in open vials which were sealed inside larger (10 mL) headspace vials (with humidity controlling solution between inner and outer vial) or held in humidity-controlled desiccators. Other samples were sealed directly in 10 mL headspace vials with no attempt to control humidity. Humidity was controlled with Drierite [considered 0 % relative humidity (RH)], saturated MgCl$_2$ (considered 30
%RH), saturated NaCl (considered 75 %RH), and distilled water (considered 100 %RH) [11]. At the completion of the aging cycle, vials were opened under 20-40 mL of acetonitrile. If the HMTD additive was an aqueous solution, magnesium sulfate was added to the sample as a drying agent; if the additive was acidic or basic, sodium bicarbonate was added to neutralize. The acetonitrile solution was sonicated for at least 30 minutes; vortex mixed for 1 minute; and if the solutions were cloudy, syringe filtered into vials for analysis.

2.8. Decomposition of HMTD with $^{15}$N Ammonium Sulfate

$^{15}$N ammonium sulfate at 15 wt% was added to HMTD (20 mg), and the mixture was heated at 80 °C under dry conditions or at 60 °C under 75 %RH. After thermolysis, samples were extracted with 30 mL of acetonitrile and analyzed by GC/MS and on LC/MS (liquid chromatography with mass spectrometric detection) in order to monitor incorporation of $^{15}$N into the condensed-phase decomposition products.

2.9. Decomposition of HMTD with deuterium oxide high humidity

HMTD (20 mg) was heated at 60°C in a small vial which was sealed in a 10mL headspace vial with 1mL of deuterium oxide (D$_2$O) between the inner and outer vials so that HMTD did not directly make contact. HMTD was decomposed in a similar configuration with a saturated NaCl/D$_2$O solution (analogous to 75 %RH conditions) between outer and inner vials for 5 days. The pH of the D$_2$O and analogous experiments with water was found to be highly acidic (pH of 1). These samples were extracted with 30mL of acetonitrile, and run on GC/MS and on LC/MS to track the exchange of deuterium into the condensed phase decomposition products. Headspace analysis was also conducted according to the method described in section 2.13 using SPME. NMR
(1H and 13C) of the D2O in the vial was used to identify formic acid (HCOOH); 1H NMR (D2O) δ 8.13 (s, 1H); 13C NMR δ 167.25.

2.10. Differential Scanning Calorimeter (DSC)

DSC samples were prepared by measuring 150 to 200 mg of sample into a glass capillary tube, which was then flame sealed. For samples with an additive, 5 to 30 wt% additive was gently stirred into a 20 mg HMTD sample, and this mixture was placed in the capillary tube. If additives were liquid, 2 mL of the liquid was added to 150-200 mg of HMTD, and then sealed in capillary tubes. The sealed micro-ampules were weighed before and after DSC analysis to verify no leakage during testing. Samples were run on a TA Instruments Q100 DSC from 25 to 300°C with a ramp rate of 20 °C/min under nitrogen flow. Results were processed via TA’s Universal Analysis software.

2.11. Monitoring Rate of HMTD Formation

Aliquots (100 μL) were removed and diluted with 5 mL of HPLC grade acetonitrile with sodium bicarbonate and magnesium sulfate added to neutralize acid and dry the solvent, respectively. This mixture was then diluted 1/10 v/v and analyzed by GC/MS.

2.12. Condensed Phase Analysis – GC/MS

Analysis of the acetonitrile samples, generated as described above, was accomplished using an Agilent 6890 gas chromatograph with a 5973 Mass Selective Detector (GC/MS) equipped with a Varian VF-200ms column (15m x 0.25mm). Two different GC/MS methods were used, one for quantification of HMTD and one for qualitative analysis of more volatile compounds. Common to both methods were the following: inlet and transfer line temperatures were maintained at 150 °C, the inlet was
kept in splitless mode; flow rate, constant at 2.5 ml/min, and the post-run oven temperature was always 310 °C for 3 min. The oven temperature program for the quantification method of HMTD started at 120 °C, and was held for 1 min, ramped 20 °C/min to 140 °C and was held for 2 min, and then ramped 10 °C/min to 250 °C. The mass spectrometer scan parameters for the quantification of HMTD were from 50-350 m/z at a rate of 4.72 scans/sec. The oven temperature program used for qualitative analysis (i.e. product identification) started at 50 °C and was held for 1 min, ramped 20 °C/min to 140 °C and was held for 2 min, then ramped 10 °C/min to 250 °C. The mass scan parameters were from 15-450 m/z at a rate of 3.35 scans/sec.

2.13. Headspace Analysis – GC/MS

Headspace of the HMTD was sampled via gas-tight syringe (5 mL or 1 mL) or Solid Phase Microextraction (SPME) fiber (SUPELCO fused silica coated with 65 μm of PDMS/DVB). The former was used for permanent gases; the latter for volatile amines. SPME fibers were flushed under helium 45 min at 250 °C prior to use. They were exposed to the samples for at least 3 hrs at room temperature and analyzed using a Thermo GC Ultra-ISQ GC/MS equipped with a PoraPlot Amines column (25 m X 0.32 mm) and a 2 m particle trap. Initial oven temperature was 100 °C, with a 20 °C/min heating ramp to 220 °C where it was held 20 minutes. Inlet temperature was 220 °C; and column was used in constant pressure mode (10 psi). MS scans were from 35-200 m/z at 5 scans/sec; transfer line and source were at 220 °C. Permanent gases were analyzed with an Agilent 6890 GC with 5973 MS detector with Molsieve 5A Plot column (10 m X 0.32 mm); initial oven temperature was 70 °C for 1 min, followed by a 50 °C/min ramp to 300 °C and held there for 15 min. Transfer line was set at 300 °C;
the flow rate, at 2.5 mL/min. Two injection methods were used. A 5 μL injection with
5:1 split ratio was used to detect O₂ and N₂ signals; a 1 mL injection with a 1:1 split
ratio was used for traces of other small molecules. The mass spectrometer scan
parameters were from 10 to 100 m/z at 12.89 scans/sec.

2.14. Condensed Phase Analysis - LC/MS

Liquid chromatography / mass spectrometry (LC/MS) analysis was conducted
using modified procedures recently published [12]. HMTD samples were typically
provided as approximately 1 mg/mL solutions in acetonitrile. Samples were diluted by
placing 10 μL of this solution into 1 mL of 50/50 (v/v) acetonitrile/water. Injections of
20 μL (~200 ng) were made onto the HPLC/MS system. Data collection and analysis
was performed with Thermo Xcalibur software version 2.2, SP 1.48. Using a Thermo
Electron (Franklin, MA, USA) Exactive Orbitrap mass spectrometer affixed with an
atmospheric pressure chemical ionization (APCI) interface, positive ions were produced
and introduced into the instrument. Tune conditions were as follows: spray voltage,
5000 V; capillary temperature, 140 °C; sheath gas (N₂), 30; auxiliary gas (N₂), 15; heater
temperature 160 °C; capillary voltage, 40 V; tube lens, 160 V; and skimmer, 15 V. Units
for sheath and auxiliary gas flow are arbitrary. Liquid chromatography was performed
using a Thermo Electron Accela quaternary pump. Sample injections were performed
by a CTC Analytics (Zwingen, Switzerland) HTS PAL autosampler.

Due to the highly polar nature of the decomposition products, three methods
were employed to identify these compounds. Initial reverse phase chromatography used
a Thermo Scientific (Franklin, MA, USA) Hypersil C-18 (2.1 x 100 mm, 5 μm) column.
This method consisted of an initial mobile phase of 95 % solvent B (0.1 % acetic acid)
and 5 % solvent C (acetonitrile). It was held for 2 minutes and then linearly ramped to 5 % B and 95 % C over 18 minutes. This was held for 2 minutes, returned to initial conditions over 1 minute and the re-equilibrated for 5 minutes. A second HPLC system was developed for optimum analysis of HMTD and hexamine; it employed an Advantage PFP column (100 x 2.1 mm, 5 μm) (Analytical Sales & Service, Pompton Plains). In order to gain some retention of hexamine, neutral pH conditions were preferable, but this caused broadening of the HMTD peak shape. To remedy this problem, three different mobile phase solvents were used to provide both pH and solvent strength gradients. Initially, 95 % solvent A (10 mM ammonium acetate, pH 6.8) and 5 % solvent C (acetonitrile) were held for 3 minutes following injection to retain hexamine. The system was then rapidly ramped to 85% solvent B (0.1 % acetic acid), 5 % solvent A and 10 % solvent C over the next 3 minutes. Organic levels increased slowly for 9 minutes to 35% C, 60% B and 5 % A, then rapidly for 3 minutes to 90 % C and 5 % of both A and B. This was held for 2 minutes before returning to initial conditions and re-equilibrated for 5 minutes prior to the next injection. Although this method revealed HMTD and most of the decomposition products, e.g. hexamine, a substantial number of species were still so polar that they were negligibly retained by this method. A third system employed an aqueous normal phase method using an Analytical Sales and Service Advantage 100 Silica column (150 mm x 2.1 mm, 5 μm). Initial conditions of 95 % solvent C and 5 % solvent D (methanol) were held for 2 minutes before ramping to 5 % C and 95 % D over 6 minutes. Solvent C was then replaced with solvent B over 1 minute and then ramped to 60 % B to 40 % D over 10 minutes. After holding this for 2 minutes, it was ramped back to 95 % D and 5 % B
over 2 minutes then 95 % D and 5 % C over 1 minute. Initial conditions were returned over 2 minutes and held for 5 minutes before the next injection. This method required the use of electrospray ionization (ESI); however, this ionization mechanism is not optimal for HMTD detection.

3. Results and Discussion

Previously reported were thermal decomposition kinetics of HMTD determined by manometry [Ea 107 kJ/mol and A =4.21 x 10^{10} s^{-1}] and HMTD fragmentation by electron impact mass spectrometry [13-15]. Here, we examine factors which influence the stability of HMTD. It is the standard protocol of this lab that following synthesis a purification step is performed to promote stability. Unfortunately, HMTD had only limited solubility even in the most polar solvent requiring large volumes of ethyl acetate and acetonitrile for recrystallization which were almost impossible to remove completely from HMTD. For that reason, many of the studies were conducted with both crude and recrystallized HMTD to ensure the presence of trace solvent had not biased results.
3.1. HMTD Headspace

Since HMTD decomposition was readily observed at 60 °C, significant decomposition at ambient temperature was probable. In fact, when HMTD was removed from storage at -15 °C (freezer temperature), it developed a noticeable odor after a couple of hours. Headspace samples of both crude and recrystallized HMTD, fresh and aged, were analyzed by GC/MS. When HMTD was heated for a week at 60 °C in 30 % relative humidity, or under a variety of conditions, the predominant decomposition products observed in the headspace were trimethylamine (TMA) and dimethylformamide (DMF) with trace quantities of ethylenimine (EN), methyl formamide (MFM), formamide (FM) and hexamine. When moisture was present 1-methyl-1H-1,2,4-triazole and pyrazine were observed. Figure 1 shows that these compounds were found in headspace of HMTD sample stored at room temperature for one year. In addition, while permanent gases, oxygen and nitrogen, were not found, carbon monoxide and carbon dioxide occurred in significant amounts. HMTD was not observed in the headspace by GC/MS under dry, moist, acidic, or basic conditions. Since HMTD could be identified in ACN solutions, either HMTD content in headspace was below the detection limits of our GC/MS system or due to its reactivity, occurrence was not sustainable in the headspace.
Figure 1.1. HMTD headspace chromatography [trimethylamine (TMA), dimethylformamide (DMF), ethylenimine (EN), methyl formamide (MFM), formamide (FM)].

3.2. Effect of Additives on HMTD Decomposition

The effect of additives on HMTD stability was screened by DSC. A general trend was readily observed: acids lower the temperature at which the exothermic maximum appeared (Table 1). We had previously demonstrated that concentrated mineral acid could be used to destroy HMTD [16]. We and others also observed that aqueous basic solutions rapidly decompose HMTD [17]. To determine the effect of select additives without water, HMTD was held at 60 °C for a week at 30 %RH, and of these additives, only citric acid markedly accelerated HMTD decomposition (Tables 2). The fact that water and citric acid, both used in the synthesis of HMTD, lowered its
thermal stability markedly emphasizes the need to thoroughly rinse and dry HMTD. Headspace monitoring revealed that water, citric acid or any acidity sped up the production of TMA and DMF in the gas phase.

Table 1.1. Effect of Solid Additives on HMTD Stability.

| HMTD Solid Additive (15%) | Average % Remaining |
|---------------------------|---------------------|
| None                      | 87                  |
| NaHCO₃                    | 87                  |
| KH₂PO₄                    | 96                  |
| NaOH                      | 75                  |
| KTButoxide                | 80                  |
| Citric Acid               | 13                  |
Table 1.2. DSC of HMTD with Additives (20°C/min).

| Material                                      | pKa of Additive | pKb of Additive | Onset Temp. of Exotherm (°C) | Exotherm Temp. Maximum (°C) | Heat Released (J/g) |
|-----------------------------------------------|-----------------|-----------------|-----------------------------|-----------------------------|-------------------|
| 18.2MΩ H2O                                   | 14.00           | 0.00            |                             |                             |                   |
| HMTD Crude                                    | N/A             | N/A             | 159                         | 161                         | 2100              |
| HMTD Rec 70/30 EA/CAN                        | N/A             | N/A             | 168                         | 171                         | 3200              |
| HMTD Crude + 2ul H2O                         | N/A             | N/A             | 136                         | 140                         | 3100              |
| HMTD Crude + 2ul pH4 Buffer                  | N/A             | N/A             | 126                         | 129                         | 3700              |
| HMTD Crude + 2ul pH7 Buffer                  | N/A             | N/A             | 134                         | 137                         | 3300              |
| HMTD Crude + 2ul pH10 Buffer                 | N/A             | N/A             | 137                         | 139                         | 3100              |
| HMTD Crude + 2ul ACN                         | N/A             | N/A             | 152                         | 178                         | 3000              |
| HMTD Crude + 2ul Benzene                     | N/A             | N/A             | 166                         | 172                         | 3200              |
| HMTD Crude + 2ul EtOH                        | N/A             | N/A             | 153                         | 164                         | 2800              |
| HMTD Crude + 2ul EtAc                        | N/A             | N/A             | 156                         | 169                         | 2800              |
| HMTD Crude + KH2PO4 15%                      | 7.21            | 6.79            | 163                         | 165                         | 2100              |
| HMTD Crude + KH Phthalate 15%                | 5.43            | 8.57            | 156                         | 157                         | 1900              |
| HMTD Crude + Benzoic Acid 15%                | 4.20            | 9.80            | 155                         | 160                         | 2600              |
| HMTD Crude + Ascorbic Acid 15%               | 4.04            | 9.96            | 146                         | 148                         | 2000              |
| HMTD Crude + Citric Acid 15%                 | 3.13            | 10.87           | 134                         | 137                         | 2800              |
| HMTD Crude + Sulfanilic Acid 15%             | 3.01            | 10.99           | 122                         | 125                         | 2400              |
| HMTD Crude + O Phthalic Acid 15%             | 2.94            | 11.06           | 143                         | 145                         | 2000              |
| HMTD Crude + Melamine 15%                    | 5.00            | 9.00            | 158                         | 159                         | 2000              |
| HMTD Crude + NaHCO3 15% *                    | 6.35            | 7.65            | 163                         | 164                         | 1300              |
| HMTD Crude + KH2PO4 15%                      | 7.21            | 6.79            | 163                         | 165                         | 2100              |
| HMTD Crude + NaOH 15%                        | 14.00           | 0.00            | 160                         | 161                         | 2300              |
| HMTD Crude + NaOH 30%                        | 14.00           | 0.00            | 162                         | 164                         | 2100              |
| HMTD Crude + K Tertbutoxide 15%              | 17.00           | -3.00           | 159                         | 160                         | 2200              |

*NaHCO3 has an endotherm which lowers the total heat released
3.3. Effect of Humidity on HMTD Decomposition

In 1924, it was reported: “That H.M.T.D. is stable at temperatures up to at least 60 °C; it is not affected by storage under water; but it is slowly affected when subjected to high humidity at maximum summer temperature...It is practically non-hygrosopic”[17]. Since DSC results did not support this statement, samples of crude HMTD were held at 60 °C with fixed humidity values of 0, 30, 75, or 100 %RH and monitored each week for four weeks (Figure 2). After 2 weeks, the samples of HMTD at high relative humidity (i.e. 75 %RH and 100 %RH) were completely degraded; HMTD was not observed by GC/MS.

![HMTD Remaining at 60°C](image)

**Figure 1.2.** Effect of humidity on HMTD.

In Figure 3 the effects of humidity on crude and recrystallized HMTD are particularly informative. Crude and recrystallized HMTD stored dry at 60 °C undergo only slight decomposition while samples stored at high humidity (i.e. 75 %RH) experience significant decomposition.
3.4. Mass Spectral Analysis of Condensed-Phase Synthesis and Decomposition Products

HMTD was heated at 60 °C under various conditions. Products were examined by GC/MS and LC/MS; and assignments are shown in Table 3 and Table 4, respectively. Assignments are based on comparison with the authentic samples [3.2, 3.5, 3.8, 3.11, 4.2, 4.8, 4.15, 4.22, and HMTD] and on the high resolution mass spectrometric results where compositions could be assigned to within 5 ppm of their calculated mass (Table 4). Examining the HMTD decomposition products, it is tempting to suggest HMTD thermolysis produces a number of small molecular fragments, e.g. CH₂O, NH₃, CH₂NH or CH(O)NH₂ which undergo further reaction, such as an aldehyde-amine condensation. The observed substituted triazine species (3.10, 3.11, 3.12) and those containing four nitrogens have been reported to be products of hexamethylenetetramine (hexamine) reactions [8,10,18]. Indeed, hexamine was found when HMTD was decomposed at 60°C with 75% or 100% RH or with added water or acidic buffer. Only tetramethylene
diperoxide diamine dialdehyde (TMDD) (4.22), matched to an authentic sample and the mono-aldehyde (3.7) suggested the original HMTD structure; and that HMTD was degraded stepwise.

In examining HMTD decomposition, we speculated the degradation products formed hexamine. Hexamine is made from ammonia and formaldehyde, and the route is via hexahydro-1,3,5-triazine[8,19]. The conversion of hexamine to 2,4,6-cyclotrimethylene-1,3,5-trinitramine (RDX) has been the subject of several studies. Thermal degradation of hexamine forms hexahydro-1,3,5-triazine, octahydro-1,3,5,7-tetrazocine, and 1,3,5,7-tetrazabicyclo-[3.3.1]-nonane [20]. Bachman found that performing the nitration of hexamine in acetic anhydride with ammonium nitrate allowed two moles of RDX to be produced rather than one via direct nitration [21]. The question was whether the extra RDX came from fragments of hexamine or nitramines CH₂NNO₂ or directly from hexamine. On the basis of the observed by-products, Aristoff et al concluded that degradation of hexamine, itself, and not combination of smaller fragments, was the route by which RDX is formed [22]. Gilbert also confirmed this later by showing that RDX can be obtained by the direct nitrolysis of substituted triazine rings [10].

