THERMAL STABILITY AND SENSITIVITY OF ENERGETIC FORMULATIONS

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THERMAL STABILITY AND SENSITIVITY
OF ENERGETIC FORMULATIONS

BY

MARIA A. DONNELLY

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OF

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ABSTRACT

Explosive mixtures have found widespread use in both military applications and as components of improvised explosive devices (IEDs). Knowledge of how the components of these formulations interact with each other will benefit both military and anti-terrorism organizations. Since there are significant differences in the explosive properties desired by the military verses those involved in illicit activities, it is important to study both military and improvised formulations.

The use of improvised explosive devices by terrorist organizations is a significant problem that has resulted in destruction of property and loss of both military and civilian lives in countries throughout the world. There are many different materials that can be used to make homemade explosives (HMEs), but they are often combinations of a fuel and an oxidizer. These materials are popular because they are generally readily available due to their use in various industrial and household processes. Knowledge of which fuel-oxidizer combinations are potentially dangerous can help anti-terrorism organizations focus resources on detecting potential threats and preventing the use of potential HME components. In the first manuscript, titled “Fuel-oxidizer Mixtures: Their Stabilities and Burn Characteristics”, various fuel/oxidizer combinations were examined by differential scanning calorimetry (DSC) and simultaneous differential scanning calorimetry/thermogravimetric analysis (SDT). It was found that the reaction between the fuel and the oxidizer was generally triggered by a thermal event such as a melt, phase change, or decomposition. When the fuel used was a polyalcohol or sulfur, the triggering event was often the melt of the fuel, which usually occurred at a lower temperature than that of the oxidizer. However,
three of the oxidizers, potassium nitrate, potassium perchlorate, and ammonium perchlorate, generally did not react until they underwent a phase change or began to decompose, and as a result, reactions with these oxidizers tended to occur at much higher temperatures. Reactions with hydrocarbon fuels containing fewer or no alcohol groups also tended to occur at higher temperatures. Regardless of the fuel used, the mixtures containing potassium chlorate, ammonium perchlorate and ammonium nitrate generally released the greatest amount of heat, around 2000 J/g, while mixtures containing potassium dichromate were the least energetic, generally releasing less than 200 J/g. For some formulations, reactions did not occur until temperatures higher than 500°C. In order to reach higher temperatures, it was necessary to use unsealed samples in the SDT rather than the sealed capillaries used in the DSC. It was noted that when samples were not in sealed capillaries, other processes such as sublimation effectively competed with the exothermic reactions experienced by the formulations. As a result, the heat release values obtained by SDT for some formulations were artificially low.

The second manuscript “Thermal Stability Studies on IMX-101 (Dinitroanisole/Nitroguanidine/NTO)” examines the interactions among the components of an insensitive munitions formulation, IMX-101, which has been developed and qualified for use as a replacement for TNT (2,4,6-trinitrotoluene). IMX-101 contains the energetic materials 2,4-dinitroanisole (DNAN), nitroguanidine (NQ), and 3-nitro-1,2,4-triazol-5-one (NTO). DNAN is a nitroarene that is very similar in structure to TNT, but with only two nitro groups, and with an anisole functional group in place of the methyl group in TNT. 2,4-Dinitrotoluene (DNT),
which also contains only two nitro groups, is even more similar to TNT, because it is a toluene rather than an anisole. DSC and isothermal analyses were used to compare DNAN and DNT, to see if increased thermal stability made the use of DNAN more appealing than DNT in IMX-101 and other insensitive munitions formulations. The isothermal studies showed that neat DNAN was more stable than neat DNT. However, when mixed with either or both of the other components of the IMX-101 formulation, the thermal stability of both DNAN and DNT was decreased, with a greater impact on DNAN. The thermal decomposition of both DNAN and DNT was significantly accelerated by the presence of NQ. NTO also enhanced the decomposition of both nitroarenes, but this compound had a significantly greater impact on DNAN than on DNT. An examination of the decomposition products from the various mixtures showed that 2,4-dinitroaniline (DNA) was produced from the decomposition of both DNAN and DNT with either of the two additives; DNA was not observed during the neat decomposition of either nitroarene. It was thought that ammonia, which has been detected in either gaseous form or as ammonium ions during decomposition studies on both NQ and NTO, might be one cause of the decreased stability imparted to the nitroarenes by the two additives. Heating DNAN and DNT in the presence of ammonia generated from ammonium carbonate produced dinitroaniline and had an accelerating effect on the decomposition of the two nitroarenes, with the greater impact, both in the acceleration level and the amount of dinitroaniline produced, on DNAN.
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PREFACE

The following research has been presented in manuscript format according to guidelines of the Graduate School of the University of Rhode Island. The dissertation is divided into two manuscripts.

The first manuscript entitled “Fuel-oxidizer Mixtures: Their Stabilities and Burn Characteristics” was presented at the NATAS Conference (Santa Fe, NM, September 2014) and has been accepted for publication in the *Journal of Thermal Analysis and Calorimetry*.

The second manuscript entitled “Thermal Stability Studies on IMX-101 (Dinitroanisole/Nitroguanidine/NTO)” is being prepared for submission to *Propellants, Explosives, and Pyrotechnics*.
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INTRODUCTION

Explosive mixtures have found widespread use both in military applications [1-4] and as components of improvised explosive devices (IEDs) [5-7]. Knowledge of how the components of these formulations interact with each other is beneficial to both military and anti-terrorism organizations. Since there are significant differences in the explosive properties desired by the military [3] and those engaged in illicit activities, it is important to study both military and improvised formulations.