In the synthesis of HMTD from hexamine the question of stoichiometry arises. Under the normal synthetic route as it is describe in equation 1; our yield, based on hexamine, was not more than 60%. However, if excess formaldehyde was added to the reaction mixture, yields of greater than 100% (based on 1 HMTD to 1 hexamine) were observed, and the reaction rate increases (precipitation of HMTD started to occur in 2 hrs compared to 5-6 hrs without formaldehyde). Equation 2 describes that reaction and
may also describe what occurs when no extra formaldehyde is added and the reaction must wait for the degradation of part of the hexamine to form formaldehyde (Figure 4). Indeed, hexamine is frequently used as a source of formaldehyde [18,23].
Table 1.3. Decomposition products GC/MS.

| #  | m/z | Identity | amount | conditions                          |
|----|-----|----------|--------|-------------------------------------|
| 3.1| 73  | ![Image](image1.png) | L      | DRY (0 %RH) & HUMID (≥75 %RH)       |
| 3.2| 75  | ![Image](image2.png) | L      | MATCHED TO AUTHENTIC SAMPLE; MAINLY SEEN IN HUMID CONDITIONS |
| 3.3| 103 | ![Image](image3.png) | M      | MAINLY SEEN IN HUMID CONDITIONS     |
| 3.4| 88  | ![Image](image4.png) | S      |                                     |
| 3.5| 84, 102 | ![Image](image5.png) | L      | MATCHED TO AUTHENTIC SAMPLE; DRY CONDITIONS |
| 3.6| 116 | ![Image](image6.png) | L      | DRY CONDITIONS                      |
| 3.8| 178 | ![Image](image7.png) | S      | BOTH IN DRY & HUMID CONDITIONS      |
| 3.9| 140 | ![Image](image8.png) | M      | MATCHED TO AUTHENTIC SAMPLE; MAINLY SEEN IN HUMID OR ACIDIC CONDITIONS |
| 3.10| 208 | ![Image](image9.png) | L      |                                     |
| 3.11| 143 | ![Image](image10.png) | S      | MATCHED TO AUTHENTIC SAMPLE; MAINLY SEEN IN HUMID CONDITIONS |
| 3.12| 171 | ![Image](image11.png) | L      | MAINLY SEEN IN HUMID CONDITIONS     |
| 3.13| 157 | ![Image](image12.png) | S      | MAINLY SEEN IN DRY CONDITIONS       |
Table 1.4. Decomposition products LC/MS.

| #  | retention time | identity | mass/charge | empirical formula | match status |
|----|----------------|----------|-------------|------------------|--------------|
| 4.1| 74.06034       | L        |             | C3H8O2N          |              |
| 4.2| 103.0603       | L        |             | C3H7O2N2         | MATCHED TO AUTHENTIC SAMPLE |
| 4.3| 106.0609       | G        |             | C3H8O3N          |              |
| 4.4| 117.0609       | L        |             | C4H9O2N2         |              |
| 4.5| 103.0603       | G        |             | C3H10O2N2        |              |
| 4.6| 120.0606       | L        |             | C3H10O3N         |              |
| 4.7| 133.0608       | M        |             | C4H9O3N2         |              |
| 4.8| 145.0608       | M        |             | C5H11O2N2        |              |
| 4.9| 155.1289       | M        |             | C7H15N4          |              |
| 4.10| 157.1289      | L        |             | C7H16O2N3        |              |
| 4.11| 160.0603      | L        |             | C4H11O2N3        |              |
| 4.12| 172.0712      | L        |             | C7H14O3N3        | MATCHED TO AUTHENTIC SAMPLE |
| 4.13| 172.1078      | S        |             | C7H13O4N4        |              |
| 4.14| 174.0873      | M        |             | C6H12O3N3        |              |
| 4.15| 201.0982      | L        |             | C7H13O3N4        |              |
| 4.16| 205.0931      | S        |             | C6H13O4N4        |              |
| 4.17| 207.0611      | TMDDD M  |             | C6H11O6N2        | MATCHED TO AUTHENTIC SAMPLE |
| 4.18| 209.0768      | HMTD M   |             | C6H13O6N2        |              |
Although not shown in the above reactions, without citric acid formation of HMTD takes days. Furthermore, the reaction is sensitive to the type and amount of acid (Table 5). Diprotic (sulfuric and oxalic) and triprotic (phosphoric) acids could be used as direct replacements for citric acid. Monoprotic acids (acetic acid, trifluoroacetic acid, formic acid, and nitric acid) gave yields comparable to citric acid only if these acids were added in 2.2 mol acid to 1 mol hexamine ratio. This aspect of the acid effect merits further examination.
Table 1.5. HMTD Reactions with additives with Scaled Yield of 0.5g.

| HMTD Reaction # | Additive            | Mol Ratio of HP (48.4wt%): Hexamine | Mol Ratio Acid (Citric): Hexamine | % Yield | MP (°C) | Purity by GC/MS |
|----------------|---------------------|------------------------------------|----------------------------------|---------|---------|---------------|
| 5              | citric acid         | 8                                  | 1.1:1                            | 44.5    | 149-150 | 87.4          |
| 6              | citric acid         | 8                                  | 1.1:1                            | 40.7    | 144-145 | 87.1          |
| 17             | citric acid         | 8                                  | 1.1:1                            | 56.3    | 153-157 | 95.8          |
| 14             | anhydrous oxalic acid | 8                               | 1.1:1                            | 45.0    | 151-153 | 94.4          |
| 15             | 85% o-phosphoric acid | 8                               | 1.1:1                            | 26.9    | 149-150 | 91.3          |
| 32             | 50% sulfuric Acid   | 8                                  | 1.1:1                            | 50.5    | 152-158 | 98.2          |
| 13             | glacial acetic acid | 8                                  | 1.1:1                            | 7.4     | 152-153 | 94.3          |
| 30             | glacial acetic acid | 8                                  | 2.2:1                            | 33.1    | 151-156 | 100.0         |
| 21             | 88% formic Acid     | 8                                  | 1.1:1                            | 6.3     | 154-158 | 94.5          |
| 25             | 88% formic Acid     | 8                                  | 2.2:1                            | 43.5    | 153-154 | 100.0         |
| 22             | 99% TFA             | 8                                  | 1.1:1                            | 3.3     | 155-159 | 93.3          |
| 26             | 99% TFA             | 8                                  | 2.2:1                            | 53.5    | 153-156 | 99.6          |
| 31             | 70% nitric Acid     | 8                                  | 2.2:1                            | 51.1    | 155-157 | 100.0         |
| Kin. #2        | no acid             | 8                                  | 0.1                              | 9.5     | 148-149 | 89.5          |
| Kin. #3        | no acid             | 8                                  | 0.1                              | 7.2     | 152-160 | 92.4          |

If HMTD is formed when hexamine breaks into smaller fragments, then it should incorporate carbon and nitrogen from outside sources. When HMTD synthesis was performed with $^{13}$C formaldehyde solution, the label appeared in both the HMTD (m/z 209, 210, 211, 212, 213) and the hexamine (m/z 140, 141, 142, 143, 144) early in the reaction (42min when precipitation was observed in 2 hr). A possible explanation is formation of bis(hydroxymethyl) peroxide (BHMP) and its incorporation into HMTD (Figure 5). Incorporation of formaldehyde into the hexamine can be explained by looking at the first two steps of decomposition of hexamine (Figure 4). Excess formaldehyde may push this reaction in the reverse direction. However, HMTD synthesized in the presence of $^{15}$N-labeled ammonium sulfate, showed little incorporation based on GC/MS and LC/MS results.
Figure 1.5. Formation of HMTD from completely dissociated hexamine.

In contrast to the lack of $^{15}$N incorporation during HMTD synthesis, it was found that under humid decomposition conditions, the $^{15}$N label was observed in the decomposition products (4.2, 4.12, 4.13, 4.14, 4.15, 4.17, 4.20) as well as in hexamine (single, double, triple and quadruple label). Yet, when the same decomposition conditions were performed dry, no hexamine was formed and the decomposition products 4.2 and 4.14 showed no label incorporation.

In deuterium oxide, HMTD decomposition products trimethylamine, dimethylformamide, hexamine, and triazines showed little incorporation of deuterium (m/z 157, 171 etc.). This suggested that hydrogen transferred during the decomposition was from the original HMTD molecule.

A mechanism for HMTD formation was proposed on data from isotopic ratio mass spectrometry [24]. Because it required the formation of a triperoxy tertiary amine and protonated methylene imine, we sought alternative proposals. Tentative proposals are illustrated in Figures 5 and 6. In Figure 5 hexamine is broken into small molecules, and from the formaldehyde/hydrogen peroxide reaction bis(hydroxymethyl) peroxide (BHMP) is formed, while from the imine/ hydrogen peroxide reaction bis(methylamine)
peroxide (BMAP) is formed. The latter reacts with 2 molecules of BHMP, forming tetramethylene diperoxide diamine (TMDD) as an intermediate, to create HMTD. The mechanism in Figure 6 also postulates the formation of BHMP but allows hexamine to remain moderately intact until fairly late in the reaction. Both mechanisms speculate that the reaction proceeds to HMTD faster in the presence of excess formaldehyde because formation does not require initial degradation of hexamine into formaldehyde. The key to both mechanisms is the formation of BHMP, first synthesized in 1914 by Fenton from hydrogen peroxide and formaldehyde and later studied by Satterfield [25]. It is likely this species was generated in situ in the reported syntheses of several caged peroxides having planar bridgehead nitrogen atoms [26]. Once a methylene is lost from hexamine as formaldehyde the resulting octahydro-1,3,5,7-tetrazocine would be subject to rapid ring inversion and isomerization from which BHMP could bridge across two nitrogens.
Figure 1.6. Formation of HMTD from intact hexamine.
To discriminate between the mechanisms proposed in Figures 5 and 6, synthesis of HMTD was done with a 1 to 1 mixture of $^{14}$N hexamine and $^{15}$N hexamine. If the formation of HMTD proceed through the route shown in Figure 5, then complete scrambling of the label would be expected, i.e. the HMTD product should show the unlabeled, single-labeled and double-labeled species [M+H], 209 to 210 to 211, in a 1 to 2 to 1 ratio. Indeed that was what was observed (Figure 7).

![Figure 1.7. Mass spectrum of HMTD formed from a mixture of N-14 and N-15 labeled hexamine.](image)

To shed light on the question of how HMTD decomposes, density functional theory (DFT) calculations were performed. The initial sequence of steps in the decomposition of a single HMTD molecule is described in Figure 8. Energy differences of the transition states and entropies of the various species along the decomposition pathway were calculated relative to the energy of the nearest intermediate or reactant to show energy barrier and entropy change for each decomposition reaction step. The
calculations were carried out for both gas phase molecule (values without parenthesis) as well as for a solvated molecule in water (values in parenthesis). The structure and properties of the various intermediate species along the decomposition pathway are summarized in Table 6.

1) First step via TS1 consist of O—O bond opening together with H-atom transfer from the methylene group (CH₂) near one of the O-atom to the O-atom farther away. The transition state is an open shell singlet state (bi-radical). This is the rate limiting step in the decomposition process. Following TS hydrogen transfer, O—O bond ruptured results in formation of –OH and –C=O groups respectively in INT1.

2) Second step via TS2 is similar to the first step (step 1) and leads to rupture of second O—O bond and a second H transfer to form two new –OH and –C=O groups in INT2.

3) Third step via TS3 involves an N—C bond opening concerted with H-atom transfer from O in CH₂OH group to O in –CH=O group to yield INT3 and a formaldehyde molecule.
Figure 1.8. Decomposition route of an isolated HMTD molecule. Energy barriers and energies of intermediates for a gas phase molecule are without parenthesis while values of solvated molecule (in water) are in parenthesis.
Table 1.6. Intermediates in the decomposition of gas phase HMTD. Calculations used PBE0PBE1/cc-pVDZ level of theory. Energy values in kcal/mol, entropy values in cal/(K mol).

| #  | mass | structure | name    | Kinetic & thermochemical | Reaction step producing intermediate |
|----|------|-----------|---------|--------------------------|-------------------------------------|
| 1  | 208  | [Image]   | CHH1206N2 | INT1                     | HMTD → INT1                         |
|    |      |           |         | \( \Delta E^a = 32.5 \) (30.2), \( \Delta S^a = 8.1 \) | One O-O bond opening together with H-atom shift from methylene group to oxy gen |
|    |      |           |         | \( \Delta E_{\text{react}} = -57.4 \) (-65.7), \( \Delta S_{\text{react}} = 9.1 \) |                                      |
| 2  | 208  | [Image]   | CHH1206N2 | INT2                     | INT1 → INT2                         |
|    |      |           |         | \( \Delta E^a = 27.3 \) (26.8), \( \Delta S^a = 8.9 \) |                                      |
|    |      |           |         | \( \Delta E_{\text{react}} = -68.3 \) (-69.0), \( \Delta S_{\text{react}} = 7.3 \) | relative INT1                        |
|    |      |           |         | \( \Delta E_{\text{react}} = -131.5 \) (-134.6), \( \Delta S_{\text{react}} = 16.4 \) | relative HMTD                        |
|    |      |           |         |                                      | Second O-O bond opening together with H-atom shift from methylene group to oxy gen |
| 3  | 178  | [Image]   | CHH1605N2 | INT2                     | INT2 → INT3HCO                      |
|    |      |           |         | \( \Delta E_{\text{react}} = 27.2 \) (28.7), \( \Delta S_{\text{react}} = 8.7 \) relative INT2 |                                      |
|    |      |           |         | \( \Delta E_{\text{react}} = -104.2 \) (-105.9), \( \Delta S_{\text{react}} = 25.0 \) | relative HMTD                        |
| 4  | 104  | [Image]   | CHH6033N (radical) | INT4                     | INT4 + INT5                         |
|    |      |           |         | \( \Delta E^a = 24.8 \) (24.0), \( \Delta S^a = 3.6 \) |                                      |
|    |      |           |         | \( \Delta E_{\text{react}} = 22.1 \) (21.6), \( \Delta S_{\text{react}} = 10.9 \) relative INT3 |                                      |
| 5  | 74   | [Image]   | CHH402N (radical) | INT5                     | INT3                                |
|    |      |           |         | \( \Delta E^a = 10.9 \) (11.3), \( \Delta S^a = -6.8 \) |                                      |
|    |      |           |         | \( \Delta E_{\text{react}} = 0.1 \) (-0.1), \( \Delta S_{\text{react}} = -6.6 \) relative INT3 |                                      |
| 6  | 178  | [Image]   | CHH1005N2 | INT6                     | INT3 → INT6                         |
|    |      |           |         | \( \Delta E^a = 10.9 \) (11.3), \( \Delta S^a = -6.8 \) |                                      |
The following step in this pathway is the decomposition of INT3 into two new species or isomerization into a 7-member ring as shown in Figure 9. The formation of two radials, INT4 and INT5, is favorable according to the entropy changes; however, INT6 formation should be favorable due to a lower energy barrier to overcome.

Figure 1.9. The next steps in the decomposition of an isolated HMTD molecule. Energy barriers and energies of intermediates for a gas phase molecule are without parenthesis while values of solvated molecule (in water) are in parenthesis.
Next, we considered the decomposition of the HMTD molecule in an acidic environment. A proton can attach to either an oxygen atom or a nitrogen atom. Protonated HMTD forms spontaneously without an appreciable energy barrier. When a proton is attached to one of the nitrogen atoms, the first step in decomposition of the cation will proceed via a C─N bond rupture. The energy barrier associated with this event is much higher than that obtained for the first step in the decomposition of a protonated oxygen atom in the HMTD molecule. Moreover, the barrier associated with the O-atom protonation is also smaller than the magnitude of the energy barrier associated with TS1 in Figure 8. A summary of the energy barriers related to the possible initial steps in the different decomposition schemes are shown in Figure 10. In the case of O-atom protonation we revealed two possible decomposition routes that are denoted as Path A and Path B. The intermediates for these two paths are named INTHOA and INTHOB, respectively. The main difference between these two decomposition routes is that Path A proceeds via C─O bond opening while path B via O─O opening. A summary of the structures and properties of all the intermediate species along Path A and Path B are described in Tables 7 and 8, respectively.
Figure 1.10. Scheme showing all the possible initial decomposition steps of HMTD molecule in different environments.
Table 1.7. Intermediates observed along path A during the decomposition of HMTD molecule with a protonated oxygen. The calculations were performed using PBE0PBE1/cc-pVDZ level of theory. Energy values in kcal/mol, entropy values in cal/(K mol).

| # | mass | structure | name   | Kinetic and thermochemical characteristics | Reaction step and comments |
|---|------|-----------|--------|--------------------------------------------|---------------------------|
| 1 | 209  | ![Structure 1](image1.png) | C6H13O6N2 INT1HOA | $\Delta E^\# = 3.5 (-0.2)$, $\Delta S^\# = 3.6$ | HMTD (protonated) $\rightarrow$ INT1HOA |
|   |      |           |        | $\Delta E_{\text{react}} = 1.4 (- 1.1)$, $\Delta S_{\text{react}} = 5.9$ | Back reaction is possible with large probability |
|   |      |           |        | $\text{C-O bond opening}$ | |
| 2 | 209  | ![Structure 2](image2.png) | C6H13O6N2 INT2HOA | $\Delta E^\# = 10.0 (14.3)$, $\Delta S^\# = 6.6$ | INT1HOA $\rightarrow$ INT2HOA |
|   |      |           |        | $\Delta E_{\text{react}} = 5.9 (6.9)$, $\Delta S_{\text{react}} = 16.5$ | |
|   |      |           |        | relative HMTD protonated | |
| 3 | 208  | ![Structure 3](image3.png) | C6H12O6N2 INT3HOA | Without barrier | INT2HOA + OH $\rightarrow$ INT3HOA + H2O |
| 4 | 104  | ![Structure 4](image4.png) | C3H6O3N INT4HOA | $\Delta E^\# = 24.6 (22.6)$, $\Delta S^\# = 9.1$ | INT3HOA $\rightarrow$ INT4HOA |
|   |      |           |        | $\Delta E_{\text{react}} = 31.9 (26.2)$, $\Delta S_{\text{react}} = 47.5$ relative | INT3HOA $\rightarrow$ INT4HOA |
Table 1.8. Structure and properties of intermediates along path B during the decomposition of HMTD molecule with protonated oxygen. Calculations used PBE0PBE1/cc-pVDZ level of theory. Energy values in kcal/mol, entropy values in cal/(K mol).

| # mass | structure | name          | Kinetic & thermochemical | Reaction step & comments |
|--------|-----------|---------------|--------------------------|--------------------------|
| 209    |           | OSH106N2 INT1HOB | ΔE° = 20.3 (17.2), ΔS° = 8.1 | HMTD (protonated) → INT1HOB |
|        |           |               | ΔE_react = -72.4 (-76.4), ΔS_react = 7.9 | |
|        |           |               | One O-O bond opening | |
| 208    |           | OSH1206N2 INT1 | Without barrier if reagent is OH | INT1HOB + OH → INT1 + H₂O |
|        |           |               | If reagent is H₂O | Or |
|        |           |               | ΔE° = 2.2 (0.9), ΔS° = -6.5 | INT1HOB + H₂O → INT1 + H₂O⁺ |
|        |           |               | ΔE_react = 1.0 (-1.4), ΔS_react = 3.9 relative INT1 + H₂O | |
| 207    |           | OSH106N2 INT2HOB | Without barrier | INTI + H⁺ → INT2HOB + H₂ |
|        |           |               | H⁺ attack to carbon in terminated CH₂OH group | |
| 209    |           | OSH106N2 INT3HOB | ΔE = -2.8 (-8.6), ΔS = -28.8 relative INT2HOB + H₂ | INTI + H⁺ → INT3HOB |
|        |           |               | H⁺ attack to nitrogen connected with terminated CH₂OH group | |
| 206    |           | OSH106N2 INT4HOB | Without barrier | INT2HOB + OH → INT4HOB + H₂O |
| 179    |           | OSH106N2 INT5HOB | ΔE° = 22.1 (29.5), ΔS° = 2.5 | INT3HOB → INT5HOB + H₂CO |
|        |           |               | ΔE_react = 11.5 (7.4), ΔS_react = 44.5 relative INT3HOB | |
| 178    |           | OSH106N2 INT6HOB | Without barrier | INT5HOB + OH → INT6HOB + H₂O |

As stated above, protonated HMTD is formed spontaneously without any appreciable energy barrier. The rupture of a C─O bond occurs with a minor energy barrier of approximately 3.5 kcal/mol (Path A). The formation of INT2HOA requires overcoming a slightly larger energy barrier; but this barrier is much smaller than that
required for HMTD decomposition as a gas phase molecule, TS1. Additional steps in the decomposition of INT2HOA require surmounting a barrier of about 35 kcal/mol. However the presences of anions in the solution suggest another possible pathway. The third intermediate, INT3HOA is formed following the stabilization of INT2HOA by an anion (OH\(^-\) in this case). This neutralization is accompanied by a large energy release. If the OH\(^-\) is replaced by H\(_2\)O, only a very low barrier is observed. The decomposition of INT3HOA requires overcoming a barrier of about 24 kcal/mol (see Table 7) and it leads to the formation of two 5-member ring radicals.

The structure and characteristics of the intermediate species in Path B of HMTD with protonated oxygen are presented in Table 8. The most important in this route is the possibility that INT1HOB is neutralized by an anion (several anions were tested, OH\(^-\), Cl\(^-\), SO\(_4^{2-}\), HSO\(_4^{2-}\)) to produce INT1 shown for neutral decomposition in Figure 8 and as entry 2 in Table 8. This pathway allows one to return to the neutral HMTD decomposition without the necessity to overcome a barrier 32.5 (30.5) kcal/mol.

Most neutral intermediates can be protonated without an appreciable energy barrier. The intermediates described in Table 8 suggest the possible intermediates with quite large molar mass similar to those presented in Tables 3 and 4. All these decomposition steps proceed without barriers or with small energy barriers; hence, most of these species are accessible. The highest barrier is related to the formation of formaldehyde (entry 6, Table 8). We also tested the fate of the relatively stable intermediate INT2 (entry 2, Table 6). The structure and properties of the intermediates observed during the decomposition of its protonated form are presented in Table 9.
Table 1.9. Intermediates observed in decomposition of gas phase HMTD starting with protonated INT2 (Fig. 8). Calculations used PBE0PBE1/cc-pVDZ. Energy in kcal/mol, entropy in cal/K mol.

| # | m/e | Structure | Name     | Kinetic &Thermochemical                  | Comments                          |
|---|-----|-----------|----------|-----------------------------------------|-----------------------------------|
|   |     |           | C6H13O6N2 | INT2_P                                  | Without barrier                   |
|   |     |           |          | D\_E\# = 27.1 (29.7), D\_S\# = -6.8   | INT2 + H\^+ \rightarrow INT2\_P   |
|   |     |           | C5H11O5N2 | INT3\_P                                  |                                   |
|   |     |           |          | D\_E\text{react} = 32.9 (29.6), D\_S\text{react} = 47.2 relative INT2\_P |                                   |
|   |     |           | C3H6O2N  | INT4\_P                                  | Without barrier                   |
|   |     |           |          | D\_E\# = 22.8 (20.7), D\_S = 6.5     | INT2\_P \rightarrow INT4\_P + H\text{\textsubscript{2}}CO |
|   |     |           | C3H7O4N  | INT7                                     |                                   |
|   |     |           | C6H13O6N2 | INT10                                    |                                   |
|   |     |           | CH3O     | INT8                                     | Without barrier                   |
|   |     |           |          | D\_E\# = 26.0 (27.8), D\_S\# = -0.4 | INT8 \rightarrow INT9 + H\text{\textsubscript{2}}CO |
|   |     |           | C2H5O3   | INT9                                     |                                   |
|   |     |           |          | D\_E\# = 13.4 (17.5), D\_S\# = 5.7 | INT6\_P \rightarrow INT10 + INT7\_P |
|   |     |           | C2H5O3   | INT10                                    |                                   |
|   |     |           |          | D\_E\text{react} = 8.5 (11.9), D\_S\text{react} = 17.3 relative INT11\_P |                                   |
|   |     |           | C2H50N   | INT7\_P                                  |                                   |
|   |     |           |          | D\_E\# = 1.4 (5.3), D\_S\# = -0.4 | INT7\_P \rightarrow INT8\_P       |
|   |     |           | C2H4N    | INT8\_P                                  |                                   |
|   |     |           |          | D\_E\text{react} = 3.4 (1.2), D\_S\text{react} = 34.6 relative INT9 |                                   |
All the decomposition steps that lead to the formation of these intermediates proceed via barriers smaller than 30 kcal/mol. In most cases a much lower barrier or even no barrier is associated with the intermediate. Most of the species listed in Table 9 are rather small and resemble some of the species listed in Tables 3 and 4. Protonation of a nitrogen in the HMTD molecule as the initial step was also considered. The attachment of a proton to nitrogen is preferred by 2.2 kcal/mol over its addition to one of the oxygen atoms in the molecule; however, there are only two nitrogen atoms compared to six oxygen atoms in an HMTD molecule. The initial steps in the decomposition of a nitrogen protonated HMTD are shown in Figure 11.

![Initial decomposition steps of a nitrogen protonated HMTD molecule.](image)

Figure 1.11. Initial decomposition steps of a nitrogen protonated HMTD molecule.
The first transition state, TS1HN, requires the system to overcome an energy barrier of about 28 kcal/mol or about 20% lower than that required to reach TS1 in gas phase HMTD decomposition. In TS1HN one C—N and one C—O bonds start to break together with a rearrangement of the molecular structure. Surmounting this energy barrier leads to the formation of a ring shape intermediate that contains three peroxide bonds. A second energy barrier, with similar magnitude to the first one, leads to TS2HN and is followed by ring opening to form INT2HN. This intermediate has two five member rings attached to each N atom, each ring connected by a \(-\text{O–O–CH}_2\text{-O–}\) chain. Further decomposition of INT2HN was examined but did not lead to the formation of stable end products.

We also examined the possible decomposition of HMTD in a basic solution. A sequence of a few steps with relatively low energy barriers separating them (highest is 17 kcal/mol) and formation of an intermediate with large (104 kcal/mol) energy release occurs. During this sequence a few formaldehyde molecules were released together with the formation of different intermediate species. The structure and the properties of the different intermediate species along the decomposition pathway are described in Table 10. Thus, HMTD decomposition is also expected to occur in basic environment as was observed in the experimental part of this study.
Table 1.10. Structure and properties of intermediate species observed during the decomposition of a HMTD-OH\(^-\) anion calculated using PBE0PBE1/cc-pVDZ level of theory. Energy values in kcal/mol, entropy values in cal/(K mol).

| # | mass  | structure | name      | Kinetic & thermochemical | Reaction step and comments |
|---|-------|-----------|-----------|--------------------------|---------------------------|
| 1 | 225   | ![Structure 1](image1) | C6H13O7N2 | INT1OH                   | HMTD +OH\(^-\) → INT1OH   |
|   |       |           |           | ΔE\(^\#\) = -2.4 (-2.6), ΔS\(^\#\) = 3.8 |                           |
|   |       |           |           | ΔE\(_{\text{react}}\) = -108.2 (-104.9), ΔS\(_{\text{react}}\) = -0.4 relative INT1OH |                           |
| 2 | 207   | ![Structure 2](image2) | C6H11O6N2 | INT2OH                   | INT1OH → INT2OH + H\(_2\)O |
|   |       |           |           | ΔE\(^\#\) = 7.0 (4.9), ΔS\(^\#\) = 4.4 |                           |
|   |       |           |           | ΔE\(_{\text{react}}\) = 6.3 (4.3), ΔS\(_{\text{react}}\) = 9.6 relative INT2OH |                           |
| 3 | 207   | ![Structure 3](image3) | C6H11O6N2 | INT3OH                   | INT2OH → INT3OH           |

4. Conclusion

Since HMTD is destabilized by water and citric acid, it is important to purify it after initial synthesis. It is recommended to rinse with water to remove acid, then with methanol to remove water. Ignoring the degrading effects of water and acid may lead to an unexpected violent reaction during storage and handling. Precautions for storage should be taken to see that HMTD remains dry and cold. Work to elucidate mechanisms of HMTD decomposition continues, but it appears that the headspace of HMTD is mainly trimethylamine (TMA) and dimethylformamide (DMF); these might be used instead of the more hazardous HMTD for canine and other vapor detection modes. It
was observed that hexamine, substituted triazines, and linear amines are formed in the condensed phase, and the observation of these products is humidity dependant. The mechanism of formation of HMTD was found to proceed through a complete breakdown of hexamine, involving formaldehyde exchange. Positive identification of synthesis intermediates remains as a future work.

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MANUSCRIPT 2

POTENTIAL BIOCIDES: IODINE-PRODUCING PYROTECHNICS

by

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Abstract

Currently there is a need for specialized pyrotechnic materials to combat the threat of biological weapons. Materials have been characterized based on their potential to produce heat and molecular iodine gas (I\(_2\)) to kill spore-forming bacteria (e.g. anthrax). One formulation, already proven to kill anthrax simulants, is diiodine pentoxide with aluminum; however, it suffers from poor stability and storage problems. The heat and iodine gas output from this mixture and candidate replacement mixtures were measured with bomb calorimetry and extraction and analysis of I\(_2\) by UV-Vis. Of the mixtures analyzed, calcium iodate and aluminum was found to be the highest producer of I\(_2\). The heat output of this mixture and others can be tuned by adding more fuel, with the cost of some iodine. Products of combustion were analyzed by thermal analysis (SDT), XPS, XRD, and LC/MS. Evidence for various metal iodides and metal oxides was collected with these methods.

1 Introduction

Previously we examined a series of oxidizers and fuels to determine their potential as explosive threats [1]. In the current work we examine, in detail, performance of oxides of iodine with the goal of determining their effectiveness as biocides. The biological threat of particular concern is spore production by *Bacillus anthracis*. While kill methods are diverse and not completely understood, it is known that a combination of heat and molecular iodine is effective [2,3]. A number of iodate and periodate salts were examined by formulating them with fuels and measuring heat evolution and molecular iodine release. Diiodine pentoxide has been used as a benchmark because it contains the highest weight percentage of iodine. Unfortunately, its long-term stability
with a favored fuel, aluminum, is poor. Herein we examine the fuels aluminum and boron carbide.

2 Experimental Section

2.1 Calorimetry and Iodine (I2) Quantification

The oxidizers KIO₃, NaIO₃, NaIO₄, KIO₄ were purchased from Acros; I₂O₅, and Ca(IO₃)₂ were purchased from Strem; the aluminum flake (23 µm) and boron carbide (8µm) fuels were from Obron and Electron Microscopy Sciences, respectively. The oxidizers were sieved to 100-200 mesh (150-75 µm). Bi(IO₃)₃ was synthesized according to Zachariah et al and used as prepared [4]. For preparation of Bi(IO₃)₃, a solution of Bi(NO₃)₃•5H₂O (4.85g in 80 mL, 2 M nitric acid) was added to HIO₃ solution (5.28 mg in 80 mL H₂O), then rinsed with 600 mL H₂O and 100 mL of methanol. Product was dried under vacuum overnight. Average particle size was 4µm (Horiba LA950 Particle Size Analyzer, wet mode).

The pyrotechnic mixtures were mixed as dry loose powders using a Resodyne Lab Ram Acoustic Mixer (acceleration 35-40 G). Heat released from the ignition of the pyrotechnic formulations was determined using a Parr 6200 Isoperibol Bomb Calorimeter. The Parr bomb was calibrated (i.e. 10 trials) with benzoic acid ignited with fuse wire and (9.6232 J/cm) and cotton string (167.36 J) in 2515 kPa oxygen (ΔH_comb = 26434 J/g). In an oxygen atmosphere, the string is in contact with the fuse wire and sample, and is ignited by the fuse wire to aid the ignition of the sample. The pyrotechnics (2-3 samples under each set of conditions) were loaded in 2 g samples and ignited with a fuse wire under argon (515 kPa). This slightly elevated pressure was chosen to simplify purging of the Parr 1108 bomb with Argon and to ensure a tight seal.
Molecular iodine (I₂) produced from each burn was quantified with ultraviolet-visible (UV-Vis) spectroscopy (Agilent 8453 spectrometer, 190 to 1100 nm, resolution 1 nm, 0.5 s integration time). Iodine was extracted from the bomb with 100 mL of an aqueous 0.5 M potassium iodide (KI) solution. The aqueous solution with excess of I⁻ was added to solubilize I₂ and transform it to I₃⁻ (absorbance 353 nm) [5]. Extracts were diluted with known amounts of 0.025 M KI for absorbance measurements at 353 nm to quantify iodine. Control samples were made by pressing solid iodine (0.8 g) with benzoic acid (1.2 g). When these control samples were ignited under 350 psi oxygen, iodine recovery was ~97%. For Bi(IO₃)₃ mixtures, an interference in the UV-Vis spectra (Figure S33-S34), attributed to a BiI₃ and KI interaction was observed [6]. For these mixtures, iodine standards and sample extractions were conducted with methylene chloride (at 506nm), which did not dissolve BiI₃. Control experiments with methylene chloride extractions showed lower recovery (73%), which was factored into the recovered iodine from Bi(IO₃)₃ mixtures.

2.2 Aging Studies

For aging studies, loose powder pyrotechnic mixtures were aged at 60°C and 75% RH (relative humidity). Time points were at 3 days and 14 days. Fresh samples and aged samples were analyzed by simultaneous differential scanning calorimetry/thermogravimetric analysis (TA Instruments, Q600 SDT, 20C/min, 50 to 1000 °C); infrared (IR) spectroscopy (Thermo Nicolet 6700 FR-IR with ATR cell, 32 scans, resolution 4 cm⁻¹, 650-4000 cm⁻¹); and visual observation. IR was used specifically to detect oxygen-hydrogen bonds, indicating uptake of water. The burn characteristics of fresh and aged samples were also noted.
2.3 Simultaneous Differential Scanning Calorimetry Thermogravimetric Analysis (SDT)

A TA instruments Q600 SDT was used to characterize the original pyrotechnic mixtures, combustion products (from bomb calorimetry, 515 kPa Argon), and standard mixtures. Samples of 3-5 mg were heated in alumina crucibles at a scan rate of 20 °C/min from 50 to 1000 °C. To remove solid iodine or solvents (in the case of water or methanol extracts for LC/MS) combustion products were dried in a vacuum oven overnight at 50 °C before the analysis. Unless stated otherwise, samples were run under nitrogen.

2.4 Titration for Oxide Content

In the case of 80/20 Ca(IO$_3$)$_2$/Al combustion products (pH 11 when mixed with water), an acid base titration was performed. Hydrochloric acid (30 mL of 0.100 M) was added to 50-150 mg of combustion products and allowed to stir for 20min. The solution was then back-titrated with 0.100 M sodium hydroxide, with bromothymol blue indicator.

2.5 X-Ray Photoelectron Spectroscopy (XPS)

A Thermo Scientific K-Alpha XPS (Aluminum source, 1486.7 eV) was used to help determine bomb calorimetry combustion products of NaIO$_3$/Al, Bi(IO$_3$)$_3$/Al, KIO$_3$/Al, Ca(IO$_3$)$_2$/Al, and I$_2$O$_5$/Al. The pass energy was 50 eV with a resolution of ±0.05eV. Samples and standards were prepared in a nitrogen glove box (from Genesis). Charge effects were corrected based on the peak signal from the corresponding cation of an appropriate standard (i.e. KIO$_3$/Al combustion products were corrected from K2p3/2 from KI).
2.6 Liquid Chromatography / Mass Spectrometry (LCMS)

Water and methanol extracts of bomb calorimetry combustion products of Ca(IO$_3$)$_2$/Al and I$_2$O$_5$/Al were prepared and infused into a Thermo Exactive Orbitrap Mass spectrometer with an electrospray ionization interface (ESI). This method was modified from a method used to analyze aluminum chloride in ESI negative mode with no additives in water [7]. The tune conditions (10 μl/min) were as follows: spray voltage 1.80 kV (for water extracts) and 2.4 kV (for methanol extracts); capillary temperature at 200 ºC; sheath gas (N$_2$) at a flow rate of 8; aux gas (N$_2$) at a flow rate of 1; capillary voltage at -10 V; tube lens at -175 V, and skimmer voltage at -25 V. The instrument passed the calibration with a mass accuracy of 2 ppm. The mass spec scanned from 128.0 to 600.0 m/z with 25,000 resolution and a maximum injection time of 50 ms. Solid combustion products were extracted with either water (60 – 75 mg in 10 mL) or methanol (500 mg in 25 mL) in falcon tubes by vortex mixing for 2 min, sonicating for 20 min, vortex mixing again for 2 min, then centrifuging for 10 min at 3.0 G. The methanol extract was decanted from the samples, and diluted with 50/50 v/v methanol/water to a concentration of 500 - 750 μg/ml. Standard solutions of calcium iodide, aluminum iodide, and calcium oxide were also prepared the same way (50 mg in 10 mL of water or 200 mg in 25 mL of methanol), then diluted to 400 μg/ml with 50/50 methanol/water.
2.7 Powder X-Ray Diffraction

A Rigaku Ultima IV XRD was used (Cu source, 40 kV, 44 mA) to help identify combustion products of the Ca(IO$_3$)$_2$/Al mixtures. The scan was 0.667 deg / min from 10 to 110 deg at a sampling width of 0.25 deg. Combustion products for 80/20 Ca(IO$_3$)$_2$/Al and 60/40 Ca(IO$_3$)$_2$/Al were handled in a glove box, then run in the instrument with containers of drierite in the analysis chamber that had pre-equilibrated for 1 hour.

2.8 Friction Testing (BAM method)

Testing was conducted according to the UN method (on an FS-12A BAM machine from OZM research) where the threshold initiation level (TIL) of a sample (in N force) is reported where 1 out of 6 samples were a “go” with a snapping sound [8]. A sample size of 10 mm$^3$ was used.

2.9 Drop-weight impact (Modified BOE method)

This test was conducted with a BOE machine manufactured by SMS (10 mg sample, 3.63 kg weight) using the UN method [8]. Ca(IO$_3$)$_2$/Al was tested seven times at the highest height of the instrument (75 cm). A Dh$_{50}$ number was obtained with an up/down method (14 samples, where 50 % of the samples were a “go”) with RDX (class 1, Holston) for comparison. A test was considered a “go” when an explosion or flash occurred.

2.10 Electrostatic Sensitivity Testing (ARDEC method 1032)

This test was conducted with a machine manufactured by UTEC Corporation, LLC using ARDEC method 1032 [9]. Testing starting at the 0.25 J level, and the energy level was stepped down until a TIL energy value was reached with 0 out of 20 samples
were a “go”. A test was considered a “go” when a flash considerably brighter than a blank occurred and the tape holding the sample down split open.

3 Results and Discussion

Choice of oxidizers was governed by availability as well as reported iodine production (Table 1). (Iodoform was considered but not examined because it was neither an oxidizer nor a good fuel.)

Table 2.1. Iodine Content of Oxidizers Employed

| Iodine Sources | mw (g/mol) | # I’s | wt % iodine | wt% oxygen |
|----------------|------------|-------|-------------|------------|
| KIO₃           | 214        | 1     | 59          | 22         |
| NaIO₃          | 198        | 1     | 64          | 24         |
| I₂O₅           | 334        | 2     | 76          | 24         |
| Ca(IO₃)₂       | 390        | 2     | 65          | 25         |
| Bi(IO₃)₃       | 734        | 3     | 52          | 20         |
| NaIO₄          | 214        | 1     | 59          | 30         |
| KIO₄           | 230        | 1     | 55          | 28         |

Because aluminum is often used to create heat-producing pyrotechnic mixtures, oxidizers were initially compared using it as the fuel (Figure 1). Boron carbide was also examined because recent studies reported when it was used in delay mixtures of periodate, iodine production was observed (Figure 2) [10].
As Figure 1 shows, diiodine pentoxide was most effective in both iodine and heat production. However, long term stability was poor. In the presence of moisture this oxide is reportedly converted to iodic acid, also a white solid [11]. The poor stability was exacerbated in the presence of aluminum. After three days, at 60 °C and 75% relative humidity, the 80/20 I₂O₅/Al mixture turned from a grey powder to a dark brown
powder (Figure 3). It may be the reaction of aluminum with iodic acid which causes the rapid color change observable in Figure 3. Evidence of the presence of iodic acid can be found in the SDT of I₂O₅ aged under the same conditions (Figure S2; water loss at 112 °C and 219 °C). At the same temperature and humidity, visual observations as well as infrared spectrometry (IR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) suggested that calcium iodate, sodium iodate, and sodium periodate, (and mixtures with fuel) were stable (Figure S1-S32). All oxidizers alone remained white solids through the aging study. When an original 75/25 calcium iodate/aluminum mixture was allowed to age two weeks under these conditions, no change is observed in its appearance, production of iodine or thermal trace, suggesting acceptable thermal stability (Figure S22-S24).

Figure 2.3. Freshly made (left) and aged 3 days at ambient pyrotechnic mixtures.

Even without considering the efficiency of I₂ production, it would be difficult for other species to match diiodine pentoxide (I₂O₅) in terms of iodine formation because they do not contain as much iodine per mass of oxidizer (Table 1). Several overall reactions are possible (eq. 1-3), where M represents the alkali metal cations in this study.

$$6 \text{MIO}_3 + 10 \text{Al} \rightarrow 5 \text{Al}_2\text{O}_3 + 3 \text{M}_2\text{O} + 3\text{I}_2$$

(1)
\[
\text{MIO}_3 + 2 \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{MI} \quad (2)
\]
\[
6 \text{MIO}_3 + 2 \text{Al} \rightarrow \text{Al}_2\text{I}_6 + 3 \text{M}_2\text{O} + 15/2 \text{O}_2 \quad (3)
\]

The alkali iodates normally decompose to make the iodide salt (eq. 2) and oxygen with perhaps up to 30% forming the oxide instead (eq. 1) [12]. The addition of a fuel eliminates the free oxygen, but in the case of aluminum fuel, excess aluminum may promote the formation of Al\(_2\)I\(_6\) [13]. Six oxidizers and I\(_2\)O\(_5\) were examined with aluminum, boron carbide and a mixture of the two (Table 2). The data reported was obtained in an argon atmosphere in a closed-bomb (Parr); iodine (I\(_2\)) was collected after combustion and usually quantified by UV-Vis spectroscopy. The reported results are averages of at least three tests. Average heat released under argon (across all mixes) was 3975 J/g; similar to heat released from 80/20 I\(_2\)O\(_5\)/Al (4414 J/g). Iodine production was more sensitive to the fuel/oxidizer ratio than was heat output (Table 3). Review of the data sorted in Table 3 indicated that as the oxidizer/fuel ratio moved from stoichiometric (roughly 80/20) to a more fuel rich formulation (60/40), I\(_2\) production decreased and heat generally increased. We attributed this to oxygen deficiency, which caused the fuel to combine with the iodine species (acting as oxidant) preventing the release of molecular iodine. Indeed, preliminary data suggested that both iodine production and heat release are improved by the presence of oxygen.
A better understanding of the pyrotechnic reactions, especially knowing why mixes like Ca(IO$_3$)$_2$/Al favor iodine production over other mixes, required identification of reaction products (by XPS, SDT, XRD, and LC/MS) and ignition mechanisms (by SDT). Measurement of heat evolved and iodine produced was obtained from ignitions in a sealed, Parr bomb calorimeter and extraction of the resulting residue with aqueous KI solution and quantification of iodine by UV-Vis. Other solid products were collected and analyzed by X-ray photoelectron spectroscopy (XPS) and simultaneous thermal gravimetric/differential scanning calorimetry (DSC/SDT). XPS results in Table 4 show electron binding energies of the combustion products, which are consistent with oxidation state assignments of I$^-$, O$^{2-}$, Al$^{3+}$, Ca$^{2+}$, N$^3$, Na$^+$, K$^+$, Bi$^{3+}$. The resulting elemental analysis is shown in Table 5, noting that all results show more oxygen than anticipated. This is attributed to the presence of moisture or surface oxidation; oxidation of iodides is explained later from SDT experiments (Table 7). The roughly 1:1 match of Na and K to I (from mixes 55, 53, and NaI) and the roughly 1:3 match for Bi to I (from mix 97) suggest that these cations become incorporated in iodide salts. However,
for Ca(IO₃)₂/Al from mix 60 (which is stoichiometric) there is not sufficient iodide (I⁻) found to support the required 1:2 ratio for CaI₂. When the aluminum fuel content was raised from 20 wt% to 40 wt%, the ratio was consistent with CaI₂ production, but this evidence was not supported by DSC/SDT of the fresh combustion products. However, SDT of dried methanol extracts of the combustion products of 60/40 Ca(IO₃)₂/Al did show both decomposition before endothermic mass loss before 200°C and a melt at 774 °C, characteristic of the presence of both Al₂I₆ and CaI₂ respectively. A dried methanol solution of 50/50 CaI₂/Al₂I₆ was very similar (Figure 4); furthermore, it was demonstrated by LC/MS that CaO (a combustion product) in the presence of Al₂I₆ and moisture can be converted to CaI₂ vide infra.
Table 2.2. Iodate salts with Various Fuels 2 g in Bomb Calorimeter (515 kPa
Argon)—Heat & I2 Evolution

Mix Info

Oxidizer

Oxidizer
(mass frac)

Al (23um)
(mass frac)

Fuel 2

Fuel 2
(mass frac)

Theoretical
Iodine tot
(wt%)

I2 Recovered
(wt%)