For many years, 2,4,6-trinitrotoluene (TNT) has been one of the most commonly used military explosives. However, there is concern about the sensitivity of munitions based on conventional explosives, which can react violently if exposed to fire or impact from an armor piercing bullet or shape charge [3, 8, 9-11]. In addition, TNT and some of its decomposition products have significant levels of toxicity and, as a result, unexploded ordnance containing TNT has become an environmental and health concern [8]. These issues have led to increased interest in the development of insensitive munitions formulations that can serve as replacements for TNT and other conventional explosives [3-4]. One of the main components of many of these formulations has been 2,4-dinitroanisole (DNAN) [3-4, 8, 12].

DNAN is similar to TNT in that it contains a phenyl ring substituted with nitro groups; however, it has one less nitro group than TNT, and it has a methoxy (\(-\text{OCH}_3\)) substituent in place of the methyl (\(-\text{CH}_3\)) group that is present in TNT [8]. DNT is even more similar to TNT; it lacks only the nitro group attached to carbon six in the phenyl ring. Both DNAN and DNT are energetic but less sensitive than TNT [12], so in theory either could serve as a potential component in insensitive replacements for
TNT based munitions. While significant research has been published verifying the explosive abilities of new DNAN-containing insensitive munitions [1, 3, 8], no information has been found explaining why 2,4-dinitroanisole was initially chosen for these formulations instead of 2,4-dinitrotoluene. The study contained herein has examined the thermal properties of DNAN and DNT, both neat and in mixtures with the other components of a recently qualified insensitive munitions formulation, IMX-101. The results show that, while neat DNAN is more thermally stable than neat DNT, this greater stability is not maintained when DNAN is combined with either nitroguanidine (NQ) or 3-nitro-1,2,4-triazol-5-one (NTO), the two other energetic materials present in IMX-101.

Military organizations are not the only groups that are interested in using explosive formulations; terrorists also make use of mixtures of materials in the manufacture of improvised explosive devices (IEDs) [6-7, 13]. However, the requirements for an IED are very different from those of military explosives. While military formulations must be safe to store and use [3-4, 8], homemade explosives (HMEs) need only cause harm to effectively serve their purpose. As a result, there are many different materials that can be used by individuals to make IEDs. Many homemade explosives are combinations of a fuel and an oxidizer [13]. Both components are generally materials that are readily available because they are used for some peaceful purpose in industry and elsewhere [6, 13-14]. For example, common fuels include sucrose (table sugar) and coal, while frequently used oxidizers include ammonium nitrate, a major component of many fertilizers, and potassium chlorate, which is used in safety matches, printing, dying, and pyrotechnics [15-16]. The
increased level of concern about terrorist attacks has led to a greater focus on the materials that can be used to make explosives; however, most published research has dealt with methods to detect HME components, either before or after an attack has occurred [6-7, 13, 17-18]. While there has been some research into the interactions between specific fuel-oxidizer pairs [19-23], there has been no comprehensive study to determine what makes an effective fuel-oxidizer combination. Through the thermal analysis of various combinations of oxidizers and fuels, the study contained herein has provided information on the ways in which fuels interact differently with different oxidizers, which combinations react at lower temperatures, and which pairs are the most energetic in terms of the amount of heat released.

Thermal analyses are essential tools in the study of energetic materials. Numerous studies have been conducted on newly developed insensitive munitions, fuel-oxidizer mixtures, components of these formulations, and other energetic materials [8, 19-21, 23-93]. Many of these studies have employed non-isothermal analyses via thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), or differential thermal analysis (DTA) [8, 19-21, 23-27, 34, 40, 42-43, 48-49, 54, 61-62, 64, 70, 72-73, 83-84, 90]. Non-isothermal DSC works by gradually heating a sample at a rate specified by the operator. Highly sensitive thermocouples in the sample cell are used to detect the flow of heat into and out of the sample during the heating process. Endothermic events, such as phase changes, are usually recorded as negative peaks, while exothermic events, including many decomposition processes, are shown as positive peaks. The temperature at which an exothermic event occurs and the amount of heat released during decomposition provide information about the
energetics and thermal stability of the material being studied. TGA is a similar technique, in which an internal balance measures the amount of material lost as the temperature is gradually increased according to a predetermined ramp rate. The amount of material lost and the temperature at which the mass loss occurs can provide information about the decomposition processes taking place.

DSC, TGA, and other related techniques are able to provide valuable information in a relatively short amount of time. As a result, they are extremely useful tools for the comparison of large numbers of different samples. Isothermal analyses, on the other hand, often involve more time consuming techniques. However, such analyses can provide in-depth information on the processes involved in thermal decomposition, and, as a result, they are also frequently employed in the study of energetic materials [38-39, 63, 68, 77, 81-82, 86-89, 91-92]. The level of decomposition that results from heating a material can be measured in various ways, including the use of chromatography, which allows mixtures of materials to be separated into their various components prior to detection and quantification. Numerous studies have demonstrated the utility of high-pressure liquid chromatography (HPLC) with either an ultra-violet (UV) or a mass spectral (MS) detector in the detection and quantification of explosives, such as DNAN, DNT, NQ, and NTO, and their decomposition products [94-104].
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Fuel-Oxidizer Mixtures:

Their Stabilities and Burn Characteristics

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Manuscript 1

Fuel-Oxidizer Mixtures: Their Stabilities and Burn Characteristics

Abstract

A survey of the stability and performance of eleven solid oxidizers and thirteen fuels was performed by differential scanning calorimetry (DSC), simultaneous differential thermolysis (SDT), and hot-wire ignition. Sugars, alcohols, hydrocarbons, benzoic acid, sulfur, charcoal, and aluminum were used as fuels; all fuels except charcoal and aluminum melted at or below 200°C. It was found that the reaction between the oxidizer and the fuel was usually triggered by a thermal event, i.e. melt, phase change, or decomposition. Although the fuel usually underwent such a transition at a lower temperature than the oxidizer, the phase change of the fuel was not always the triggering event. When sugars or sulfur were the fuels, their phase change usually triggered their oxidation. However, three oxidizers, KNO₃, KClO₄, and NH₄ClO₄, tended to react only after they underwent a phase change or began to decompose, which meant that their oxidization reaction, regardless of the fuel, was usually above 400°C. KClO₄/fuel mixtures decomposed at the highest temperatures, often over 500°C, with the ammonium salt decomposing almost 100°C lower. Mixtures with ammonium nitrate also decomposed at much lower temperatures than those with the corresponding potassium salt. With the exception of the oxidizers triggered to react by the phase changes of the polyols and sulfur, the oxidizer/fuel mixtures generally decomposed between 230°C and 300°C, with ammonium nitrate (AN) formulations
generally decomposing at the lowest temperature. In terms of heat release, potassium dichromate/fuel mixtures were the least energetic, generally releasing less than 200 Jg\textsuperscript{-1}. Most of the mixtures released 1000 to 1500 Jg\textsuperscript{-1}, with potassium chlorate, ammonium perchlorate, and ammonium nitrate releasing significantly more heat, around 2000 Jg\textsuperscript{-1}. When the fuel was aluminum most of the oxidizers decomposed below 500°C leaving the aluminum to oxidize at over 800°C. Only two oxidizers reduced the temperature of the aluminium exotherm—chlorate and potassium nitrite. To go to temperatures above 500°C, unsealed crucibles were necessary, and with these containers, the endothermic volatilization of reactants and products effectively competed against the exothermic decomposition so that heat release values were artificially low.

**Key Words:** Fuel-oxidizer mixtures, Thermal analysis, Differential scanning calorimetry (DSC), Simultaneous differential thermolysis (SDT), Hot-wire ignition

**Introduction**

Fuel-Oxidizer (FOX) mixtures are commonly used in the pyrotechnic and mining industries, with applications ranging from oxygen sources to sources of energy and propulsion. Examples of such uses include ammonium perchlorate with hydroxy-terminated polybutadiene for rocket fuel and ammonium nitrate with fuel oil for commercial mining. The wide availability of many fuels and oxidizers has also resulted in their illicit use as components of improvised explosive devices (IEDs) [1,2].
In this study, a number of solid oxidizers, with varying oxidizing power, were tested on lab-scale in mixtures with a variety of fuels. The purpose of these tests was to assess the hazard and threat potential of the different mixtures, and to allow assessment of the usefulness of small-scale tests. Many of the oxidizers were oxyhalide salts. The potassium salts were used because they tend to be less hygroscopic than those of sodium. Since ammonium salts have different chemical behavior than the potassium salts of the same anion, because they carry and use, if required, their own fuel, the ammonium salts of nitrate and perchlorate were also included in the study. The choice of fuels was limited to solids, including poly-alcohols, hydrocarbons, benzoic acid, sulfur, charcoal, and aluminum.

**Materials and Methods**

Eleven oxidizers and twelve fuels were used in various different combinations. All materials were reagent grade with the exception of the charcoal, which was purchased locally, and aluminum, which was pyrotechnic grade. The oxidizer/fuel mixtures were examined fuel-rich at 50/50 mass% and closer to stoichiometric at 80/20 mass%. Benzoic acid, which is often used as a burn rate modifier, and aluminum were added only at the 20 mass% level. Individual components with larger particle sizes (i.e. sugars and most oxidizers) were ground prior to mixing. Those materials that were already fine powders, such as sulfur, were used as received. Materials used to make the 80/20 sucrose mixtures were sieved to 50-100 mesh. Mixtures were generated by gently stirring the fuel and oxidizer together with a wooden stick or by mixing in a Resodyn LabRAM acoustic mixer (two minutes, 50%
intensity, auto frequency). Batch sizes ranged from 100 mg to 1 g depending on the analyses to be performed.