60/40 Bi(IO3)3/Al

Bi(IO3)3

0.60

0.40

--

--

31%

1%

--

2%

80/20 Bi(IO3)3/Al
80/20 Bi(IO3)3/Al (2515 kPa)
80/20 Bi(IO3)3/B4C

Bi(IO3)3
Bi(IO3)3
Bi(IO3)3

0.80
0.80
0.80

0.20
0.20

--0.20

42%
42%
42%

4%
0%
0%

1%

--

7%
1%
0%

80/10/10 Bi(IO3)3/Al/B4C

Bi(IO3)3

0.80

-0.10

--B4C
B4C

0.10

42%

0%

0%

60/40 Ca(IO3)2/Al

Ca(IO3)2

0.60

0.40

--

--

39%

2%

1%

70/30 Ca(IO3)2/Al

Ca(IO3)2

0.70

0.30

--

--

46%

15%

75/25 Ca(IO3)2/Al
80/20 Ca(IO3)2/Al

Ca(IO3)2
Ca(IO3)2

0.75
0.80

0.25
0.20

---

---

49%
52%

36%
42%

80/20 Ca(IO3)2/Al (2515 kPa)
70/10/20 Ca(IO3)2/B4C/Al

Ca(IO3)2
Ca(IO3)2

0.80
0.70

0.20
0.20

-B4C

-0.10

52%
46%

45%
23%

2%

80/20 Ca(IO3)2/B4C

Ca(IO3)2

0.80

B4C

0.20

52%

B4C

0.10

C
C

0.10

Std
Dev

I2 Yield /
Theory Std Dev

Heat Rxn
(J/g)

Std
Dev

--

4129

56

2.5%

30

--

4410
4367
2863

1%

0.8%

3552

76

5%

2.2%

4444

147

5.9%

34%

12.8%

4667

44

3%

73%
81%

7.0%

4491
3563

136

3.0%
--

3551
4073

292

--

86%
50%

15%

3%

29%

6.6%

3526

71

52%

40%

2%

78%

4.7%

3867

58

47%
49%

6%
23%

2%

14%
46%

3.3%
10.4%

3237
3535

38

39%

0%

--

0%

--

4461

50

47%

7%

2%

15%

3.4%

3871

226

47%
47%

8%

0%

0.8%

2962
3754

55

0%

18%
30%

0.3%

14%

0%

1%

1.2%

1.8%

9
71

208

--

80/10/10 Ca(IO3)2/Al/B4C

Ca(IO3)2

0.80

80/20 Ca(IO3)2/Al +10% C
80/20 Ca(IO3)2/Al +5% C

Ca(IO3)2
Ca(IO3)2

0.72
0.76

-0.10
0.18
0.19

60/40 KIO3/Al

KIO3

0.60

0.40

--

80/20 KIO3/Al

KIO3

0.80

0.20

--

80/20 KIO3/B4C
80/10/10 KIO3/Al/B4C

KIO3
KIO3

0.80
0.80

-0.10

B4C
B4C

--0.20
0.10

70/20/10 KIO4/B4C/Al

KIO4

0.70

0.10

B4C

0.20

39%

8%

--

20%

--

4608

--

80/20 KIO4/Al

KIO4

0.80

0.20

--

44%

4%

0%

9%

0.7%

4578

490

80/20 KIO4/B4C

KIO4
KIO4

0.80
0.80

-0.10

B4C
B4C

44%
44%

10%
20%

2%

3.5%

3903
4946

139

2%

22%
46%

3.9%

80/10/10 KIO4/Al/B4C

-0.20
0.10

60/40 NaIO3/Al

NaIO3

0.60

0.40

--

--

39%

0%

--

0%

--

4881

151

75/25 NaIO3/Al

NaIO3

0.75

0.25

--

--

48%

6%

--

12%

--

5182

--

80/20 NaIO3/Al
80/20 NaIO3/Al (2515 kPa)
85/15 NaIO3/Al
75/5/20 NaIO3/Al/B4C

NaIO3
NaIO3
NaIO3
NaIO3

0.80
0.80
0.85
0.75

0.20
0.20
0.15
0.05

---B4C

---

16%
28%
15%
11%

6%

2.9%

4074
4058
2911
3765

51

1%

30%
54%
28%
23%

11.7%

-0.20

51%
51%
55%
48%

80/5/15 NaIO3/Al/B4C

NaIO3

0.80

0.05

B4C

0.15

51%

26%

1%

51%

1.3%

3592

26

85/5/10 NaIO3/Al/B4C

NaIO3

0.85

0.05

B4C

0.10

55%

28%

1%

51%

0.9%

3219

24

75/10/15 NaIO3/Al/B4C
80/10/10 NaIO3/Al/B4C

NaIO3
NaIO3

0.75
0.80

0.10
0.10

B4C
B4C

0.15
0.10

48%
51%

17%
22%

--

--

3%

35%
43%

5.1%

4014
3997

34

85/10/5 NaIO3/Al/B4C
80/20 NaIO3/B4C

NaIO3
NaIO3

0.85
0.80

0.10

B4C
B4C

0.05
0.20

55%
51%

30%
19%

1%

55%
36%

2.8%

3511
3427

87

65/35 NaIO4/B4C

NaIO4

0.65

B4C

0.35

39%

3%

2%

7%

4.0%

4044

95

70/30 NaIO4/B4C

NaIO4

0.70

---

B4C

0.30

42%

4%

0%

10%

1.1%

4204

72

75/25 NaIO4/B4C
70/20/10 NaIO4/B4C/Al

NaIO4
NaIO4

0.75
0.70

-0.10

B4C
B4C

0.25
0.20

44%
42%

9%
11%

2%

3.4%
--

4468
4932

30

--

20%
28%

80/20 NaIO4/Al

NaIO4

0.80

0.20

--

47%

10%

1%

21%

2.9%

4134

73

80/10/10 NaIO4/B4C/Al
80/20 NaIO4/B4C

NaIO4
NaIO4

0.80
0.80

0.10

B4C
B4C

47%
47%

31%
22%

-5%

66%
47%

--

--

-0.10
0.20

11.5%

5038
4434

55

80/20 I2O5/Al

I 2 O5

0.80

0.20

--

--

61%

55%

1%

90%

1.8%

4414

114

60/40 I2O5/Al

I 2 O5

0.60

--

--

46%

0%

--

0%

--

5789

173

80/20 I2/Al

I2

0.80

0.40
0.20

--

--

80%

0%

--

0%

--

882

--

--

0.05

5%

1%
--

--

1.1%
--

--

9

84

71

21
-13

--

--

--

--

Theoretical iodine (wt%) is iodine content of original mixture; I 2 recovered (wt%) is mass I2 extracted from combustion products (quantification by UV-Vis) relative to original
mix mass; I2 yield /theory is mass of I2 relative to theoretical amount.

59


Table 2.3. Select Parr Calorimetry Results: Effect of Oxidizer/ Fuel Ratio on Iodine and Heat Production

| Mix Info | Oxidizer (mass frac) | Oxidizer (mass frac) | Al 23um (mass frac) | Fuel 2 (mass frac) | Theoretical Iodine tot (wt%) | % I2/g mix | Std Dev | I2 Yield/Theory | Std Dev | Heat Rxn (J/g) | Std Dev |
|----------|----------------------|----------------------|---------------------|-------------------|-----------------------------|------------|---------|-----------------|---------|----------------|---------|
| 85/15 NaIO3/Al | NaIO3 | 0.85 | 0.15 | -- | -- | 55% | 15% | -- | 28% | -- | 2911 | -- |
| 80/20 NaIO3/Al | NaIO3 | 0.80 | 0.20 | -- | -- | 51% | 16% | 6.0% | 30% | 11.7% | 4074 | 51 |
| 75/25 NaIO3/Al | NaIO3 | 0.75 | 0.25 | -- | -- | 48% | 6% | -- | 12% | -- | 5182 | -- |
| 60/40 NaIO3/Al | NaIO3 | 0.60 | 0.40 | -- | -- | 39% | 0% | -- | 0% | -- | 4881 | 151 |
| 80/20 NaIO3/B4C | NaIO3 | 0.80 | -- | B4C | 0.20 | 47% | 22% | 5.5% | 47% | 11.5% | 4434 | 55 |
| 75/25 NaIO3/B4C | NaIO3 | 0.75 | -- | B4C | 0.25 | 44% | 9% | 15% | 1.5% | 20% | 3.4% | 4468 | 30 |
| 70/30 NaIO3/B4C | NaIO3 | 0.70 | -- | B4C | 0.30 | 42% | 4% | 0.4% | 10% | 1.1% | 4204 | 72 |
| 65/35 NaIO3/B4C | NaIO3 | 0.65 | -- | B4C | 0.35 | 39% | 3% | 1.6% | 7% | 4.0% | 4044 | 95 |
| 80/20 Ca(IO3)2/Al | Ca(IO3)2 | 0.80 | 0.20 | -- | -- | 52% | 42% | 0.9% | 81% | 1.8% | 3563 | 208 |
| 75/25 Ca(IO3)2/Al | Ca(IO3)2 | 0.75 | 0.25 | -- | -- | 49% | 36% | 3.4% | 73% | 7.0% | 4491 | 136 |
| 70/30 Ca(IO3)2/Al | Ca(IO3)2 | 0.70 | 0.30 | -- | -- | 46% | 15% | 5.9% | 34% | 12.8% | 4667 | 44 |
| 60/40 Ca(IO3)2/Al | Ca(IO3)2 | 0.60 | 0.40 | -- | -- | 39% | 2% | 0.9% | 5% | 2.2% | 4444 | 147 |
| 85/10/5 NaIO3/Al/B4C | NaIO3 | 0.85 | 0.10 | B4C | 0.05 | 55% | 30% | -- | 55% | -- | 3511 | -- |
| 85/10/5 NaIO3/Al/B4C | NaIO3 | 0.85 | 0.05 | B4C | 0.10 | 55% | 28% | 0.5% | 51% | 0.9% | 3219 | 24 |
| 80/10/5 NaIO3/Al/B4C | NaIO3 | 0.80 | 0.10 | B4C | 0.10 | 51% | 22% | 2.6% | 43% | 5.1% | 3997 | 34 |
| 80/5/15 NaIO3/Al/B4C | NaIO3 | 0.80 | 0.05 | B4C | 0.15 | 51% | 26% | 0.7% | 51% | 1.3% | 3592 | 26 |
| 75/10/15 NaIO3/Al/B4C | NaIO3 | 0.75 | 0.10 | B4C | 0.15 | 48% | 17% | -- | 35% | -- | 4014 | -- |
| 75/20 NaIO3/Al/B4C | NaIO3 | 0.75 | 0.05 | B4C | 0.20 | 48% | 11% | 1.4% | 23% | 2.9% | 3765 | 13 |
### Table 2.4. XPS on Combustion Products- 2 g Iodates with Al in Bomb Calorimeter (Argon)

| Combustion Product | Oxidizer | % I | % Al | I3d5/2 | I3d3/2 | O1s | Al2p | Al2p | N1s | Ca2p3/2 | Ca2p1/2 | Na1s | K2p3/2 | Bi4f5/2 | Bi4f7/2 | Corrections | Type |
|--------------------|----------|-----|-----|--------|--------|-----|------|------|-----|--------|--------|------|--------|--------|--------|-------------|------|
| Mix 60 Ca(IO3)2  | 80       | 20  | 619.6 | 630.0  | 531.0 | 74.0 | 347.2 | 350.9 | -0.91 Ca2p3/2 CaO3 |
| Mix 78 Ca(IO3)2  | 60       | 40  | 618.7 | 630.2  | 531.5 | 74.2 | 347.2 | 350.9 | -0.91 Ca2p3/2 CaO3 |
| Mix 54 | O2O5  | 80       | 20  | 619.9 | 631.4 | 532.4 | 75.5 | 0.57 Al2p AlI3 |
| Mix 95 | O2O5  | 60       | 40  | 619.1 | 630.6 | 532.8 | 75.4 | 0.36 Al2p AlI3 |
| Mix 97 | Na(IO3)3 | 80     | 20  | 619.4 | 630.9 | 531.8 | 75.1 | 164.6 | 159.3 | 0.22 Bi4f5/2 BiI3 |
| Mix 116 Bi(IO3)3 | 60       | 40  | 619.4 | 630.9 | 533.0 | 75.6 | 164.6 | 159.3 | -0.01 Bi4f5/2 BiI3 |
| Mix 55 | K2O3  | 80       | 20  | 619.3 | 630.8 | 530.1 | 73.2 | -0.17 K2p3/2 KI |
| Mix 115 | K2O3  | 60     | 40  | 619.3 | 630.8 | 530.8 | 73.9 | 293.1 | -0.94 K2p3/2 KI |
| Mix 53 | Na(IO3)  | 80     | 20  | 619.2 | 630.7 | 531.2 | 73.9 | 1071.9 | -1.12 Na1s NaI |
| Mix 114 | Na(IO3)  | 60     | 40  | 618.8 | 630.3 | 530.1 | 73.6 | 1071.9 | -1.48 Na1s NaI |

#### Standards

| Product        | Oxidation State | I- | O-2 | Al3+ | N3- | Ca2+ | Na+ | K+ | Bi3+ |
|----------------|-----------------|----|-----|------|-----|------|-----|----|------|
| Al             |                 | 531.3 | 74.0 | 71.3 |     |      |     |    |      |
| Al heated in Air |                | 531.3 | 74.2 |     |     |      |     |    |      |
| Al heated in N2 |                 | 531.3 | 73.7 | 396.7 |     |      |     |    |      |
| CaO3           |                 | 531.5 |     |      |     |      |     |    |      |
| CaI3           |                 | 531.4 |     |      |     | 347.2 | 350.8 |    |      |
| Si             |                 | 531.3 |     |      |     |      |     |    |      |
| Si heated in Air |                | 531.3 |     |      |     | 293.1 |     |    |      |
| Si heated in N2 |                | 531.3 |     |      |     | 293.1 |     |    |      |
| NaI            |                 | 619.3 | 630.7 | 532.8 | 75.4 |      |     |    |      |
| NaI heated in Air |            | 619.3 | 630.7 | 532.5 | 75.6 |      |     |    |      |
| NaI heated in N2 |            | 619.3 | 630.7 | 532.8 | 75.4 |      |     |    |      |
| NaI heated in O2 |            | 619.3 | 630.7 | 532.8 | 75.4 |      |     |    |      |
| NaI heated in N2 |            | 619.3 | 630.7 | 532.8 | 75.4 |      |     |    |      |

**Combustion and Qualitative Analysis of Peak Binding Energy (eV)**

| Product | Oxidizer | % I | % Al | I3d5/2 | I3d3/2 | O1s | Al2p | Al2p | N1s | Ca2p3/2 | Ca2p1/2 | Na1s | K2p3/2 | Bi4f5/2 | Bi4f7/2 | Corrections | Type |
|---------|----------|-----|-----|--------|--------|-----|------|------|-----|--------|--------|------|--------|--------|--------|-------------|------|
| Mix 60  | Ca(IO3)2 | 80  | 20  | 619.6 | 630.0 | 531.0 | 74.0 | 347.2 | 350.9 | -0.91 Ca2p3/2 CaO3 |
| Mix 78  | Ca(IO3)2 | 60  | 40  | 618.7 | 630.2 | 531.5 | 74.2 | 347.2 | 350.9 | -0.91 Ca2p3/2 CaO3 |

**Corrections**

-0.91 Ca2p3/2 CaO3
Table 2.5. XPS Elemental Analysis of Combustion products of Iodate Salts with Aluminum and Standards

| Product | Oxidizer | % I | % O | % Al | % N | % Ca | % Na | % K | % Bi | Sum |
|---------|----------|-----|-----|------|-----|------|------|-----|------|------|
| Mix 60  | Ca(IO3)2 | 80  | 20  | 4    | 60  | 32   | 3    | 100 |      |      |
| Mix 78  | Ca(IO3)2 | 60  | 40  | 15   | 53  | 26   | 7    | 100 |      |      |
| Mix 54  | I2O5     | 80  | 20  | 2    | 59  | 40   |      | 100 |      |      |
| Mix 95  | I2O5     | 60  | 40  | 8    | 60  | 32   |      | 100 |      |      |
| Mix 97  | Bi(IO3)3 | 80  | 20  | 8    | 56  | 34   | 2    | 100 |      |      |
| Mix 116 | Bi(IO3)3 | 60  | 40  | 17   | 58  | 24   | 2    | 100 |      |      |
| Mix 55  | K(IO3)   | 80  | 20  | 17   | 40  | 25   | 19   | 100 |      |      |
| Mix 115 | K(IO3)   | 60  | 40  | 16   | 42  | 26   | 16   | 100 |      |      |
| Mix 53  | Na(IO3)  | 80  | 20  | 17   | 41  | 22   | 20   | 100 |      |      |
| Mix 114 | Na(IO3)  | 60  | 40  | 10   | 51  | 31   | 8    | 100 |      |      |

| Standards | | | | | | | | | |
| Bi(IO3)3  | | 22  | 68  | 10  | 100 | | | | |
| Al        | | 62  | 38  | 0   | 100 | | | | |
| Al heated in Air | | 62  | 38  | 0   | 100 | | | | |
| Al heated in N2 | | 36  | 43  | 21  | 100 | | | | |
| Al2O3     | | 63  | 37  | 100 | | | | | |
| CaO       | | 74  | 26  | 100 | | | | | |
| CaI2      | | 54  | 26  | 21  | 100 | | | | |
| AlI3      | | 15  | 58  | 27  | 100 | | | | |
| NaI       | | 53  | 47  | 100 | | | | | |

The SDT allowed observation of heat released or absorbed concomitant with weight loss in the iodine-containing samples during heating as opposed to burning with fuel. Table 6 summarizes the observations when these fresh samples were heated in unsealed SDT pans. Table 7 analyzes the remaining solid products produced from the reactions outlined in Table 6 although the actual residue was collected from the bomb calorimetry experiments (Table 2). Neat I₂O₅ decomposed at ~438 °C and did not appear to react with aluminum (Figure S4). With or without fuel, both sodium and potassium periodate exothermically reduced to the iodate; for NaIO₄ at ~312 °C and for KIO₄ at ~350 °C. After that the thermal scans of both salts were identical to those of
their respective iodates [12]. Sodium iodate melts at ~422 °C and decomposes to oxygen and the iodide salt NaI ~600 °C; while potassium iodate undergoes a melt with decomposition to KI at ~550 °C. These changes are endothermic. If aluminum alone is the fuel, the formation of NaI occurs 50 °C earlier at 550 °C, but that of KI remains at 550 °C and both decompositions remain endothermic. When boron carbide was present alone or with aluminum, the reaction at 550 °C for both NaIO3 and KIO3 became extremely exothermic (1700 to 2400 J/g) with sodium salt being more energetic than potassium salt. Evidence for KI formation in these boron carbide mixtures was seen by the presence of its melt at 673 °C and evaporation at 750 °C. Comparable evidence of NaI in the boron carbide mixtures was not observed. Boron carbide reacted with the alkali iodates at temperatures (i.e. ~550 °C) much lower than it reacted with air (~770 °C). However, if aluminum alone was the fuel, then NaI and KI melts were observed; the latter, KI at ~676 °C, separated from the Al melt. NaI and Al both exhibit endotherms near 650 °C. This endotherm was interpreted as the melt of NaI if continued heating resulted in significant weight loss. When Al was heated with no added salt it exhibited a neat melting endotherm at 650 °C, but also an exotherm near 850 °C, which we interpret as the formation of AlN. This exotherm was also observed when Al was the only fuel combined with sodium or potassium iodates/periodates. If aluminum was heated in air, the exotherm is observed much earlier just above 600 °C, and was interpreted as the formation of Al2O3. For the iodates equation 2 can be broken into several steps where M is either sodium or potassium cation:

\[ \text{MIO}_3 + 2 \text{Al} \rightarrow \text{MI} + 2 \text{Al} + 3/2 \text{O}_2 \rightarrow \text{Al}_2\text{O}_3 + \text{MI} \]  \hspace{1cm} (4)
While NaI and KI have been identified from the DSC melt and XPS examination of the combustion products, we know also from the basicity of the combustion products and presence of molecular iodine that equation 1 is also operative [12,14]. The sodium and potassium salts show an increase in iodine production when boron carbide, rather than aluminum, was used as the fuel (Figures 12 and 13).

Bismuth triiodate, upon heating, exhibited two modest endotherms at 550 °C and at 579 °C [4,15]. These are assigned as the stepwise oxidation of bismuth iodate to the oxide Bi₂O₃ with release of I₂ (eq. 5, 6). Indeed there was also one small endotherm at 817 °C, the melting point of Bi₂O₃ [16].

\[
5\text{Bi(IO}_3\text{)}_3 \rightarrow \text{Bi}_5\text{O}_7\text{I} + 7\text{I}_2 + 19\text{O}_2 \quad (5)
\]

\[
2\text{Bi}_5\text{O}_7\text{I} + \text{O}_2 \rightarrow 5\text{Bi}_2\text{O}_3 + \text{I}_2 \quad (6)
\]

When aluminum was added the two endotherms were visible at slightly lower temperatures, 528 °C and 566 °C (accompanied by ~40% weight loss), and an exotherm near the melting point of aluminum (641°C) appeared. There is little heat released at this exotherm and almost no weight loss (Table 6). This cannot be explained by a direct reaction of Bi₂O₃ with Al. When reagent grade Bi₂O₃ and Al were examined under the same experimental conditions, no reaction was observed until the oxide melted (814 °C). The combustion of bismuth triiodate with aluminum in a sealed vessel under argon yielded a black product that exhibited only one endotherm at ~365 °C. This melt as well as its UV-Vis spectrum confirmed this product as BiI₃ (m.p. 390 °C) [6,16]. Indeed, little molecular iodine was produced if the combustion was in an inert atmosphere. Unlike the alkali iodate salts, less, rather than more, molecular iodine was
produced when the bismuth or calcium iodates were burned with boron carbide rather than aluminum (Table 2).

Calcium iodate, like the bismuth iodate, exhibited two modest endotherms at 656 °C and 736 °C. The first endotherm is ascribed to the decomposition of Ca(IO₃)₂ to Ca₅(IO₆)₂, iodine and oxygen and the second endotherm to the complete oxidation of the calcium salt to calcium oxide with further generation of iodine and oxygen [12,17]. When aluminum is mixed with the calcium iodate, where the decomposition of Ca(IO₃)₂ and melt of aluminum coincide at 650 °C, an exothermic reaction occurs which forms both calcium and aluminum oxide as well as iodine (Table 6). The formation of calcium oxide is claimed based on the basicity of the combustion product (from closed bomb calorimetry in argon) from the 80/20 Ca(IO₃)₂/Al mixture (pH 11), the ratio of elements in the XPS (Table 5, mix 60); and the fact that when the residue from the combustion was examined by SDT, neither endotherms nor exotherms were observed and weight loss was only 6%. These combustion products were shown by titration to form 11% CaO (assuming this is the product). Some XRD peaks characteristic of γ-Al₂O₃ were observed in the 80/20 Ca(IO₃)₂/Al combustion products, but no good matches for a particular iodide (although some peaks match for CaI₂•6.5H₂O). If aluminum was introduced into the calcium iodate in excess, e.g. 60/40 Ca(IO₃)₂/Al, then the DSC/SDT scan of the product mixture showed an endotherm at 652 °C, characteristic of the melt of excess aluminum. XRD peaks of these products match γ-Al₂O₃ and more closely with CaI₂•6.5H₂O than the products of the 80/20 Ca(IO₃)₂/Al mix (Figure 5). Furthermore, the SDT of the combustion products shows a mass loss of 31%, rather than 6%, and the pH was pH 5, instead of 11. These observations along with the great
reduction in produced I$_2$ (42% with 20% Al down to 2% with 40% Al, see Tables 2 and 3) suggest some formation of Al$_2$I$_6$, a Lewis acid. The peak binding energies of the iodine signal from XPS suggests that the combustion products from Ca(IO$_3$)$_2$/Al (both 80/20 and 60/40) as well as other iodate/Al mixtures, contain iodine present as iodide (Table 4). [A similar trend was observed when combustion products from a 60/40 I$_2$O$_5$/Al mixture were analyzed on DSC/SDT, with a mass loss at 300 °C of 21%. No I$_2$ was observed from the extraction of the mixture with KI solution (and pH of the water solution was 4), which also suggests the formation of Al$_2$I$_6$.]
Table 2.6. SDT Scans of Various Iodates and Fuels (20 °C/min, 3-5 mg in N₂ unless otherwise stated)

| wt% / material | °C | J/g | wt% / loss | °C | J/g | wt% / loss | °C | J/g | wt% / loss | °C | J/g |
|----------------|----|-----|------------|----|-----|------------|----|-----|------------|----|-----|
| NaIO₃ | 100 | 553 | 747 | -25 | 676 | 76 | 0 | 847 | 323 | -68 |
| NaIO₃/Al | 80/20 | 551 | 363 | -15 | 654 | 47 | 0 | 865 | 40 | 0 | 850 | -48 | -860 | -59 | 3 |
| NaIO₃/Bi₂O₃ | 80/10/10 | 570 | 862 | -25 | 653 | 11 | 0 | 672 | 38 | 0 | 850 | -46 | -900 | -87 | 0 |
| KIO₃ | 100 | 566 | -1106 | -26 | 673 | 23 | 0 | 750 | -40 |
| KIO₃/Al | 80/20 | 551 | 363 | -15 | 654 | 47 | 0 | 865 | 40 | 0 | 850 | -48 | -860 | -59 | 3 |
| KIO₃/Bi₂O₃ | 80/10/10 | 570 | 862 | -25 | 653 | 11 | 0 | 672 | 38 | 0 | 850 | -46 | -900 | -87 | 0 |
| Bi₂O₃/Al | 80/20 | 552 | 311 | -12 | 655 | 30 | 0 | 677 | 35 | 0 | 862 | 195 | 40 |
| Bi₂O₃/Bi₂O₃ | 80/10/10 | 562 | -770 | -19 | 653 | 8 | 0 | 673 | 23 | 0 | 850 | -31 | -900 | -37 | 0 |
| CuIO₃ | 100 | 557 | 738 | -19 | 674 | 18 | 0 |
| CuIO₃/Al | 80/20 | 552 | 24 | -27 | 566 | 101 | -16 | 641 | -196 | 0 |
| CuIO₃/Bi₂O₃ | 80/10/10 | 547 | -49 | -28 | 583 | 31 | -17 | 620 | -90 | 0 |
| Al in N₂ | 200 | -59 | 438 | 840 | -99 | 818 | 6 | -5 |
| Al in air | 80/20 | 656 | 586 | -64 | 736 | 329 | -19 |
| Al in air | 75/25 | 646 | -842 | -73 |
| Al in air | 80/10/10 | 657 | -572 | -80 |
| Al in air | 80/20 | 682 | 155 | -53 | 752 | -35 | -14 |
| Al in air | 100 | 656 | -586 | -64 | 736 | 329 | -19 |
| Al in air | 80/20 | 656 | 586 | -64 | 736 | 329 | -19 |
| Al in air | 80/10/10 | 657 | -572 | -80 |
| Al in air | 80/20 | 682 | 155 | -53 | 752 | -35 | -14 |
| Al in air | 100 | 656 | 586 | -64 | 736 | 329 | -19 |
| Al in air | 80/20 | 656 | 586 | -64 | 736 | 329 | -19 |
| Al in air | 80/10/10 | 657 | -572 | -80 |
| Al in air | 80/20 | 682 | 155 | -53 | 752 | -35 | -14 |
| Al in air | 100 | 656 | 586 | -64 | 736 | 329 | -19 |
| Al in air | 80/20 | 656 | 586 | -64 | 736 | 329 | -19 |
| Al in air | 80/10/10 | 657 | -572 | -80 |
| Al in air | 80/20 | 682 | 155 | -53 | 752 | -35 | -14 |
| Al in air | 100 | 656 | 586 | -64 | 736 | 329 | -19 |
Table 2.7. SDT Solid Bomb Combustion Products (20 °C/min, 3-5 mg in N₂ unless otherwise stated)

| wt% | material                  | °C | J/g | wt % loss | °C | J/g | wt % loss | ³C | J/g | wt % loss | XPS                  | pH |
|------|---------------------------|----|-----|-----------|----|-----|-----------|----|-----|-----------|-----------------------|----|
| 80/20| Ca(IO₃)₂/Al               | 300| 652 | 48        | 0  | a   | -6        | Ca²⁺, Al³⁺, I⁻, O²⁻ | 11 |
| 60/40| Ca(IO₃)₂/Al               | 300| 652 | 48        | 0  | a   | -31       | Ca²⁺, Al³⁺, I⁻, O²⁻ | 5  |
| 100  | CaI₂ in N₂                | 179| 142 | -7        | -H₂O| 783 | 123       | -38                      |    |
| 100  | CaI₂ in Air               | 177| 104 | -8        | 520| -40 | -70       |                          |    |
| 80/20| NaIO₃/Al                  | 653| 42  | -34       | Na⁺, Al³⁺, I⁻, O²⁻ | 13 |
| 60/40| NaIO₃/Al                  | 656| 28  | -46       | Na⁺, Al³⁺, I⁻, O²⁻ | 6  |
| 100  | NaI in N₂                 | 657| 171 | -100      |                          |    |
| 100  | NaI in Air                | 659| 104 | -93       |                          |    |
| 80/20| KIO₃/Al                   | 681| 31  | -53       | K⁺, Al³⁺, I⁻, O²⁻ | 6  |
| 60/40| KIO₃/Al                   | 680| 28  | -42       | K⁺, Al³⁺, I⁻, O²⁻ | 6  |
| 100  | KI in N₂                  | 681| 64  | -98       |                          |    |
| 100  | KI in Air                 | 682| 108 | -96       |                          |    |
| 80/20| Bi(IO₃)₃/Al               | 365| 39  | -44       | b  | Bi³⁺, Al³⁺, I⁻, O²⁻ | 4  |
| 60/40| Bi(IO₃)₃/Al               | 320| 8   | -23       | 648| 10  | 0         | Bi³⁺, Al³⁺, I⁻, O²⁻ | 4  |
| 100  | BiI₃ in N₂                | 390| 199 | -100      | b  | Bi³⁺, Al³⁺, I⁻, O²⁻ | 4  |
| 100  | BiI₃ in Air               | 379| 136 | -97       | b  | Bi³⁺, Al³⁺, I⁻, O²⁻ | 4  |
| 80/20| I₂O₅/Al                   | 300| 21  | 648       | 16 | 0   | c         | -24 Al³⁺, I⁻, O²⁻ | 6  |
| 60/40| I₂O₅/Al                   | 300| 21  | 648       | 16 | 0   | c         | -24 Al³⁺, I⁻, O²⁻ | 6  |
| 100  | AlI₃ in N₂                | 190| 19  | -18       | 235| 16  | -58       | 649| 5   | 0         | Al³⁺, I⁻, O²⁻ | 4  |
| 100  | AlI₃ in Air               | 150| 84  | -43       | 238| -524| -29       |                          |    |

a. CaI₂ melt at 783°C was not observed; b. DSC melt & UV-Vis suggests BiI₃; c. AlI₃ observed when aluminum in excess.
Figure 2.5. XRD of combustion products of 80/20 Ca(IO$_3$)$_2$/Al (left) and 60/40 Ca(IO$_3$)$_2$/Al (right)

The occurrence of iodides in combustion products of Ca(IO$_3$)$_2$/Al and I$_2$O$_5$/Al, was confirmed by LC/MS of methanol and water extracts. Methanol extracts of 60/40 Ca(IO$_3$)$_2$/Al combustion products showed peaks consistent with CaI$_2$ (dominant) and Al$_2$I$_6$ (peaks of which were more prominent in methanol compared to water extracts, Figure S95), where methanol extracts of 80/20 Ca(IO$_3$)$_2$/Al combustion products showed peaks consistent with only CaI$_2$ (Figure 6). Similar peaks were observed in a standard methanol solution of 50/50 CaI$_2$/Al$_2$I$_6$. However, adding CaO to an aqueous or methanol standard solution of Al$_2$I$_6$ showed a decrease in Al$_2$I$_6$ signals, and the formation of CaI$_2$, suggesting that moisture might adversely affect the composition of the products if they contained a mixture of CaO and Al$_2$I$_6$ (Figure 7), promoting the
formation of CaI₂. LC/MS of the water extract of 60/40 I₂O₅/Al combustion products shows peaks consistent with Al₂I₆ (Figure 8), but they were not observed in the 80/20 I₂O₅/Al combustion products. What is also interesting to note, is that the extract of a fresh mixture of 80/20 I₂O₅/Al produced LC/MS peaks consistent with known hydration products of I₂O₅ (IO₃⁻ from HIO₃, and I₂O₅•IO₃⁻ from I₂O₅•HIO₃) [11]. The methanol extract of fresh 80/20 Ca(IO₃)₂/Al did not contain any identifiable peaks (Figures 6 and 8).

Figure 2.6. LC/MS of the Methanol Extract of 60/40 Ca(IO₃)₂/Al Combustion products
Figure 2.7. LC/MS of extracts of CaO and Al\textsubscript{2}I\textsubscript{6}
Impact, friction, and electrostatic discharge (ESD) sensitivity tests were conducted on the mixtures of Ca(IO₃)₂/Al because this mixture shows the most promise to be included in final formulations with polymers. Compared with RDX, this mixture is not sensitive to friction or impact, but does have a similar and sometimes more sensitive response than RDX to ESD (Table 8). Adding a binder did not change the impact or friction sensitivity, and seemed to improve the ESD sensitivity.
Table 2.8. Sensitivity Testing

| Composition | % | % Al | BOE Impact $H_{50}$ (cm) | BAM Friction TIL 1/6 (N) | ESD TIL 0/20 (J) |
|-------------|---|------|--------------------------|--------------------------|------------------|
| RDX         | 100 | 0    | 21.9                     | 120                      | 0.074            |
| Ca(IO$_3$)$_2$ (-325mesh) Al (23um Obron) | Ca(IO$_3$)$_2$ | 75 | 25 | >75 | 360 | 0.085 |
| Ca(IO$_3$)$_2$ (-325mesh) Al (23um Obron) | Ca(IO$_3$)$_2$ | 90 | 10 | >75 | 360 | 0.074 |
| Ca(IO$_3$)$_2$ (-325mesh) Al (23um Obron) | Ca(IO$_3$)$_2$ | 95 | 5 | >75 | >360 | 0.045 |
| Ca(IO$_3$)$_2$ (-325mesh) Al (23um Obron) + 20% Polyurethane Foam (50-100mesh) | Ca(IO$_3$)$_2$ | 72 | 8 | >75 | >360 | 0.19 |

4 Conclusions

As a replacement for I$_2$Os, calcium iodate [Ca(IO$_3$)$_2$] was unique among the iodine-containing salts examined (sodium, potassium, calcium and bismuth iodates and periodates of the alkali metals). When combusted with aluminum under argon, Ca(IO$_3$)$_2$ released the most molecular iodine and trapped the smallest amount of iodine as an iodide salt in an 80/20 mix with aluminum. In this mixture, calcium iodate reacted exothermically but did not release as much heat as some of the other iodate salts. More heat could be obtained by increasing the amount of aluminum, but this would have been at the cost of some molecular iodine. When 60/40 mixtures of I$_2$Os/Al or Ca(IO$_3$)$_2$/Al were combusted, little or no molecular iodine was recovered. This and other evidence (SDT, XPS, XRD, LC/MS) suggested that with excess aluminum, aluminum triiodide (Al$_2$I$_6$) may have been formed from a reaction of the unburned aluminum and free iodine in this inert atmosphere. It has been reported that the completeness of reaction of a stoichiometric mixture of I$_2$Os/Al is pressure dependent (at pressures less than atmospheric). The reaction forms more Al$_2$O$_3$ rather than Al$_2$I$_6$ as atmospheric pressure
is approached [18]. We have studied 80/20 Ca(IO₃)₂/Al, Bi(IO₃)₃ /Al, and NaIO₃/Al at both 515 kPa (60 psig) and 2515 kPa (350 psig) pressures (Table 2) to determine if the reaction can be driven to produce more molecular iodine. Interestingly, 80/20 Bi(IO₃)₃/Al produced very little free iodine (possibly further combination of Bi + I₂); 80/20 Ca(IO₃)₂/Al produced slightly more iodine (45% vs. 42%); and 80/20 NaIO₃/Al produced considerably more iodine (28% vs. 16%). The increase in iodine produced from 80/20 NaIO₃/Al would likely be coming from further oxidation of NaI.

Table 9 summarizes the reactions observed with the various iodate and periodate salts. The production of molecular iodine is opposed by both the potential for the original cation (Na⁺, K⁺, Ca²⁺, Bi³⁺) as well as the aluminum to form the iodide salts. Aluminum preferentially forms the oxide if there is sufficient oxygen available in the mixture, but the alkali ions preferentially form the iodide (MI), reducing molecular iodine formation. Calcium and bismuth form oxides, but bismuth oxide undergoes a metathesis reaction with aluminum to form, ultimately, bismuth iodide, which probably forms through elemental bismuth reacting with elemental iodine. In aluminum heavy mixtures, calcium iodate may form calcium iodide and aluminum iodide, although it is difficult to tell the difference between having calcium oxide and aluminum iodide in the products (with post reaction with moisture to form CaI₂•6.5H₂O), or having a mixture of calcium and aluminum iodides. In general, excess aluminum reduces I₂ formation.

The fact that more molecular iodine is released when there is more oxygen available to the fuels indicates that most of the metals would rather be oxides than iodides. This is supported by the Gibbs free energy and enthalpy of oxidation of iodide salts to metal oxides (Table 10). The oxidation of the alkali iodide salts is endothermic,
with a positive Gibbs free energy suggesting that they are less likely to produce iodine gas than the other iodide salts listed. The oxidation of the alkali earth iodides, aluminum iodide, and bismuth iodide is exothermic, with a negative Gibbs free energy suggesting release of iodine to be more favorable than that of the alkalis. All the iodide salts (KI, NaI, CaI$_2$, BiI$_3$, and Al$_2$I$_6$) were run on SDT under air as well as under nitrogen. Under air, calcium iodide and aluminum iodide produced traces with small exotherms and large mass losses. In contrast, under nitrogen, calcium iodide showed no decomposition as heat flow and mass loss below its melting point, and aluminum iodide produced an endotherm during its melt with some significant mass loss (moderate sublimation). These differences suggest significant oxidation in air for these two salts. The sodium, potassium, and bismuth iodide salts showed little difference between air and nitrogen, with their melts accompanying almost total mass loss, which is presumed to be mostly sublimation (Table 7).

Table 2.9. Reactions of Iodine-Containing Salts with 20% Al in Argon
(observed dominant products are highlighted)

| Reaction | Products |
|----------|----------|
| MIO$_3$ + Al $\rightarrow$ Al$_2$O$_3$ Al$_2$I$_6$ MI MO I$_2$ |
| I$_2$O$_5$ + Al $\rightarrow$ Al$_2$O$_3$ I$_2$ |
| NaIO$_4$ $\downarrow$ NaIO$_3$ + Al $\rightarrow$ Al$_2$O$_3$ + NaI + Na$_2$O + I$_2$ |
| KIO$_4$ $\downarrow$ KIO$_3$ + Al $\rightarrow$ Al$_2$O$_3$ + KI + K$_2$O + I$_2$ |
| Ca(IO$_3$)$_2$ + Al $\rightarrow$ Al$_2$O$_3$ + CaO + I$_2$ |
| Bi(IO$_3$)$_3$ + Al $\rightarrow$ Al$_2$O$_3$ + Bi + BiI$_3$ + Bi$_2$O$_3$ + I$_2$ |
The potential for molecular iodine to be released may depend on the relative oxophilicity of aluminum relative to the cation accompanying the iodate (Table 10). This would especially be important in oxygen deficient situations such as experiments performed under inert atmosphere. With insufficient oxygen the iodide may be formed instead. We believe this to be the case with bismuth iodate, due to the favorable reaction between bismuth oxide and aluminum, which frees up bismuth for a reaction with iodine. Because the reaction of some metal oxides (calcium and magnesium) with aluminum is not as favorable, it is likely that excess aluminum in this case would react with iodine directly in an oxygen deficient environment.

We have noted that use of a combination of boron carbide (B₄C) and aluminum as fuels resulted in more iodine formation from the alkali iodates than the use of either fuel alone (Table 2). The exact nature of the reactions have not been ascertained. Boron carbide has been examined by bomb calorimetry, and diboron trioxide and carbon dioxide were formed [19,20].

\[
B_4C + 4O_2 \rightarrow 2B_2O_3 + CO_2 \quad (7)
\]
Furthermore, the combustion products of boron with potassium nitrate and potassium perchlorate under argon were found to be $\text{KB}_5\text{O}_8\cdot4\text{H}_2\text{O}$ and $\text{KB}_5\text{O}_6(\text{OH})_4\cdot2\text{H}_2\text{O}$, respectively [21]. The authors of that article speculate that reaction 8 occurs:

$$2\text{KClO}_4 + 2\text{B} \rightarrow 2\text{KBO}_2 + \text{Cl}_2 + 2\text{O}_2 \quad (8)$$

Using that model we suggest a similar reaction (eq 9). Indeed, over time a boron carbide mixture with sodium iodate evolved molecular iodine at room temperature. Perhaps the reason the combination fuel Al/B$_4$C results in higher amounts of evolved I$_2$ can be attributed to the alkali metal being removed from the competition with aluminum for the freed oxygen. Thus, both the alkali metal and the aluminum are incorporated in a stable species allowing molecular iodine to be evolved.

$$4\text{KIO}_3 + \text{B}_4\text{C} \rightarrow 4\text{KBO}_2 + \text{CO}_2 + 2\text{I}_2 + \text{O}_2 \quad (9)$$

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MANUSCRIPT 3

CORRELATION OF EXPLOSIVE PROPERTIES OF
FUEL/OXIDIZER MIXTURES

by

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Abstract

As seen in multiple cases, including the Boston Marathon bombing, improvised explosives may be as simple as a fuel/oxidizer (FOX) mixture initiated by a hot wire. The knowledge of large scale explosive potential of fuel/oxidizer (FOX) mixtures is incomplete. Predicting this explosive potential from small scale test data is desirable. Herein the explosive properties of fuel/oxidizer mixtures (FOX) were measured at both the small scale (2 g) with bomb calorimetry and large scale (5 kg) with high speed photography and pressure probe. Properties measured at the small scale such as the energy and pressure of reaction were compared to detonation velocity and air blast TNT equivalence measured at the large scale and predictions by Cheetah thermochemical code.
1 Introduction

Hundreds of years ago the field of energetic materials began with the creation of a fuel-oxidizer mixture of charcoal, sulfur, and potassium nitrate, which became known as black powder [1]. Within the last century the fuel-oxidizer mixture of ammonium nitrate and fuel oil (ANFO) became popular as a commercial blasting agent [2] and later as a terrorist tool [2,3]. In the intervening period, the discovery of nitration resulted in a number of high-density organic molecules—nitrate esters, nitroarenes, nitramines. Because these molecules have become the basis of military weaponry much effort has been expended in modeling their detonation performance. Fuel/oxidizer (FOX) mixtures, when examined by the same protocols, have been termed “non-ideal” explosives because the models usually over-predict performance. Nevertheless, it has become imperative that we understand FOX mixtures since their ease of creation—simply mixing a fuel and oxidizer together—has made them a common choice in illicit bombing.

We have previously reported a series of 11 oxidizers and 13 fuels examined by differential scanning calorimetry (DSC), simultaneous DSC/TGA (SDT), and by open burn. DSC is usually the first step in evaluating the energy content of an energetic formulation because the technique can use less than a milligram of material. In preparing the fuel/oxidizer DSC samples, great care was taken to make the samples homogeneous. Nevertheless, the DSC traces were difficult to interpret due to the small size of the prepared batches and the presence of multiple thermal events [4]. Herein we report a re-investigation of these and other FOX mixtures using isoperibol calorimetry—a Parr bomb-recording heat release and dynamic pressure rise of 2 gram samples during reaction under argon. Initiation of detonation of select formulations was attempted on
the pound-scale (~10 lb FOX with 1 lb C4 Military Explosive), and data was recorded by high-speed photography and pressure transducer.