A TA Q100 differential scanning calorimeter (DSC) was used with a ramp rate of 20°C/minute. Samples of about 0.25 mg were flame sealed in glass capillaries (borosilicate, 0.06 in. ID, 0.11 in. OD) held on a liquid nitrogen cooled metal post to ensure that decomposition did not occur during sample preparation [3]. To verify the integrity of the capillary sealing (i.e. no leaks) capillaries were weighed before and after DSC analysis. A TA Instruments Q600 simultaneous TGA/DSC (SDT) was used with unsealed samples held in ceramic crucibles. About 5 mg of sample was placed in an empty crucible previously tared by the internal balance of the SDT. Ceramic caps (not tightly sealed) were placed on the crucibles for samples which might eject material or for highly volatile samples, such as the sulfur mixtures. The SDT was used because of its extended temperature range (1000°C versus 500°C for DSC); however, the thermograms obtained with sealed DSC capillaries did not necessarily match those observed with the unsealed ceramic pans used in the SDT. In contrast to the open pans, which allowed samples to volatilize, there was considerable pressure build-up in the sealed samples. Differences noted in the SDT traces included somewhat smaller exotherms; some smaller exotherms became endotherms; and larger exotherms were sometimes split by an endotherm. Since a build-up of pressure is representative of real explosive events, the sealed DSC capillaries were used for temperatures below 450°C; if temperatures above that are reported, they are SDT results. In most cases, both DSC and SDT analyses were run under nitrogen.
Samples were usually run in triplicate, but where marked variations in the thermograms were apparent, up to seven samples were run. Variations in the detailed appearance of the DSC thermograms were likely a result of inhomogeneities in the oxidizer and fuel mix, especially considering that samples were usually less than a milligram. Because multiple endotherms and exotherms were often observed in the DSC and SDT traces, and because many of the exotherms covered a wide temperature range, the major exotherm of a trace is usually reported with either the onset temperature or the temperature at which a deviation from baseline was initially detected, followed by the temperature(s) at which “peak maxima” were observed, with the highest in bold, and the heat of reaction in parentheses (J g\(^{-1}\)) calculated from peak area using baselines established by the operator.

For burn tests the oxidizers and sucrose were dried overnight in a vacuum oven at 50°C, then ground and sieved to 50-100 mesh. Pyrotechnic-grade (median particle size 23 μm) aluminum powder (Obron) was used. Samples were mixed with a Resodyn LabRAM acoustic mixer at 50% intensity for 2 minutes. Approximately 0.25 g samples were placed in a pile on a ceramic plate over a loop of 22-gauge nichrome wire (30 cm long for power requirements of 150W) attached to a variable autotransformer (set to 20V) with a 25 amp internal fuse for the burn. Light output was recorded with a DET36A detector (Thor Labs) and recorded using a National Instruments USB-6210 data acquisition module. Light data was recorded at 10-100 kHz by measuring voltage across a 350 ohm resistor. The detector was unfiltered for mixtures producing low levels of light (oxidizer with sucrose). To resolve the brightest events (oxidizer with aluminum), a 90% neutral density filter (ND10A, optical density
of 1.0) was applied behind an Iris (6.33 mm diameter opening, Iris SM1D12). The data acquisition card was set to sampling rate of at least 10 kHz, with pre-trigger of 50-100ms.

Results and Discussion

Neat Species: Oxidizing power can be assessed in various ways. Intrinsic oxidizing ability, given by the standard reduction potential in Volts (1M aq solution against H₂ as zero), is one approach to quantifying oxidizing power. Standard reduction potentials are listed below starting from the left with species having most positive potential [4,5]:

\[
\begin{align*}
\text{H}_2\text{O}_2 & (1.8) > \text{IO}_4^- (1.7-1.6) > \text{MnO}_4^- (1.7-1.5) > \text{BrO}_3^- (1.5-1.4) > \text{ClO}_3^- (1.5) > \\
\text{Cr}_2\text{O}_7^{2-} (1.4-1.3) > \text{ClO}_4^- (1.4-1.2) > \text{IO}_3^- (1.2-1.1) > \text{NO}_3^- (1.0-0.8) > \text{NO}_2^- (-0.46)
\end{align*}
\]

Actual potentials depend on the pH of the solution and the final products:

\[
\text{NO}_3^- \rightarrow \text{NO, HNO}_2, \text{NH}_4^+ \text{, NO}_2; \quad 0.96, 0.94, 0.87, 0.80 \text{ V, respectively}
\]

An alternative approach to rating oxidizing power is a burn test. The U.N. Manual of Tests and Criteria rates an oxidizer by comparing its burn rate in admixture with cellulose (2:3 and 3:7 ratios) to mixtures of potassium bromate/cellulose [6]. Our burn tests used 250 mg instead of 30 g of material, and sucrose or aluminum powder instead of cellulose. Burn rates are shown in Table 1.
Thermal stability was assessed via the temperature at peak maximum of the DSC exotherm. The higher the exotherm temperature, the more thermally stable the species. Some salts decomposed with an exclusively endothermic response (Table 2).

Among salts releasing heat (exothermic response), the amount of heat varied from more than 1000 J g\(^{-1}\) for ammonium salts, which can undergo self-oxidation, to a few hundred joules per gram for other oxidizers. Thermal traces of the oxidizers alone were not simple; they included phase change(s), decompositions, and heats of fusion of the decomposition product. In systems where oxygen was not allowed to escape, the pairs perchlorate/chlorate [7-9] and nitrate/nitrite [10,11] can establish a pseudo-equilibrium (eq 1-2) [10]. At high temperatures the melts of KCl, K\(_2\)O, and KI were

### Table 1 Burn time /seconds of a 4:1 Oxidizer: Sucrose Mix

| Oxidizer | KIO\(_3\) | KMnO\(_4\) | KBrO\(_3\) | KClO\(_3\) | K\(_2\)CrO\(_7\) | NH\(_4\)Cl | KClO \(_4\) | KBrO \(_3\) | NH\(_2\)ClO | KIO\(_3\) | KNO\(_3\) | NH\(_2\)NO\(_3\) | KNO\(_3\) |
|----------|------------|------------|------------|------------|----------------|-----------|------------|------------|-------------|------------|------------|---------------|------------|
| Burn Test 8:2 Oxidizer/Al | | | | | | | | | | | | | | |
| Arc Peak Light Signal Thor (mV) | 5764 | 3530 | 1113 | 1179 | 140 | 144 | 397 | | | | | | |
| Rel. | 75 | 57 | 41 | 74 | 92 | 71 | 11 | | | | | | |
| Notes | liquid flash | liquid flash | liquid flash | liquid flash | liquid flash | liquid flash | | | | | | | | |