2 Experimental Section

2.1 Sample Preparation for Bomb Calorimetry with Pressure Transducer, DSC, and SDT

The fuels chosen were sucrose from Fisher Scientific, 23 μm flake coated aluminum powder from Obron, and a 5 μm magnesium powder from Firefox. Oxidizers were ground and sieved 100-200 mesh (150-75 μm). Sucrose was ground with a small coffee grinder and sieved 100-200 mesh or 150-75 μm. Fuel/oxidizer (FOX) mixtures were prepared as dry loose powders placed in plastic pop-top containers, for differential scanning calorimetry (DSC) samples in 500 mg batches and for bomb calorimetry as individual 2 g samples. Mixing was then conducted with a Resodyn Lab Ram acoustic mixer at 35 - 40 G acceleration for 2 min. Individual DSC samples ~0.25 mg were taken from the 500 mg batch. Sample preparation for SDT was similar, but with sample sizes of 4 to 6 mg.

2.2 Differential Scanning Calorimetry (DSC)

Samples were flame sealed (~0.25 mg) in glass capillaries (borosilicate, 0.06 in. ID, 0.11 in OD) on a metal post cooled by liquid nitrogen to prevent decomposition during sample preparation. Scans were conducted at a ramp rate of 20 °C/min on a TA Q100 DSC. The temperature range was usually 30 °C to 450 °C, and the nitrogen flow rate was set to 50 mL/min. The temperature was calibrated by running indium with a melting point of 156.6 °C. This technique was chosen for oxidizer / sucrose mixtures
because exotherms of these mixtures typically fall within the temperature limits of the instrument.

2.3 Simultaneous DSC/TGA (SDT)

A TA Q600 simultaneous DSC/TGA was used to run samples of 4-6 mg in open aluminum oxide pans, and scanned at 20 °C/min under 100 mL/min nitrogen flow. The temperature was calibrated by running Zinc with melting point of 419.5 °C. The temperature range was usually 50 °C to 1000 °C. Oxidizer / aluminum mixtures were analyzed with this technique due to exotherms appearing at higher temperatures than the DSC limits.

2.4 Bomb Calorimetry with Pressure Transducer

Heat output and pressure/time curves were determined using a Parr 6200 calorimeter and Parr 1108 bomb, fitted with a pressure transducer (Parr 6976 pressure recording system, including a 5108A Kistler piezoelectric coupler, and a 211B2 Kistler piezoelectric pressure transducer with a calibrated sensitivity of 1.096 mV/psi). The Parr bomb was calibrated (i.e. 10 trials) with benzoic acid ignited with fuse wire (9.6232 J/cm) and cotton string (167.36 J) in 2515 kPa oxygen ($\Delta H_{\text{comb}} = 26434$ J/g). In an oxygen atmosphere, the string was in contact with the fuse wire and sample and was ignited by the fuse wire to aid ignition of the sample. The FOX samples (three to six 2 g samples under each set of conditions) were ignited with a fuse wire under argon (2859 kPa, 400 psig). This pressure represented the maximum initial pressure in which the regulator could handle. It appeared to be a good balance allowing rapid initiation of burn, and minimizing heat losses with the walls of the Parr bomb [5]. With some energetic materials, it has been observed that there is a critical pressure of ignition
associated with a specified input energy [6,7]. Igniting samples at a higher initial pressure is more likely to overcome the critical pressure of the sample. A National Instruments USB-6210 data acquisition card (maximum sample rate of 250 kS/s) and LabView software were used to collect the pressure/time data at a rate of 10 kS/s. This sample collection rate of 100 µs between pressure points was high enough resolution to result in pressure/time plots that appeared continuous on the ms time-scale (see Figures 9 and 10). Figure 1 outlines the protocol followed.

Figure 3.1. Schematic of Protocol for Parr Bomb Calorimetry Tests

2.5 Sample Preparation for Detonation Diagnostics

Sucrose and oxidizers were prepared separately by grinding with a Vita-Mix 5000 blender and sieving each to 100-200 mesh (150-75 µm). The aluminum flake (23 µm) from Obron was used as received. Fuel/oxidizer samples of approximately 5 kg were manually mixed in a 37.9 L (10 gal) plastic bag for about 2 minutes (Figure 2).
For the detonation studies, schedule-40 clear, polyvinyl chloride (PVC) tubes of 4 inch diameter (10.16 cm) were purchased from McMaster Carr in 8 foot lengths and cut to 24 inches (60.96 cm) long. PVC booster cups were assembled by gluing a 4 inch PVC sewer and drain endcap to a 4 inch PVC coupler. Into the booster cup were placed two sheets (30 g) of #2 PETN sheet explosive which had been cut into circle shape to fit tightly into the booster cup. On top of the sheet explosive, C4 (546 g) was packed and then three more circles of the PETN sheet explosive. Booster cups (Figure 3) were taped with duct tape directly to the clear PVC tube so that there was direct contact with the sample mixture. The FOX mixture was added by pouring from the plastic mixing bag, using a kraft paper funnel (Figure 4). The test device was placed in a vertical position (booster end down) on a wooden test stand; the bottom of the test device was 91.4 cm (36 in) from the ground. The detonator was inserted last before initiation from a blasting machine.
2.6 Detonation Diagnostics

Detonation velocity was determined visually using a Phantom V7.11 camera with a frame rate of 66,019 fps, interframe time of 15.15 μs, resolution of 160 X 304 pixels, exposure of 0.4 μs (0.29 μs exposure for aluminum mixtures), 1 s of pre-trigger,
and 1 s of post-trigger. A twisted pair of duplex wire, taped to the detonator, was used as a falling edge camera trigger (i.e. “make” trigger). Phantom PCC 2.8 software was used to process the camera data, tracking the detonation front and setting the distance scaling calibration for each file to obtain a detonation velocity. The detonation front was assumed to be the forward most position of the emitted band of light, following the contribution of the booster (Figure 5). The initiation of the booster produces a significant fire ball, present even in samples that do not detonate, and is defined herein as the “booster cloud” (Figure 5).

Figure 3.5. Illustration of how detonation front was determined to calculate detonation velocity, $D_v$ (Sample shown is 70:30 KClO$_3$:Sucrose)
After using the Phantom PCC 2.8 software to track the scaled detonation front (x,y) in time, a correction was made for the angle of incidence (to align the shot to a vertical position). The following equations for rotating the image were used where (X’,Y’) are the new coordinates:

\[
X' = X \cos(\alpha) - Y \sin(\alpha) \quad (1)
\]
\[
Y' = X \sin(\alpha) + Y \cos(\alpha) \quad (2)
\]

Where \(\alpha\) (Figure 6) is the incident angle from vertical, measured by taking the inverse tangent of two points on the side of the pipe \((X_1, Y_1)\) and \((X_2, Y_2)\):

\[
\alpha = -\tan^{-1}\left(\frac{X_2 - X_1}{Y_2 - Y_1}\right) \quad (3)
\]

If two points are taken from the calibrated coordinate system (i.e. for 70:30 KClO\textsubscript{3}:Sucrose) in mm \((X_1, Y_1) = (89,30)\) and \((X_2, Y_2) = (68,210)\), then \(\alpha = 0.116\) rad, and \(Y'(t)\) can be plotted for each time point (using equation 2) to find the detonation velocity (the slope in Figure 7).

Figure 3.6. Correction for angle (\(\alpha\)) for detonation velocity
Figure 3.7. Detonation front tracking of rotation corrected $Y'$ points. The slope of the curve is the detonation velocity in mm/$\mu$s.

The detonation velocity was taken as the slope of the newly rotated points $Y'(t)$ distance vs. time curve. The distance vs. time curves were linear ($R^2 > 0.99$) for all of the samples that detonated.

A pencil gauge pressure transducer (Kistler 6233A, 25 psi limit, calibrated sensitivity of 200 mV/psi, 5 V limit) with coupler (Kistler 5134B, 0.05 Hz high pass filter, gain of 1) measured blast overpressure. Fifty foot coax cables connected the pencil gauge to the coupler, and coupler to a Tektronix oscilloscope. The pencil gauge was mounted 1.29 m high, positioned 6.096 m (20 ft) from the test device on a wooden stand weighted with sand bags. The Tektronix oscilloscope (model MSO4014B, max bandwidth of 100 MHz) was set with a typical sampling rate between 5-100 MSa/s; it
was automatically triggered on the rising edge of the pressure signal. Figure 8 shows the overall test arena setup.

![Figure 8. Overall Test Arena Setup](image)

2.7 Predictive Tools

Cheetah 7.0 from Lawrence Livermore National Laboratory (product library: sandia, jczs revision 1923) was used to predict detonation velocity, detonation pressure, and total energy of reaction. Each mixture was run with Cheetah using the density that was measured for its large scale test [8].

The blast effects calculator (BEC V5.1) was used to obtain air blast TNT equivalence from the measured peak air blast pressures [9,10,11]. For each experiment, a goal seek method was used with the empirical fits for pressure (as a function of scaled distance, m/kg\(^{1/3}\)) to find the total amount of TNT needed to achieve the same peak pressure. However, the booster also has a contribution to the air blast pressure. This contribution must be subtracted in terms of energy or TNT equivalent weight, not in terms of pressure. An experiment with the booster and sand as the sample (no energy contributed from the sand) allowed the TNT equivalent weight of only the booster to be
calculated with goal seek in the blast effects calculator. The booster TNT equivalent weight from this experiment was subtracted from the total TNT equivalent weight (Table 4) of each test to find the TNT equivalence of the sample (TNT Equivalence = TNT equivalent mass of sample / sample weight).

3 Results

3.1 Parr Bomb Calorimetry

A Parr bomb calorimeter was used primarily to estimate the energy available from FOX mixtures. Combustion was accomplished under argon gas instead of oxygen gas to determine heat of reaction without excess oxygen (Table 1). The calorimeter had been fitted with a pressure transducer to observe the pressure response as a function of time due to reaction. Closed volume pressure measurement is a common tool for propellant applications. Thus, it was possible to compare the response of a number of common gun propellants (Red Dot, Pyrodex, black powder) to FOX mixtures of interest. (Figure 9). In general the propellants exhibit a larger and faster change in pressure, but the FOX mixtures release more heat. Pressure responses of ammonium nitrate and potassium nitrate with sucrose were significantly delayed compared to other FOX (Figure 10). It is interesting to note that KNO₃:sucrose burned slower and with slightly less energy than a similar mixture with added KClO₃ (63:7:30 KNO₃:KClO₃:sucrose); KNO₃:sucrose did not detonate on the large scale but mixtures with added KClO₃ did.
Figure 3.9. Continuous pressure vs. time: fuel:oxidizer mixtures & propellants from 2g 2859 kPa argon
Figure 3.10. Continuous pressure vs time curves of fuel:oxidizer mixtures from 2g 2859 kPa argon. In parentheses the result of the large scale test (D = Detonation; NO = No Detonation). The ammonium nitrate:sugar mixture is so slow that it has its own time axis (above plot).
Table 3.1. Bomb Calorimetry Outputs from Fuel:Oxidizer Mixtures Burned 2g 2859

kPa argon

| Mixture wt,wt | Δ Time (ms) | RSD | Δ Pressure (kPa) | RSD | Δ P/Time (kPa/ms) | RSD | Δ U (kJ/g) | RSD | DSC/SDT |
|---------------|-------------|-----|-----------------|-----|------------------|-----|-------------|-----|---------|
| **Oxidizer, Sucrose** | | | | | | | | | |
| K2Cr2O7, Sucrose 70,30 | 2084 | 29% | 776 | 2% | 0.4 | 29% | 1.14 | 2% | DSC |
| AN, Sucrose 70,30 | 7687 | 10% | 1531 | 9% | 0.2 | 20% | 2.70 | 1% | 1.79 |
| KMnO4, Sucrose 70,30 | 641 | 5% | 1985 | 2% | 3.1 | 3% | 2.07 | 0% | 1.80 |
| KIO3, Sucrose 70,30 | 334 | 13% | 2514 | 3% | 7.6 | 15% | 1.47 | 1% | 0.84 |
| KNO2, Sucrose 70,30 | 509 | 19% | 2702 | 3% | 5.4 | 20% | 2.61 | 3% | 1.69 |
| KNO3, Sucrose 70,30 | 509 | 3% | 3685 | 1% | 7.2 | 3% | 2.81 | 1% | 0.68 |
| KClO3, KNO, Sucrose 70,30 | 703 | 3% | 3605 | 1% | 7.2 | 3% | 2.81 | 1% | 0.68 |
| KClO4, Sucrose 70,30 | 703 | 3% | 3605 | 1% | 7.2 | 3% | 2.81 | 1% | 0.68 |
| **Oxidizer, Al** | | | | | | | | | |
| K2Cr2O7, Al 70,30 | 474 | 7% | 3261 | 6% | 6.9 | 13% | 4.18 | 1% | SDT |
| AN, Al 70,30 | 696 | 21% | 4370 | 14% | 6.5 | 31% | 5.20 | 8% | 2.40 |
| KMnO4, Al 70,30 | 254 | 8% | 5089 | 9% | 20.1 | 10% | 5.31 | 2% | 0.73 |
| KIO3, Al 70,30 | 241 | 38% | 5682 | 8% | 26.6 | 46% | 4.94 | 0% | 0.49 |
| KNO3, Al 70,30 | 403 | 13% | 6307 | 1% | 15.8 | 12% | 5.98 | 3% | 1.30 |
| KIO4, Al 70,30 | 153 | 30% | 8301 | 5% | 58.6 | 38% | 6.32 | 1% | 0.17 |
| KClO4, Al 80,20 | 75 | 19% | 9578 | 5% | 132.6 | 26% | 5.11 | 1% | 0.80 |
| KBrO3, Al 70,30 | 105 | 21% | 10215 | 5% | 100.1 | 23% | 6.53 | 1% | 0.45 |
| AN, Al 70,30 | 195 | 19% | 10367 | 4% | 54.1 | 14% | 7.85 | 0% | 0.64 |
| KClO4, Al 50,50 | 135 | 17% | 11045 | 1% | 84.0 | 19% | 8.22 | 1% | 0.45 |
| KClO3, Al 70,30 | 96 | 11% | 11929 | 5% | 126.3 | 15% | 7.18 | 5% | 1.50 |
| KClO4, Al 70,30 | 78 | 18% | 12272 | 3% | 161.6 | 20% | 7.52 | 1% | 0.74 |
| KClO4, Al 60,40 | 97 | 19% | 12727 | 5% | 136.4 | 22% | 9.36 | 2% | 1.60 |
| AP, Al 70,30 | 81 | 15% | 15813 | 4% | 199.7 | 20% | 9.36 | 1% | 1.60 |
| **Oxidizer, Na Benzoate** | | | | | | | | | |
| KNO3, NaBenzoate 70,30 | 471 | 7% | 3045 | 2% | 6.5 | 8% | 2.25 | 2% | DSC |
| KClO3, NaBenzoate 70,30 | 64 | 6% | 6815 | 2% | 105.8 | 4% | 3.19 | 1% | 1.30 |
| KClO4, NaBenzoate 70,30 | 65 | 25% | 7636 | 2% | 123.8 | 30% | 3.70 | 0% | 0.74 |
| AP, NaBenzoate 70,30 | 490 | 12% | 7814 | 1% | 16.1 | 14% | 4.13 | 2% | 1.60 |
The change in internal energy of the formulations, as judged by the heat of decomposition measured at the sub-milligram-scale by DSC (far right column, Table 1) and heat of reaction observed in the 2 g Parr bomb samples (penultimate right column, Table 1), differ. Heat of reaction (i.e. Parr bomb data) is greater than heat of decomposition, particularly when the fuel is aluminum. However, the aluminum/oxidizer formulations were tested in open pans by SDT where there were ample opportunities for sample evaporation/sublimation, thus heat loss.

A comparison of the same oxidizers with different fuels shows the energy input from the choice of fuel is aluminum > sucrose > sodium benzoate (Table 1). Other fuel/oxidizer mixtures were also examined in the Parr bomb (Table 2). In terms of energy output neither the thermites nor the gun propellants released more energy than the examined FOX mixtures.

Table 3.2. Parr Bomb Calorimetry Output for Thermites vs. Gun Propellants

| Mixture wt,wt | Δ Time (ms) | RSD | Δ Pressure (kPa) | RSD | Δ P/Time (kPa/ms) | RSD | Δ U (kJ/g) | RSD |
|---------------|-------------|-----|-----------------|-----|------------------|-----|------------|-----|
| **Thermites** |
| Fe3O4, Mg 80,20 | 1501 | 9% | 424 | 10% | 0.3 | 19% | 2.12 | 0% |
| Fe3O4, Mg 70,30 | 1322 | 3% | 970 | 7% | 0.7 | 9% | 3.22 | 1% |
| Fe3O4, Mg 60,40 | 1043 | 17% | 1539 | 3% | 1.5 | 16% | 3.73 | 0% |
| Bi2O3, Al 70,30 | 288 | 13% | 1810 | 8% | 6.3 | 4% | 1.75 | 1% |
| Bi2O3, Al 90,10 | 210 | 50% | 2277 | 12% | 12.8 | 46% | 1.61 | 1% |
| Bi2O3, Al 80,20 | 113 | 6% | 2704 | 8% | 23.9 | 13% | 1.90 | 2% |
| **Gun Propellants** |
| BP Meal | 183 | 6% | 4812 | 9% | 26.4 | 13% | 2.83 | 1% |
| BP 07 Mesh | 139 | 9% | 5000 | 3% | 36.1 | 6% | 2.78 | 1% |
| BP 20 Mesh | 127 | 16% | 5033 | 3% | 40.4 | 13% | 2.79 | 2% |
| Pyrodex | 116 | 8% | 5143 | 1% | 44.6 | 9% | 2.87 | 1% |
| Red Dot | 86 | 13% | 9761 | 3% | 115.1 | 15% | 4.40 | 0% |
3.2 Detonation Testing

Table 3 shows FOX mixtures for which initiation of detonation was attempted. Four of the mixtures failed to propagate detonation although the velocity of the burn front is recorded under the velocity of km/s. Figure 11 provides screen captures of the reactions observed. The detonation front was taken to be the bright line running ahead of the booster debris cloud (bottom). A detonation rather than a burn was judged by the rapid PVC wall expansion immediately behind the front. Figure 12 shows KNO₃:sucrose as an example of a mixture which failed to support detonation. Figure 12 also shows KNO₃:aluminum as an example of a mixture where the detonation failed and transited to a rapid burn. In this case the mixture is more flammable than detonable. Figure 13 shows an enlarged picture of three FOX mixtures known to be improvised explosive mixtures which detonated (NH₄NO₃:Sucrose, NH₄NO₃:Al, and KClO₃:Sucrose) and one more example of one which did not detonate (KMnO₄:Sucrose).
Figure 3.11. One frame from video of each FOX mixture tested. Frame was chosen when reaction was about 75% along the 24 inch pipe in order to allow the detonation
front (samples 5 to 16) to be clearly separated from the booster cloud. (D=Detonation, NO=NO Detonation).

Figure 3.12. Comparison of detonation of KNO₃:Sucrose mix spiked with KClO₃ to KNO₃ mixes which failed to detonate. (KNO₃:Al transited to a burn.)
Figure 3.13. Detonation tests showing three steady detonations (left three) and one which failed to propagate (right).

Table 3.3. Detonation Testing Summary

| Mixture               | Mass (kg) | Density (g/mL) | Heat (cal/g) | Heat (kJ/g) | ΔP (psi) | ΔP/Δt (psi/ms) | ΔP (kPa) | ΔP/Δt (kPa/ms) | ΔP/Δt (kJ/g) | Phantom V7.11 Det Velocity (km/s) | Peak Airblast ΔP 20ft (psi) | Peak Airblast ΔP 20ft (kPa) |
|-----------------------|-----------|----------------|--------------|-------------|----------|----------------|----------|----------------|--------------|----------------------------------|-----------------------------|-----------------------------|
| 70:30 KIO3:Sucrose (no Det) | 6.833     | 1.49           | 352          | 1.47        | 365      | 1.11           | 2517     | 7.7            | 0.00         | 7.90                             | 54.43                       |                            |
| 70:30 KNO3:Sucrose (no Det) | 5.216     | 1.10           | 494          | 2.07        | 228      | 0.45           | 1572     | 3.1            | 0.00         | 6.47                             | 44.57                       |                            |
| 70:30 KNO3:Al (no Det) | 4.711     | 0.97           | 672          | 2.81        | 534      | 1.05           | 3682     | 7.2            | 0.67         | 8.20                             | 56.54                       |                            |
| 70:30 KNO3:Al (no Det) | 3.636     | 0.75           | 1428         | 5.98        | 915      | 2.30           | 6307     | 15.8           | 1.67         | 13.10                            | 90.32                       |                            |
| 70:30 KNO3:Al (no Det) | 1.709     | 0.97           | 692          | 2.89        | 570      | 1.72           | 3928     | 11.8           | 1.71         | 14.54                            | 100.25                      |                            |
| 4.704                 | 0.88      | 701            | 2.93         | 607         | 1.27     | 4186           | 8.8      | 1.77           | 12.06        | 83.12                            |                            |                            |
| 5:66:28.5 RDX:KNO3:Sucrose | 4.254     | 1.01           | 815          | 3.41        | 809      | 5.53           | 5778     | 38.1           | 2.24         | 14.97                            | 103.18                      |                            |
| 5:66:28.5 RDX:KNO3:Sucrose | 4.768     | 1.01           | 815          | 3.41        | 809      | 5.53           | 5778     | 38.1           | 2.24         | 14.97                            | 103.18                      |                            |
| 70:30 NH4ClO4:Al       | 3.132     | 0.69           | 2238         | 9.36        | 2293     | 28.97          | 15813    | 199.7          | 2.24         | 16.32                            | 112.49                      |                            |
| 70:30 KClO3:Sucrose    | 4.788     | 0.99           | 967          | 4.05        | 1037     | 10.53          | 7150     | 72.6           | 2.34         | 16.70                            | 115.14                      |                            |
| 70:30 NH4ClO4:Al       | 3.140     | 0.68           | 1876         | 7.85        | 1504     | 7.85           | 10367    | 54.1           | 2.70         | 18.60                            | 128.24                      |                            |
| 70:30 KClO3:Sucrose    | 5.246     | 1.10           | 967          | 4.05        | 1037     | 10.53          | 7150     | 72.6           | 3.07         | 14.80                            | 102.04                      |                            |
| 70:30 NH4ClO4:Al       | 4.121     | 0.87           | 645          | 2.70        | 222      | 0.03           | 1531     | 0.2            | 3.49         | 11.87                            | 81.84                       |                            |
| Flake TNT              | 3.663     | 0.77           | 1093*        | 4.57        | LLNL     | --             | --       | 3.84           | --          | LLNL                            |                            |                            |
| 70:30 NH4ClO4:Sucrose  | 4.662     | 0.98           | 1167         | 4.88        | 1347     | 13.94          | 9287     | 96.1           | 3.89         | 19.30                            | 133.07                      |                            |
| Flake TNT              | 4.003     | 0.81           | 1093*        | 4.57        | LLNL     | --             | --       | 4.50           | 12.73        | 87.76                            |                            |                            |
| 50:35:15 RDX:KNO3:Sucrose | 4.986     | 1.05           | 1013         | 4.24        | 1139     | 5.48           | 7853     | 37.7           | 4.80         | 13.50                            | 93.08                       |                            |
| Booster                | --        | --             | --           | --          | --       | --             | --       | --             | --           | LLNL                            |                            |                            |

~23” x 4” charge; C4 booster=0.546kg; PETN = 0.15 kg; (no Det = no Detonation observed); distance Pressure Trans 20 ft
* LLNL Detonation Calorimeter
4 Discussion

FOX mixtures were chosen to examine three issues: 1) relative detonability of oxidizers as judged from small-scale tests; 2) role of the fuel; and 3) importance of small adjustments in energy input to performance. The FOX mixtures in Table 3 are ordered top to bottom by increasing detonation velocity. Among the FOX mixtures studied, chlorate and perchlorate with sucrose had the highest performance although density variations make it difficult to quantify the extent to which they are superior.

Cheetah, a Lawrence Livermore National Laboratory (LLNL) thermochemical code was used to calculate detonation velocity, Chapman-Jouguet (CJ) pressure, and energies of combustion and detonation at the densities used in the field detonation studies (Table 4). For the FOX formulations with aluminum, the calculated energy of combustion was only slightly higher than that of detonation (Cheetah calculations were run assuming all aluminum reacted.) For the FOX mixtures with sucrose fuel, the combustion energy was about 30% higher than detonation; and for TNT the combustion energy was approximately 4 times as high as the detonation energy. For air blast calculations where TNT equivalence was required, the heat of TNT reaction, rather than combustion, was used. The total heat of detonation calculated from Cheetah correlates linearly with the heat released in the Parr calorimeter (Figure 14). Since it was not feasible to create intact samples of controlled density of the powdery FOX mixtures, it was reassuring that isoperibol bomb calorimetry gave proportional results to detonation calorimetry (heat of detonation of TNT from [12]).
### Table 3.4: Detonation Testing Summary with Analysis

| Mixture                      | Density (g/mL) | Heat (kJ/g) | ΔP (psi) | ΔP/Δt (psi/ms) | Phantom V7.11 Det Velocity (km/s) | Peak Airblast ΔP 20ft (psi) | Mass eq TNT (kg) | TNT Eq | TNT eq booster corrected | Air Blast Energy (kJ/g) | Air Blast Energy Comb (kJ/g) | CJ Pressure (GPa) | Energy Detonation (kJ/g) | Heat Combustion (kJ/g) |
|------------------------------|----------------|-------------|----------|----------------|----------------------------------|-----------------------------|---------------------|--------|--------------------------|-----------------------|-----------------------------|------------------|------------------------|----------------------|
| 70:30 KIO₃:Sucrose (no Det)  | 1.49           | 1.47        | 365      | 1.11           | 0.00                             | 7.90                        | 2.67                | 0.39   | 0.18                     | 0.80                  | 2.5                         | 3.60             | 3.86                  | 1.39                 | 3.92                 |
| 70:30 KMnO₄:Sucrose (no Det) | 1.10           | 2.07        | 228      | 0.45           | 0.00                             | 6.47                        | 1.91                | 0.37   | 0.08                     | 0.38                  | 1.2                         | 2.12             | 1.20                  | 2.83                 | 4.76                 |
| 70:30 KNO₃:Sucrose (no Det)  | 0.97           | 2.81        | 534      | 1.05           | 0.67                             | 8.20                        | 2.84                | 0.60   | 0.29                     | 1.33                  | 4.2                         | 3.04             | 1.94                  | 2.69                 | 3.68                 |
| 70:30 KNO₃:Al (no Det)       | 0.75           | 5.98        | 915      | 2.30           | 1.67                             | 13.10                       | 5.87                | 1.62   | 1.21                     | 0.39                  | 1.33                        | 1.23             | 0.38                  | 7.24                 | 7.83                 |
| 7:63:30 KClO₃:KNO₃:Sucrose   | 0.97           | 2.89        | 570      | 1.72           | 1.71                             | 14.54                       | 6.84                | 1.45   | 1.14                     | 0.52                  | 0.63                        | 3.08             | 0.20                  | 2.78                 | 3.79                 |
| 566:528.5 RDX:KNO₃:Sucrose   | 0.88           | 2.93        | 607      | 1.27           | 1.77                             | 12.06                       | 5.19                | 1.22   | 0.87                     | 3.99                  | 12.6                        | 2.89             | 1.67                  | 2.82                 | 3.94                 |
| 35:35:30 KClO₃:KNO₃:Sucrose  | 1.01           | 3.41        | 809      | 5.53           | 2.24                             | 14.97                       | 7.13                | 1.50   | 1.19                     | 5.42                  | 17.2                        | 3.47             | 3.12                  | 3.14                 | 4.20                 |
| 7:30 NH₄ClO₄:Al              | 0.69           | 9.36        | 2293     | 28.97          | 2.24                             | 16.32                       | 8.07                | 2.58   | 2.11                     | 9.62                  | 30.5                        | 2.75             | 1.72                  | 10.21                | 10.41                |
| 7:30 KClO₃:Sucrose           | 0.99           | 4.05        | 1037     | 10.53          | 2.34                             | 16.70                       | 8.34                | 1.74   | 1.43                     | 6.55                  | 20.8                        | 3.78             | 3.19                  | 3.59                 | 4.17                 |
| 7:30 NH₄NO₃:Al               | 0.68           | 7.85        | 1504     | 7.85           | 2.70                             | 18.60                       | 9.71                | 3.09   | 2.62                     | 11.98                 | 38.0                        | 3.58             | 2.45                  | 9.11                 | 10.32                |
| 7:30 KClO₃:Sucrose           | 1.10           | 4.05        | 1037     | 10.53          | 3.07                             | 14.80                       | 7.02                | 1.34   | 1.06                     | 4.83                  | 15.3                        | 4.23             | 4.99                  | 3.61                 | 4.71                 |
| 7:30 NH₄NO₃:Sucrose          | 0.87           | 2.70        | 222      | 0.03           | 3.49                             | 11.87                       | 5.07                | 1.23   | 0.87                     | 3.99                  | 12.6                        | 4.50             | 4.65                  | 2.64                 | 5.53                 |
| Flaké TNT                    | 0.77           | 4.57        | LLNL     | --             | 3.84                             | --                          | --                  | --     | --                       | --                    | --                          | 4.34             | 3.91                  | 3.42                 | 14.48                |
| 7:30 NH₄ClO₄:Sucrose         | 0.98           | 4.88        | 1347     | 13.94          | 3.89                             | 19.30                       | 10.23               | 2.19   | 1.88                     | 8.58                  | 27.2                        | 4.83             | 6.13                  | 3.93                 | 5.61                 |
| Flaké TNT                    | 0.81           | 4.57        | LLNL     | --             | 4.50                             | 12.73                       | 5.63                | 1.41   | 1.04                     | 4.74                  | 15.0                        | 4.50             | 4.45                  | 3.47                 | 14.48                |
| 50:35:15 RDX:KNO₃:Sucrose    | 1.05           | 4.24        | 1139     | 5.48           | 4.80                             | 13.50                       | 6.14                | 1.23   | 0.94                     | 4.28                  | 13.5                        | 4.83             | 6.20                  | 4.02                 | 6.28                 |

- Clear PVC pipe Shots (4" Dia x 24" L)
- Detonation Testing Calculations
- Cheetah Predictions

- Phantom V7.11 Det Velocity
- Peak Airblast ΔP 20ft
- Mass eq TNT
- TNT Eq
- TNT eq booster corrected
- Air Blast Energy
- Air Blast Energy Comb
- CJ Pressure
- Energy Detonation
- Heat Combustion

* LLNL Detonation Calorimeter

~23" x 4' charge; C4 booster=0.546kg; PETN = 0.15 kg; (no Det = no Detonation observed); distance Pressure Trans 20 ft

* LLNL Detonation Calorimeter
Figure 3.14. Heat of Detonation from Parr Bomb Calorimeter vs Calculated by Cheetah. (Error bars in heat are too small to be seen; Table 1 shows relative standard deviation.)

Observed detonation velocities tracked with the Cheetah predicted detonation velocities. Figure 15 shows the non-detonations (i.e. potassium nitrate formulations) with an X and separates the shots done with aluminum fuel from those done with sucrose and from those done with formulations including high explosives (in red, two TNT shots and one that was 50% RDX).
Figure 3.15. Observed Detonation Velocities (km/s) vs Cheetah Calculation Thereof (X failed to detonate).

Since the heat released measured by calorimetry and detonation velocities measured by camera track with Cheetah predictions, it is not surprising that the measured heat of reaction under argon correlated with observed detonation velocities (Figure 16). Interestingly, the outliers (above the line on both the oxidizer/sucrose and oxidizer/aluminum formulations) are the formulations with ammonium nitrate. Part of this is certainly due to the fact that it is difficult for the sucrose formulation to burn under argon, but this does not explain the AN/Al formulation.
Figure 3.16. Heat of Reaction measured by calorimetry vs. Detonation Velocity. (Error bars in heat are too small to be seen; Table 1 shows relative standard deviation.)

Figure 16 suggests there may be a minimum energy (~2.8 kJ/g) needed for detonation. However, the data as well as detonation theory dictates that energy alone does not guarantee detonation. The rate of energy release by the formulation must be fast enough to support detonation. If we make the rather speculative assumption that the rates of all the oxidizer/sucrose reactions are similar because the rate of reaction in these low density powders is diffusion controlled, then we might expect a linear relationship between energy of reaction and detonation velocity.

Figure 16 also shows that the aluminum-fueled oxidizers follow a different trend than the sucrose-fueled formulations. Given the idea of minimum energy, it could be
speculated that aluminum can provide enough additional energy during its oxidation to push a low-energy formulation to detonation; this was not the case in these studies. Ammonium nitrate and perchlorate sucrose mixtures were detonable; substitution of aluminum for sucrose increased the heat released in the calorimeter, but detonation velocity decreased. We attribute this result to the lower density of the aluminum formulation due to the small aluminum particle size. Not surprisingly the air blast in terms of TNT equivalence increased with the addition of aluminum. It is well known that aluminum does not react rapidly enough to contribute all its energy to the detonation front; hence, the provision in Cheetah to make some of the aluminum content “inert.” In fact, air blast in terms of TNT equivalence is proportional to the heat observed in the Parr calorimeter (Figure 17).
Figure 3.17. Air Blast TNT equivalence large scale vs. heat from bomb calorimetry.

(Error bars in heat are too small to be seen; Table 1 shows relative standard deviation.)

5 Conclusions

Measurement or calculation (Cheetah) of heat of reaction is a useful first step in determining whether a formulation is potentially detonable. It appears there is some minimum energy which a formulation must possess to be detonable. However, examination of Table 4 clearly shows that some materials with high reaction energy (i.e. KNO$_3$/Al) do not detonate, while others with low reaction energy (i.e. AN/sucrose) do. Clearly any small-scale test or model must take into account the rate of reaction as well as energy. The potassium nitrate/sucrose mixture exhibited low heat release in the Parr bomb, and it did not detonate in the field-scale configuration. The substitution of aluminum for sucrose dramatically increased the energy released (as measured in the calorimeter), but the mixture (KNO$_3$:Al) still did not detonate in field trials. The rate recorded in Table 3 is a burn, as judged by video record and discussed above (Figure 12). The potassium nitrate/sucrose mixture was prodded into detonation by spiking it with 5wt% RDX or 7wt% potassium chlorate. Both these chemicals were capable of rapidly adding energy to the mixture. However, the total energy released by these potassium nitrate/sucrose mixture with these additives was only a little over half that of potassium nitrate / aluminum. This observation points to the importance of the rate at which the energy is provided. Figure 18 recasts the Parr data found in Figures 9 and 10 colorizing Parr pressure data to reflect the outcome in the large-scale tests. In general, FOX mixtures, which exhibited a rapid rise to peak pressure, detonated on the large
scale. Those FOX mixtures, which reached peak pressure more slowly, did not detonate at the large scale, with the exception of ammonium nitrate and sucrose.

Figure 3.18. Pressure vs. time curves of fuel:oxidizer mixes from Figures 9 & 10. Ultimate outcome at the 5 to 6 kg scale is shown by color – red for FOX which detonated; blue for FOX which did not detonate. The ammonium nitrate:sugar mixture is so slow that it has its own time axis (above plot).

With aluminum mixtures at the large scale, it has already been mentioned that due to the slowness of the reaction only some fraction of the energy released in the aluminum oxidation can support the detonation front [13]. The rest is manifest in the Taylor wave expansion, i.e. air blast. The fuel/oxidizer mixture has as similar problem with reaction rate. Detonation velocity is strongly dependent on density [14]. FOX mixtures are far from dense, and a significant amount of time must be spent in diffusion
and compaction of the fuel and oxidizer. High explosives, such as PETN or RDX, have reaction zone lengths of approximately 1-2 mm, reacting rapidly enough so that much of their energy can support the detonation front [15]. This in contrast to a non-ideal explosive, such as ANFO, with a reaction zone length estimated as 8-12 mm [15]. With these FOX mixtures the fraction of energy released to the front must be significantly less. How much less and the role of compaction in these composite materials will be the subject of a number of future studies.

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Gurney Energies typically 70% of heat of Detonation, TNT is 61% of its heat of detonation.

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Estimation of Cj pressure as a function of the initial density of the explosive and detonation velocity. $P_{CJ} = \rho_0D^2(1-0.713\rho_0^{0.07})$ where $D$ is detonation velocity in mm/usec and $\rho_0$ is the initial density in g/cm$^3$.

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From shock theory it is known $P_{CJ} = \rho_0D^2/(\gamma + 1)$ and $\rho_{CJ} = \rho_0(\gamma + 1)/\gamma$ ($\gamma$ being useful for describing the PV isentrope from the product gases in the Taylor wave). Koch shows
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BEC V5.0 fits our data a little better. The BEC V5.0 calculator is headed by Michael Swisdak, and is based on empirical fit parameters from Kingery and Bulmash 1984. Kingery and Bulmash numbers come from measurements taken from 4 events 1959-1964 from TNT shots of 5, 20, 100, and 500 tons.

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Important to note that the open tray propagation rate of a MoO3/Al thermite (m/s) was directly proportional to the pressurization rate dp/dt of the same mixture inside a closed bomb. The open burn rate and closed volume pressurization rate peaked at the same wt % aluminum. This shows that dp/dt is an important metric for burn rate.
Solid propellants were run for their P/t traces. In a simplified equation, it was shown that the g/s burn rate, \(\frac{dC}{dt} = \frac{C_b}{P_{\text{max}}} \frac{dP}{dt}\) (where \(\frac{dC}{dt}\) is the burn rate, \(C_b\) is the total sample mass, and \(P_{\text{max}}\) is the maximum difference in pressure achieved). The assumptions were that heat losses were minimal and high surface area allowed the burn to become complete when peak pressure is reached. If heat losses are large, \(P_{\text{max}}\) may occur before the burn is complete. They ran propellant samples that pass through a 30 mesh sieve to maximize the burn rate and minimize heat losses. Impetus (\(F\)) is the ability of the sample to do work based on the volume of the sample, peak pressure reached, and amount of sample. This reference supports what was taught in the Picatinny pyrotechnics class from closed bomb testing. \(F \ (J/g) = P_{\text{max}} \frac{V}{W}\) (\(P_{\text{max}}\) is the maximum difference in pressure in Pa, \(V\) is the volume of the bomb in m\(^3\), and \(W\) is the weight of the sample in g).
APPENDIX 4: DATA FOR MANUSCRIPT 1

Figure 4.1. Mass spectrum of HMTD from GC/MS
Figure 4.2. $^1$H NMR spectrum of HMTD in CDCl$_3$.

Figure 4.3. IR Spectrum of crude and recrystallized HMTD.
Figure 4.4. DSC thermogram of recrystallized HMTD with and without water.
Figure 4.5. DSC thermogram of crude HMTD with and without water.
Figure 4.6. GC/MS mass spectrum of HMTD extracted during synthesis in the presence of $^{13}$C formaldehyde.
Figure 4.7. GC/MS mass spectrum of hexamine extracted during HMTD synthesis in the presence of $^{13}$C formaldehyde.

Figure 4.8. LC/MS mass spectrum of HMTD extracted during synthesis in the presence of $^{13}$C formaldehyde.
Figure 4.9. LC/MS mass spectrum of hexamine extracted during HMTD synthesis in the presence of $^{13}$C formaldehyde.
Figure 4.10. GC/MS mass spectrum of HMTD recovered after synthesis in the presence of $^{15}$N ammonium sulfate.
Figure 4.11. LC/MS mass spectrum of HMTD recovered after synthesis in the presence of $^{15}$N ammonium sulfate.

**HMTD**

with $^{15}$NH$_3$

$^{210.0744}$

$\text{C}_6\text{H}_{13}\text{O}_6\text{N}^{15}\text{N}^+$

$^{210.0807}$

$\text{C}_5\text{H}^{13}\text{CH}_{13}\text{O}_6\text{N}_2^+$

$^{210.0304}$

$\text{C}_5\text{H}^{13}\text{CH}_{13}\text{O}_6\text{N}_2^+$
Figure 4.12. $^1$H NMR spectrum of $^{15}$N hexamine in CDCl$_3$. 
Figure 4.13. GC/MS Mass Spectrum of 1:1 $^{14}$N:$^{15}$N hexamine extracted during synthesis of HMTD.