### Table 2 Burn time /seconds of a 4:1 Oxidizer: Sucrose Mix

| Oxidizer | KIO\(_3\) | KMnO\(_4\) | KBrO\(_3\) | KClO\(_3\) | K\(_2\)CrO\(_7\) | NH\(_4\)Cl | KClO \(_4\) | KBrO \(_3\) | NH\(_2\)ClO | KIO\(_3\) | KNO\(_3\) | NH\(_2\)NO\(_3\) | KNO\(_3\) |
|----------|------------|------------|------------|------------|----------------|-----------|------------|------------|-------------|------------|------------|---------------|------------|
| Burn Test 8:2 Oxidizer/Al | | | | | | | | | | | | | | |
| Arc Peak Light Signal Thor (mV) | 56 | 25 | 206 | 164 | 3 | 11 | 22 | | | | | | | |
| Rel. | 12 | 12 | 31 | 41 | 4 | 11 | 22 | | | | | | | |
| Notes | purple | blue | blue | blue | blue | blue | blue | | | | | | | | |

### Table 3 Burn time /seconds of a 4:1 Oxidizer: Sucrose Mix

| Oxidizer | KIO\(_3\) | KMnO\(_4\) | KBrO\(_3\) | KClO\(_3\) | K\(_2\)CrO\(_7\) | NH\(_4\)Cl | KClO \(_4\) | KBrO \(_3\) | NH\(_2\)ClO | KIO\(_3\) | KNO\(_3\) | NH\(_2\)NO\(_3\) | KNO\(_3\) |
|----------|------------|------------|------------|------------|----------------|-----------|------------|------------|-------------|------------|------------|---------------|------------|
| Burn Test 5:5 Oxidizer/Al | | | | | | | | | | | | | | |
| Arc Peak Light Signal Thor (mV) | 18 | 450 | 118 | 18 | 58 | 43 | 43 | | | | | | | |
| Rel. | 9 | 22 | 11 | 9 | 22 | 22 | 22 | | | | | | | |
| Notes | yellow, orange | yellow | yellow, orange | yellow | yellow | yellow, orange | yellow | | | | | | | |

### Table 4 Burn time /seconds of a 4:1 Oxidizer: Sucrose Mix

| Oxidizer | KIO\(_3\) | KMnO\(_4\) | KBrO\(_3\) | KClO\(_3\) | K\(_2\)CrO\(_7\) | NH\(_4\)Cl | KClO \(_4\) | KBrO \(_3\) | NH\(_2\)ClO | KIO\(_3\) | KNO\(_3\) | NH\(_2\)NO\(_3\) | KNO\(_3\) |
|----------|------------|------------|------------|------------|----------------|-----------|------------|------------|-------------|------------|------------|---------------|------------|
| Burn Test 6:0 Oxidizer/Benzonic Acid | | | | | | | | | | | | | | |
| Arc Peak Light Signal Thor (mV) | 1113 | 157 | 2228 | 762 | 26 | 226 | 737 | 221 | 91 | 11 | 160 | | | |
| Rel. | 172 | 12 | 441 | 236 | 5 | 230 | 144 | 112 | 1 | 1 | | | | |
| Notes | yellow, orange | yellow | yellow, orange | yellow | yellow | white | white | orange | yellow | | | | | | |
observed, and the DSC traces showed the decomposition of periodate to iodate around 330°C (eq 3); thereafter, their thermograms were identical [12-17].

\[
\begin{align*}
K\text{ClO}_4 & \iff K\text{ClO}_3 \rightarrow K\text{Cl} + 1.5 \text{O}_2 & (1) \\
K\text{NO}_3 & \iff K\text{NO}_2 + 0.5\text{O}_2 & (2) \\
K\text{IO}_4 & \rightarrow K\text{IO}_3 \rightarrow K\text{I} + 1.5 \text{O}_2 & (3)
\end{align*}
\]

Ammonium perchlorate (AP, NH₄ClO₄) did not melt but exhibited an endotherm around 245°C (~70 J g⁻¹) as a result of an orthorhombic to cubic phase change. [Ammonium chlorate is thermally unstable and has been reported to spontaneously ignite at temperatures as low as 100°C [18]; for this reason it was not used in this study.] Continued heating of AP in sealed DSC ampules resulted in a single exotherm which began around 350°C and reached a maximum about 400°C (~1300 J g⁻¹). The SDT results appeared quite different. Immediately after the 245°C phase change, a small exotherm (~360 J g⁻¹) at ~318°C was observed followed by a second endotherm centered around 435°C (Fig. 1). This apparent difference in AP behavior has been explained by the sublimation of AP above 350°C competing with its decomposition [19, 20]. Sublimation can be dramatically reduced by pressure; thus, when possible sealed DSC pans were used [20]. As heating of the open pan in SDT was continued, a small endotherm at 757°C was observed for the melt of KCl.
All the fuels, except charcoal and aluminum, melted below 208°C; some showed exothermic decomposition especially when heated under air. Endothermic and exothermic temperature minima or maxima, onset temperatures for exotherms, and heat release as found by DSC or SDT (scan rate 20°C/min) are shown in Table 2.

An advantage of SDT thermal analysis was that it allowed scanning to higher temperatures. However, since the crucibles were not sealed, the SDT thermal traces differed markedly from sealed DSC thermal analyses. For example, the exotherm at 316°C in the DSC thermal trace of AN became an endotherm at 292°C when examined by SDT due to the volatilization of the AN. This same observation was made with a number of compounds and formulations. Sulfur, in the open pans, exhibited an exotherm around 400°C when run under air. This was evidently a reaction with the oxygen in air since no exotherm was observed when the samples were scanned under nitrogen. Similar large exotherms were also observed when charcoal and sucrose were scanned under an air atmosphere.
Table 2. Temperature Endotherms & Exotherms DSC & SDT (20°/min, Heat Release/ Jg⁻¹)

| Compound | KClO₃ | KMnO₄ | KIO₃ | KNO₃ | KBrO₃ | KClO₄ |
|----------|-------|-------|------|------|-------|-------|
| Snout    | 110   | 100   | 100  | 100  | 100   | 100   |
| Bucephos | 100   | 100   | 100  | 100  | 100   | 100   |
| PNP      | 100   | 100   | 100  | 100  | 100   | 100   |
| Lactone  | 100   | 100   | 100  | 100  | 100   | 100   |
| Chiosene | 100   | 100   | 100  | 100  | 100   | 100   |
| Xyloglo   | 100   | 100   | 100  | 100  | 100   | 100   |
| Xyloglon  | 100   | 100   | 100  | 100  | 100   | 100   |
| Cystodea  | 100   | 100   | 100  | 100  | 100   | 100   |
| Canthax   | 100   | 100   | 100  | 100  | 100   | 100   |
| Sperma    | 100   | 100   | 100  | 100  | 100   | 100   |
| Nannosa   | 100   | 100   | 100  | 100  | 100   | 100   |
| Nannosum  | 100   | 100   | 100  | 100  | 100   | 100   |
| Nannosol  | 100   | 100   | 100  | 100  | 100   | 100   |
| Charcoal  | 100   | 100   | 100  | 100  | 100   | 100   |
| Al 20%    | 100   | 100   | 100  | 100  | 100   | 100   |
Table 2 cont. Temperature Endotherms & Exotherms DSC & SDT (20°/min, Heat Release/ g⁻¹)

| Sample | Temperature (°C) | Heat Release (J/g) |
|--------|------------------|--------------------|
| Sample A | 100 | 1000 |
| Sample B | 200 | 2000 |
| Sample C | 300 | 3000 |

Note: Additional columns and rows may be present in the table.
Oxidizer/Fuel Mixtures

Numerous kinetic studies have examined the decomposition of individual oxidizers [7-24], and several kinetic and mechanistic studies exist that have examined the oxidation of alcohols by iodate and periodate [25-34], bromate [35], chlorate and perchlorate [36-38], permanganate [39,40], and dichromate [41] (Table 3). Most of the eleven oxidizers (KIO₄, KMnO₄, KBrO₃, KClO₃, K₂Cr₂O₇, KIO₃, AN, KNO₂) reacted with the sugars immediately after their melt, and a large exotherm was observed, as can be seen in Figure 2 (DSC thermogram of KIO₄ mixed with 50 mass% sucrose). This behavior was observed regardless of whether the sugar was a disaccharide, i.e. sucrose and lactose, or a monosaccharide, i.e. glucose and fructose (Fig. 3, 4).

Table 3 Oxidation Products of Some Alcohols

| Oxidizer   | Alcohol                  | Products                      | Reference |
|------------|--------------------------|-------------------------------|-----------|
| KBrO₃      | propan-2-ol              | acetone                       | 35        |
| KClO₃      | sucrose                  | KCl, CO₂, H₂O                | 38        |
| KClO₃      | lactose                  | KCl₂, CO₂, H₂O, CO₃, C₂H₂     | 36, 37    |
| KClO₃      | fructose                 | KCl₁₂, O₂, H₂O               | 38        |
| KIO₃       | pea cannaery waste       | fructose, iodate, carboxylic acid | 37    |
| KIO₃       | diacetyl disobutyl, benzil, camphorquinone | iodate, carboxylic acid, KIO₃, 38 |
| KIO₃       | fructose, glucose, galactose, maltose, sucrose | formic acid & lower sugars | 39      |
| NaIO₄      | dextran (an anhydroglucose polymer) | formic acid, dimer of intermediate via Diels-Alder | 30, 39 |
| NaIO₄      | salicyl alcohol          | dimer of intermediate via Diels-Alder | 30      |
| NaIO₄      | glucose                  | HCO₂-H, HClO₃, H₂O           | 25        |
| NaIO₄      | cellulose                | dglaldehyde                   | 32        |
| NaIO₄      | cellulose                | dglaldehyde                   | 33        |
| NaIO₄      | catechol                 | o-benzoglucinquinone          | 34        |
Fig. 2 $\text{KIO}_4 + 50$ mass% Sucrose

Fig. 3 $\text{KClO}_3 + 50$ mass% disaccharide: Sucrose (3a) & Lactose (3b)

Fig. 4 $\text{KClO}_3 + 50$ mass% monosaccharide: Glucose (4a) & Fructose (4b)
The fact that the majority of oxidizers reacted immediately after the melt of the sugar suggested that molten sugars can solublize, or at least mobilize, the oxidizer, promoting reaction. We labeled these oxidizers "sugar-controlled." A detailed examination of the reaction between KClO$_3$ and lactose noted the importance of liquid lactose and its solubilization of the chlorate; it also noted no disproportionation into perchlorate [36-38].