Figure 4.14. LC/MS Mass Spectrum of 1:1 $^{14}$N:$^{15}$N hexamine extracted during synthesis of HMTD.
Figure 4.15. GC/MS mass spectrum of HMTD extracted during synthesis with 1:1 $^{14}$N:$^{15}$N hexamine.
Figure 4.16. GC/MS of Hexamine formed after 6 days when HMTD is decomposed in the presence of 15N Ammonium Sulfate at 60 °C and 75 %RH.
Figure 4.17. LC/MS of Hexamine formed after 6 days when HMTD is decomposed in the presence of 15N Ammonium Sulfate at 60 °C and 75 %RH.
Figure 4.18. $^1$H NMR of D$_2$O in outside vial after 5 days during decomposition of HMTD at 60 $^\circ$C 100% RD.
Figure 4.19. $^{13}$C NMR of D$_2$O in outside vial after 5 days during decomposition of HMTD at 60 °C 100% RD.
APPENDIX 5: DATA FOR MANUSCRIPT 2

SDT from Aging Studies

Figure 5.1. $\text{I}_2\text{O}_5$ fresh

Figure 5.2. $\text{I}_2\text{O}_5$ after 3 days 75 %RH at 60 °C
Figure 5.3. I$_2$O$_5$ after 14 days 75 %RH at 60 °C

Figure 5.4. 80/20 I$_2$O$_5$/Al fresh mixture
Figure 5.5. 80/20 I₂O₅/Al after 3 days 75 %RH at 60 °C (does not burn)

Figure 5.6. 80/20 I₂O₅/Al after 14 days 75 %RH at 60 °C (does not burn)
Figure 5.7. NaIO₄ fresh

Figure 5.8. NaIO₄ after 3 days 75 %RH at 60 °C
Figure 5.9. NaIO₄ after 14 days 75%RH at 60 °C

Figure 5.10. 80/10/10 NaIO₄/B₄C/Al fresh mixture
Figure 5.11. 80/10/10 NaIO₄/B₄C/Al after 3 days 75 %RH at 60 °C

Figure 5.12. 80/10/10 NaIO₄/B₄C/Al after 2 weeks 75 %RH at 60 °C (burns slower, decreased brightness)
Figure 5.13. NaIO$_3$ fresh

Figure 5.14. NaIO$_3$ after 3 days 75 %RH at 60 °C
Figure 5.15. NaIO₃ after 14 days 75 %RH at 60 °C

Figure 5.16. 80/10/10 NaIO₃/B₄C/Al fresh mixture
Figure 5.17. 80/10/10 NaIO₃/B₄C/Al after 3 days 75 %RH at 60 °C

Figure 5.18. 80/10/10 NaIO₃/B₄C/Al after 2 weeks 75 %RH at 60 °C (burns slower, decreased brightness)
Figure 5.19. Ca(IO$_3$)$_2$ fresh

Figure 5.20. Ca(IO$_3$)$_2$ after 3 days 75 %RH at 60 °C
Figure 5.21. Ca(IO$_3$)$_2$ after 14 days 75 %RH at 60 °C

Figure 5.22. 75/25 Ca(IO$_3$)$_2$/Al fresh mixture
Figure 5.23. 75/25 Ca(IO₃)₂/Al after 3 days 75 %RH at 60 °C

Figure 5.24. 75/25 Ca(IO₃)₂/Al after 14 days 75 %RH at 60 °C (burns with a bright flash and purple smoke)
IR from Aging Studies

Figure 5.25. I$_2$O$_5$ fresh (blue) and after 3 days 75 %RH at 60 °C (red)

Figure 5.26. 80/20 I$_2$O$_5$/Al fresh (blue) and after 3 days 75 %RH at 60 °C (red)
Figure 5.27. NaIO₄ fresh (blue) and after 3 days 75 %RH at 60 °C (red)

Figure 5.28. 80/10/10 NaIO₄/B₄C/Al fresh (blue) and after 3 days 75 %RH at 60 °C (red)
Figure 5.29. NaIO₃ fresh (blue) and after 3 days 75 %RH at 60 °C (red)

Figure 5.30. 80/10/10 NaIO₃/B₄C/Al fresh (blue) and after 3 days 75 %RH at 60 °C (red)
Figure 5.31. Ca(IO$_3$)$_2$ fresh (blue) and after 3 days 75 %RH at 60 °C (red)

Figure 5.32. 75/25 Ca(IO$_3$)$_2$/Al fresh (blue) and after 3 days 75 %RH at 60 °C (red)
UV-Vis Data

Figure 5.33. 0.5 M KI extraction of 80/20 Bi(IO₃)₃/Al combustion products compared to a BiI₃ standard and a standard curve made with KI and I₂ (KI₃)

Figure 5.34. 0.5 M KI extraction of 60/40 Bi(IO₃)₃/Al combustion products compared to a BiI₃ standard and a standard curve made with KI and I₂ (KI₃)
SDT Data of Other Fresh Mixtures

Figure 5.35. 80/20 NaIO₃/Al

Figure 5.36. 80/20 NaIO₃/B₄C
Figure 5.37. 80/20 NaIO₄/Al

Figure 5.38. 80/20 NaIO₄/B₄C
Figure 5.39. 80/20 KIO₃/Al

Figure 5.40. 80/10/10 KIO₃/B₄C/Al
Figure 5.41. 80/20 KIO₃/B₄C

Figure 5.42. 80/20 KIO₄/Al
Figure 5.43. 80/10/10 KIO₄/B₄C/Al

Figure 5.44. 80/20 KIO₄/B₄C
Figure 5.45. 80/20 Bi(IO₃)₃/Al

Figure 5.46. 80/10/10 Bi(IO₃)₃/B₄C/Al
Figure 5.47. 80/20 Bi(IO₃)₃/B₄C

Figure 5.48. 80/10/10 Ca(IO₃)₂/B₄C/Al
Figure 5.49. 80/20 Ca(IO₃)₂/B₄C

SDT Data of Other Oxidizers

Figure 5.50. KIO₃
Figure 5.51. KIO₄

Figure 5.52. Bi(IO₃)₃
SDT Data of Fuels

Figure 5.53. Aluminum in nitrogen

Figure 5.54. Aluminum in air
Figure 5.55. 50/50 Aluminum/iodine run in nitrogen

Figure 5.56. B₄C in nitrogen
Figure 5.57. $\text{B}_4\text{C}$ in air

Figure 5.58. 50/50 $\text{B}_4\text{C}$/iodine run in nitrogen
Figure 5.59. 80/20 Bi₂O₃/Al

SDT Data of Combustion Products

Figure 5.60. 80/20 Ca(IO₃)₂/Al combustion products
Figure 5.61. 60/40 Ca(IO$_3$)$_2$/Al combustion products

Figure 5.62. 80/20 NaIO$_3$/Al combustion products
Figure 5.63. 60/40 NaIO₃/Al combustion products

Figure 5.64. 80/20 KIO₃/Al combustion products
Figure 5.65. 60/40 KIO₃/Al combustion products

Figure 5.66. 80/20 Bi(IO₃)₃/Al combustions products
Figure 5.67. 60/40 Bi(IO$_3$)$_3$/Al combustion products

Figure 5.68. 80/20 I$_2$O$_5$/Al combustion products
Figure 5.69. 60/40 I$_2$O$_5$/Al combustion products

SDT Data of Iodides

Figure 5.70. CaI$_2$ in nitrogen
Figure 5.71. CaI$_2$ in air

Figure 5.72. NaI in nitrogen
Figure 5.73. NaI in air

Figure 5.74. KI in nitrogen
Figure 5.75. KI in air

Figure 5.76. BiI$_3$ in nitrogen
Figure 5.77. BiI$_3$ in air

Figure 5.78. Al$_2$I$_6$ in nitrogen
Figure 5.79. Al$_2$I$_6$ in air

**XPS Data**

![Graph showing XPS data](image)

Figure 5.80. 80/20 Ca(IO$_3$)$_2$/Al combustion products I 3d high resolution spectra
Figure 5.81. 60/40 Ca(IO₃)₂/Al combustion products 13d high resolution spectra

Figure 5.82. Ca(IO₃)₂/Al combustion products Ca 2p high resolution spectra
Figure 5.83. 80/20 I₂O₅/Al combustion products I 3d high resolution spectra

Figure 5.84. 60/40 I₂O₅/Al combustion products I 3d high resolution spectra
Figure 5.85. 80/20 Bi(IO₃)₃/Al combustion products 13d high resolution spectra

Figure 5.86. 60/40 Bi(IO₃)₃/Al combustion products 13d high resolution spectra
Figure 5.87. 80/20 Bi(IO₃)₃/Al combustion products Bi 4f high resolution spectra

Figure 5.88. 60/40 Bi(IO₃)₃/Al combustion products Bi 4f high resolution spectra
Figure 5.89. 80/20 KIO₃/Al combustion products I 3d high resolution spectra

Figure 5.90. 60/40 KIO₃/Al combustion products I 3d high resolution spectra
Figure 5.91. 80/20 NaIO₃/Al combustion products I 3d high resolution spectra

Figure 5.92. 60/40 NaIO₃/Al combustion products I 3d high resolution spectra
Figure 5.93. Aluminum heated in air and nitrogen Al 2p high resolution spectra

Figure 5.94. Aluminum heated in air and nitrogen O 1s high resolution spectra
### Table 5.1: XPS extended table with FWHM for each binding energy

| Sample | Oxidizer % | Fuel % | I3d5/2 | I3d3/2 | O 1s | Al 2p | Ca 2p3/2 | Ca 2p1/2 | Na 1s | K2p3/2 | Bi4f5/2 | Bi4f7/2 | Correction Type |
|--------|------------|--------|--------|--------|------|-------|----------|----------|------|-------|--------|--------|----------------|
| Mix 60 Comb Prod Ca(IO3)2 | 60 | Al | 20 | 618.8 | 1.9 | 630.0 | 2.0 | 531.0 | 2.8 | 740.0 | 2.0 | 347.2 | 1.8 | 350.8 | 1.6 | -0.9 Ca2p3/2 CaO |
| Mix 78 Comb Prod Ca(IO3)2 | 60 | Al | 40 | 618.7 | 2.2 | 630.2 | 2.1 | 531.5 | 2.5 | 742.0 | 2.0 | 347.2 | 1.6 | 350.8 | 1.6 | -0.9 Ca2p3/2 CaO |
| Mix 95 Comb Prod | 60 | Al | 40 | 619.1 | 1.7 | 630.6 | 1.7 | 532.8 | 2.3 | 754.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Al2p Al3 |
| Mix 54 Comb Prod | 80 | Al | 20 | 619.8 | 2.0 | 631.4 | 2.0 | 532.4 | 2.4 | 754.0 | 1.7 | 347.2 | 1.6 | 350.8 | 1.6 | 0.5 Al2p Al3 |
| Mix 97 Comb Prod | 60 | Al | 20 | 619.4 | 1.6 | 630.9 | 1.5 | 531.8 | 2.0 | 754.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.5 Al2p Al3 |
| Mix 66 Comb Prod | 60 | Al | 20 | 619.4 | 1.5 | 630.9 | 1.5 | 533.0 | 2.1 | 756.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.6 Bi4f7/2 Bi3 |
| Mix 55 Comb Prod KIO3 | 60 | Al | 20 | 619.5 | 1.7 | 630.8 | 1.8 | 530.1 | 2.6 | 733.1 | 1.9 | 347.2 | 1.6 | 350.8 | 1.6 | -0.1 K2p3/2 KI |
| Mix 80 Comb Prod | 60 | Al | 20 | 619.5 | 2.0 | 630.8 | 2.0 | 530.8 | 2.7 | 733.1 | 2.0 | 347.2 | 1.6 | 350.8 | 1.6 | -0.1 K2p3/2 KI |
| Mix 57 Comb Prod NaO3 | 60 | Al | 20 | 619.2 | 2.1 | 630.7 | 2.2 | 531.2 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | -0.3 Na2p Al3 |
| Mix 114 Comb Prod NaO3 | 60 | Al | 20 | 618.8 | 2.0 | 630.3 | 2.2 | 530.7 | 2.4 | 736.9 | 2.0 | 347.2 | 1.6 | 350.8 | 1.6 | -0.3 Na2p Al3 |
| Mix 53 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | -0.3 Na2p Al3 |
| Mix 115 Comb Prod | 60 | Al | 40 | 619.8 | 1.9 | 630.3 | 1.9 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.0 Na2p Al3 |
| Mix 116 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | -0.0 Na2p Al3 |
| Mix 95 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 117 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 95 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 118 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 95 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 118 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 95 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 118 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |
| Mix 95 Comb Prod | 60 | Al | 40 | 619.8 | 2.0 | 630.3 | 2.0 | 530.8 | 2.1 | 739.0 | 1.6 | 347.2 | 1.6 | 350.8 | 1.6 | 0.3 Na2p Al3 |

#### Qualitative Analysis of Peak Binding Energy (eV)

- **Oxidizer**: Oxidizer %
- **Fuel**: Fuel %
- **I3d5/2 FW**: I3d5/2 Full Width at Half Maximum (FWHM)
- **I3d3/2 FW**: I3d3/2 Full Width at Half Maximum (FWHM)
- **O 1s FW**: O 1s Full Width at Half Maximum (FWHM)
- **Al 2p FW**: Al 2p Full Width at Half Maximum (FWHM)
- **Ca 2p3/2 FW**: Ca 2p3/2 Full Width at Half Maximum (FWHM)
- **Ca 2p1/2 FW**: Ca 2p1/2 Full Width at Half Maximum (FWHM)
- **Na 1s FW**: Na 1s Full Width at Half Maximum (FWHM)
- **K2p3/2 FW**: K2p3/2 Full Width at Half Maximum (FWHM)
- **Bi4f5/2 FW**: Bi4f5/2 Full Width at Half Maximum (FWHM)
- **Bi4f7/2 FW**: Bi4f7/2 Full Width at Half Maximum (FWHM)
- **Correction Correction Type**: Correction Type

- **Correction**: Correction Value
- **Type**: Type of Correction

#### Oxidation State in Combustion Products

- **I-**: Iodide
- **O-2**: Oxygen
- **Al+3**: Aluminum
- **N-3**: Nitrogen
- **Ca+2**: Calcium
- **Na+**: Sodium
- **K+**: Potassium
- **Bi+3**: Bismuth

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**Note**: The table presents the XPS peak binding energies with full width at half maximum (FWHM) values for various samples, including combinations of oxidizers and fuels, along with qualitative analysis of peak binding energies and oxidation states in combustion products.
Figure 5.95. LCMS - Ca(IO$_3$)$_2$/Al extracted with H$_2$O. Blank (top), Ca(I$_2$) in H$_2$O (middle top), CaO added to a solution of Al$_2$I$_6$ in H$_2$O (middle bottom), and 60/40 Calcium Iodate/Al combustion products extracted in H$_2$O (bottom).
APPENDIX 6: DATA FOR MANUSCRIPT 3

Pressure vs. Time Curves from Bomb Calorimetry

Figure 6.1. Pressure vs. Time curve of \( \text{Fe}_3\text{O}_4: \text{Mg} \) 80:20 wt:wt (2 g in 2859 kPa Argon)
Figure 6.2. Pressure vs. Time curve of Fe₃O₄:Mg 70:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.3. Pressure vs. Time curve of Fe$_3$O$_4$:Mg 60:40 wt:wt (2 g in 2859 kPa Argon)
Figure 6.4. Pressure vs. Time curve of Bi$_2$O$_3$:Al 70:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.5. Pressure vs. Time curve of Bi$_2$O$_3$:Al 90:10 wt:wt (2 g in 2859 kPa Argon)
Figure 6.6. Pressure vs. Time curve of Bi$_2$O$_3$:Al 80:20 wt:wt (2 g in 2859 kPa Argon)
Figure 6.7. Pressure vs. Time curve of KNO$_3$:Nabenzoate 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.8. Pressure vs. Time curve of KClO$_3$-Nabenzoate 70:30 wt:wt (2 g) Pressure vs Time Ignited in 2859 kPa Argon

(2 g in 2859 kPa Argon)
Figure 6.9. Pressure vs. Time curve of KClO$_4$:Nabenzoate 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.10. Pressure vs. Time curve of NH₄ClO₄:Nabenzoate 70:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.11. Pressure vs. Time curve of K$_2$Cr$_2$O$_7$:Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.12. Pressure vs. Time curve of NH$_4$NO$_3$:Sucrose 70:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.13. Pressure vs. Time curve of KMnO₄:Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.14. Pressure vs. Time curve of KIO₃:Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.15. Pressure vs. Time curve of KNO\(_2\):Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.16. Pressure vs. Time curve of KNO₃:Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.17. Pressure vs. Time curve of KNO₃:KClO₃:Sucrose 63:7:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.18. Pressure vs. Time curve of KIO$_4$:Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.19. Pressure vs. Time curve of RDX:KNO₃:Sucrose 5:66.5:28.5 wt:wt (2g) Pressure vs Time Ignited in 2859 kPa Argon

(2 g in 2859 kPa Argon)
Figure 6.20. Pressure vs. Time curve of KClO₃:KNO₃:Sucrose 17:53:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.21. Pressure vs. Time curve of RDX:KNO₃:Sucrose 10:63:27 wt:wt (2 g) Pressure vs Time Ignited in 2859 kPa Argon

(2 g in 2859 kPa Argon)
Figure 6.22. Pressure vs. Time curve of KNO₃:KClO₃:Sucrose 35:35:30 wt:wt (2g) Pressure vs Time Ignited in 2859 kPa Argon

(2 g in 2859 kPa Argon)
Figure 6.23. Pressure vs. Time curve of KBrO₃:Sucrose 70:30 wt:wt
(2 g in 2859 kPa Argon)
Figure 6.24. Pressure vs. Time curve of KClO$_4$:Sucrose 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.25. Pressure vs. Time curve of KClO₃:Sucrose 70:30 wt:wt
(2 g in 2859 kPa Argon)
Figure 6.26. Pressure vs. Time curve of RDX:KNO₃:Sucrose 50:35:15 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.27. Pressure vs. Time curve of $\text{K}_2\text{Cr}_2\text{O}_7$:$\text{Al}$ 70:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.28. Pressure vs. Time curve of KNO$_2$:Al 70:30 wt:wt (2g) Pressure vs Time Ignited in 2859 kPa Argon
Figure 6.29. Pressure vs. Time curve of KMnO₄:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.30. Pressure vs. Time curve of KIO$_3$:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.31. Pressure vs. Time curve of KNO₃:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.32. Pressure vs. Time curve of KIO$_4$:Al 70:30 wt:wt (2 g in 2859 kPa Argon)
Figure 6.33. Pressure vs. Time curve of KClO₄:Al 80:20 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.34. Pressure vs. Time curve of KBrO$_3$:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.35. Pressure vs. Time curve of NH$_4$NO$_3$:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.36. Pressure vs. Time curve of KClO₄:Al 50:50 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.37. Pressure vs. Time curve of KClO₃:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.38. Pressure vs. Time curve of KClO₄:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.39. Pressure vs. Time curve of KClO₄:Al 60:40 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.40. Pressure vs. Time curve of NH₄ClO₄:Al 70:30 wt:wt

(2 g in 2859 kPa Argon)
Figure 6.41. Pressure vs. Time curve of 7 mesh granulated Black Powder

(2 g in 2859 kPa Argon)
Figure 6.42. Pressure vs. Time curve of 20 mesh granulated Black Powder

(2 g in 2859 kPa Argon)
Figure 6.43. Pressure vs. Time curve of Meal Black Powder

(2 g in 2859 kPa Argon)
Figure 6.44. Pressure vs. Time curve of Pyrodex (2 g in 2859 kPa Argon)
Figure 6.45. Pressure vs. Time curve of Red Dot (2 g in 2859 kPa Argon)
Figure 6.46. Airblast pressure vs. time curve from large scale testing with the booster only (sand as the sample)
Figure 6.47. Airblast pressure vs. time curve from large scale testing with TNT as the sample.
Figure 6.48. Airblast pressure vs. time curve from large scale testing with KClO$_3$:Sucrose 70:30 wt:wt as the sample
Figure 6.49. Airblast pressure vs. time curve from large scale testing with KNO₃:Sucrose 70:30 wt:wt as the sample
Figure 6.50. Airblast pressure vs. time curve from large scale testing with NH₄NO₃:Sucrose 70:30 wt:wt as the sample.
Figure 6.51. Airblast pressure vs. time curve from large scale testing with

$\text{NH}_4\text{ClO}_4$:Sucrose 70:30 wt:wt as the sample
Figure 6.52. Airblast pressure vs. time curve from large scale testing with 

\( \text{KClO}_3: \text{KNO}_3: \text{Sucrose} \ 35:35:30 \ \text{wt:wt} \) as the sample.
Figure 6.53. Airblast pressure vs. time curve from large scale testing with KMnO$_4$:Sucrose 70:30 wt:wt as the sample
Figure 6.54. Airblast pressure vs. time curve from large scale testing with KIO$_3$:Sucrose 70:30 wt:wt as the sample
Figure 6.55. Airblast pressure vs. time curve from large scale testing with KCIO$_3$:Sucrose 70:30 wt:wt as the sample.
Figure 6.56. Airblast pressure vs. time curve from large scale testing with RDX:KNO₃:Sucrose 50:35:15 wt:wt as the sample
Figure 6.57. Airblast pressure vs. time curve from large scale testing with
KNO₃:KClO₃:Sucrose 63:7:30 wt:wt as the sample
Figure 6.58. Airblast pressure vs. time curve from large scale testing with KNO₃:RDX:Sucrose 66.5:5:28.5 wt:wt as the sample
Figure 6.59. Airblast pressure vs. time curve from large scale testing with NH₄NO₃:Al 70:30 wt:wt as the sample
Figure 6.60. Airblast pressure vs. time curve from large scale testing with KNO$_3$:Al 70:30 wt:wt as the sample.
Figure 6.61. Airblast pressure vs. time curve from large scale testing with NH$_4$ClO$_4$:Al 70:30 wt:wt as the sample.
High Speed Camera Records of Large Scale Tests

Figure 6.62. High speed camera record from large scale testing with the booster only and sand as the sample (20161220 shot 1)

Figure 6.63 High speed camera record from large scale testing with TNT as the sample (20161220 shot 2)
Figure 6.64. High speed camera record from large scale testing with TNT as the sample (20161221 shot 1)
Figure 6.65. High speed camera record from large scale testing with KClO₃:Sucrose 70:30 wt:wt as the sample (20170113 shot 1)
Figure 6.66. High speed camera record from large scale testing with KNO₃:Sucrose 70:30 wt:wt as the sample (20170113 shot 2)
Figure 6.67. High speed camera record from large scale testing with NH\textsubscript{4}NO\textsubscript{3}:Sucrose 70:30 wt:wt as the sample (20170125 shot 1)
Figure 6.68. High speed camera record from large scale testing with NH₄ClO₄:Sucrose 70:30 wt:wt as the sample (20170125 shot 2)
Figure 6.69. High speed camera record from large scale testing with KNO$_3$:KClO$_3$:Sucrose 35:35:30 wt:wt as the sample (20170125 shot 3)
Figure 6.70. High speed camera record from large scale testing with KMnO₄:Sucrose 70:30 wt:wt as the sample (20170206 shot 1)
Figure 6.71. High speed camera record from large scale testing with KIO₃:Sucrose 70:30 wt:wt as the sample (20170206 shot 2)
Figure 6.72. High speed camera record from large scale testing with KClO₃:Sucrose 70:30 wt:wt as the sample (20170206 shot 3)
Figure 6.73. High speed camera record from large scale testing with RDX:KNO₃:Sucrose 50:35:15 wt:wt as the sample (20170206 shot 4)
Figure 6.74 High speed camera record from large scale testing with KNO$_3$:KClO$_3$:Sucrose 63:7:30 wt:wt as the sample (20170302 shot 1)
Figure 6.75. High speed camera record from large scale testing with KNO₃:RDX:Sucrose 66.5:5:28.5 wt:wt as the sample (20170302 shot 2)
Figure 6.76. High speed camera record from large scale testing with NH$_4$NO$_3$:Al 70:30 wt:wt as the sample (20170302 shot 3)
Figure 6.77 High speed camera record from large scale testing with KNO₃:Al 70:30 wt:wt as the sample (20170303 shot 1)
Figure 6.78. High speed camera record from large scale testing with NH$_4$ClO$_4$:Al 70:30 wt:wt as the sample (20170303 shot 2)