![Fig. 5 KIO$_4$ + 20 mass% Sucrose](image)

For three oxidizers this general trend with sugars was not observed. These oxidizers may have exhibited a small exotherm immediately after the sugar melt, but the majority of the exothermic reaction only occurred after the oxidizer underwent a melt, phase change, or decomposition, and we labeled them "oxidizer-controlled." The two resistant anions were perchlorate and nitrate, but for the latter, nitrate, only the potassium salt failed to react immediately after the sugar melt. This counter-trend was true regardless of the type of sugar (Fig. 6 and Fig. 7).
Generally, the thermograms did not change drastically in appearance when 20 mass% rather than 50 mass% sucrose was used (compare Fig. 2 and 5 or see Fig. 8). The exception was ammonium perchlorate (AP), one of the three oxidizers resistant to sugar melt. With 50 mass% sucrose a wide exotherm was observed immediately after the melt of sucrose and a second exotherm started about 270°C. With only 20 mass% sucrose, no exotherm was observed until ~ 470°C, in dramatic contrast to the thermogram with 50 mass% sucrose (Fig 9).
With ammonium nitrate (AN) and the sugars, it was difficult to assign the decomposition trigger as the sugars and the AN both melted in the 150 to 170°C range. With the higher level of sucrose (50 mass%) the main exotherm was observed around 180°C, while with sucrose closer to stoichiometric (20%), large exotherms were observed at 170 and 340°C, with the latter at the normal decomposition temperature of AN (Fig. 10).
The heat released from the oxidizers with 20 mass% sucrose was comparable (~1400 Jg$^{-1}$) to the heat released with 50 mass% sucrose (Table 4). There was a large deviation in observed heat released (±25%) run to run which we have attributed to the slow response of the DSC thermocouples. K$_2$Cr$_2$O$_7$ fuel mixtures were notably low in energy release, averaging less than a tenth of the other fuel/oxidizer mixtures (Table 4).
Table 4 Heat Released/ Jg\textsuperscript{-1} below 500°C from Oxidizer/Fuel Mixes

| Oxidizer | KIO\textsubscript{4} | KMnO\textsubscript{4} | KBrO\textsubscript{3} | KClO\textsubscript{4} | KClO\textsubscript{3} | KIO\textsubscript{3} | KNO\textsubscript{3} | AN | KNO\textsubscript{2} |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|---|----------------|
| Exotherm Jg\textsuperscript{-1} | 94 | 142 | 217 | 465 | 1233 | 290 | 1407 | SDT |
| Sulfur | 2054 | 1964 | 1110 | 2037 | 127 | 2253 | 1125 | 1243 | 1016 | 2092 | 1981 |
| Sulfur 20% | 1405 | 1798 | 1718 | 2091 | 102 | 1357 | 1698 | 838 | 681 | 1792 | 5280 |
| Glucose | 2086 | 2686 | 697 | 696 | 1480 | 666 | 2217 |
| Pentaaerythritol | 1427 | 2058 | 1638 | 2118 | 1009 | 2238 | 1758 | 1209 |
| Erythritol | 1140 | 1702 | 2272 | 129 | 3822 | 573 | 871 | 2438 | 1758 | 1009 |
| Cyclododecanol | 790 | 768 | 876 | 1329 | 276 | 19/ | not seen | 354 | not seen |
| Surfact | 2353 | 2360 | 815 | 723 | 1747 | 1512 | 2299 | 1054 | 2328 | 2094 |
| Naphthalene | 1205 | 531 | 1779 | 500 | 60 | 1527 | not seen | 829 | not seen |
| Benzoic acid 20% | 1500 | 1309 | 835 | 5648 | 138 | 2400 | not seen | 18/9 | not seen |
| Charcoal | 600 | 792 | 454 | 1585 | 156 | 1718 | 1172 | 300 | 1361 | 1607 | 625 |
| Aluminum 20% all SDT | 170 | 726 | 1454 | 1495 | 38 | 1600 | 800 | 490 | 1300 | 640 | 2400 |

Average all fuel - Al 1452 | 1331 | 1235 | 2011 | 136 | 2038 | 1057 | 978 | 1131 | 1892 | 1281 |

Since there was not much differentiation among the sugars, we chose to examine a more diverse group of alcohols: erythritol (mp 122°C), pentaerythritol (mp 190°C), and cyclododecanol (mp 78°C). Erythritol has been shown to be a suitable substitute for sucrose in the preparation of chiffon cake [42]. Only two oxidizers with erythritol (KMnO\textsubscript{4} and KIO\textsubscript{4}) showed immediate decomposition after the melt of erythritol, although all the "sugar-controlled" oxidizers that were examined with this fuel decomposed at lower temperatures than their own phase changes or decomposition point (Fig. 11). Five of the oxidizers were heated with pentaerythritol. KClO\textsubscript{3} and KBrO\textsubscript{3}, which had been labeled "sugar-controlled", remained triggered by the fuel, while KNO\textsubscript{3} remained oxidizer controlled. AN, which
with the four sugars exhibited an exotherm around 170°C, did not react with the melt of pentaerythritol (PE) at 190°C. Instead it began to release heat around 260°C, a phase change for PE. In some thermograms the exotherm at 260°C was the only peak; in others a second peak was observed at the normal decomposition temperature of AN (Fig. 12). Potassium dichromate, which was one of the “sugar controlled” oxidizers, did not react near the melting point of pentaerythritol, but showed a small exotherm following its own melting point around 400°C.

Fig. 11 KMnO₄ + Erythritol

Fig. 12 AN + 50 mass% Pentaerythritol (12a & 12b)
Cyclododecanol had a melting point lower than the other alcohols, but as a mono-alcohol it appeared to have little ability to solvate the oxidizers. Two of the oxidizers, KClO₄ and KNO₃, showed no reaction with cyclododecanol when monitored up to 500°C.

To examine samples that did not exhibit heat releases in the temperature range of the DSC, SDT was used. Because the SDT was designed to allow monitoring of mass loss as well as heat flow, samples were scanned unsealed. This immediately proved to be a problem. In some cases exothermic events appeared as endothermic events; a classic example is a scan of an unsealed sample of AN. When not contained in a sealed ampoule, AN will show an endotherm around its 300°C decomposition rather than the actual exotherm (Fig. 13). Occassionally the exothermic event was only partially countered by the endothermic evaporation of the reactant or products; in such cases the exotherm was observed, but heat release was significantly lower than it would have been in a sealed sample. Therefore, whenever possible, sealed samples were examined by DSC. To date we have found no satisfactory method for sealing DSC samples that remains gas tight over 550°C.

![Figure 13 Ammonium nitrate DSC (13a) vs. SDT (13b)](image-url)
To examine fuels other than alcohols, naphthalene, hexatriacontane, benzoic acid, charcoal, sulfur, and aluminum were added to the study. Neither naphthalene nor hexatriacontane, both of which are hydrocarbons with melting points around 80°C, exhibited reactions with the oxidizers at temperatures below 200°C, and in the mixtures with benzoic acid, only potassium permanganate reacted near the fuel’s melting point of 121°C. Charcoal, which does not melt, also tended to react at higher temperatures; only with ammonium nitrate did it have an exothermic peak maximum below 300°C. Sulfur, which exists as a number of allotropes [43], and has long been used in energetic formulations [44,45], exhibited behavior much more similar to that of the sugars. We observed two, and sometimes three, endotherms between 107 and 120°C, assigned to phase change and melting, and there was also a small endotherm around 180°C. The oxidizers that were initiated by the sugar melt also showed exothermic decomposition with sulfur beginning around 180°C. A common characteristic of this exothermic decomposition was slow heat release rising to a recognizable exotherm (Fig. 14). The same three oxidizers classified as oxidizer-controlled do not show an exotherm until higher temperatures (Fig. 15).

![Graph showing DSC analysis](image)

**Fig. 14** KMnO₄ + 50 mass% Sulfur
Table 5 records the temperature at which the exotherms were first observed to rise above the baseline (ramp rate of 20°C/min). These temperatures are different than those recorded in Table 2, which tabulates the onset temperatures of the exothermic peaks as calculated by the TA Universal Analysis DSC software. When DSC exotherms are very broad, onset temperatures are often misleading. For example, when KBrO₃ is mixed with naphthalene (Fig. 16), the difference between the onset and first deviation from baseline is not large (~30°C), but for KIO₃ and sulfur (Fig. 17) the difference between the calculated onset and the deviation from baseline is huge (~160°C). (Note that this trace of oxidizer and sulfur is typical for sulfur mixtures.)
Table 5 Temperature at which Principle Exotherm is First Observed/°C

| Oxidizer phase change | KIO₃ | K₂MnO₄ | KBrO₃ | KClO₃ | K₂Cr₂O₇ | AP | KClO₄ | KNO₃ | KNO₂ | AN | KNO₃ |
|-----------------------|------|---------|-------|-------|---------|----|-------|------|------|----|------|
| Oxidizer decomposition | 310  | 277     | 428   | 574   | 365     | 636| 555   | 703  | 254  | 510|
| Sucrose               | 185  | 238     | 148   | 194   | 179     | 167| 224   | 203  | 443  | 159| 372  |
| Pentanol              | 359  |         |       |       |         |    |       | 420  |      |    |      |
| Diphenylmethane       | 722  | 297     | 119   | 117   | 142     | 393| 258   | 515  | 595  | 141| 350  |
| Sulfur                | 187  | 119     | 182   | 180   | 193     | 149| 391   | 428  | 169  | 294| 172  |
| Cyclohexanol          | 79   |         |       |       |         |    |       | 414  |      |    |      |
| Cyclohexane           | 79   |         |       |       |         |    |       |      |      |    |      |
| Naphthalene           | 80   |         |       |       |         |    |       | 400  | 600  | 600| 219  |
| Benzoic acid 20%      | 121  |         |       |       |         |    |       | 403  | NR<500| 270| NR<500|
| Charcoal              | 164  | 277     | 300   | 367   | 363     | 393| 403   | 410  | 261  | 368|
| Al (78%)              | 662  |         |       | 419   | 264     | 900| 563   | 581  | 747  | 846| 679  |
| Al                   | 280  |         |       |       |         |    |       | 435  |      |    |      |

The temperature at which an oxidizer/fuel mixture begins to react depends on both the susceptibility of the fuel to oxidation and the oxidizer’s tendency to be reduced. In comparing the carbonaceous fuels, cyclohexanol, hexatriacontane, naphthalene, benzoic acid, and charcoal, we had hoped to see a reactivity trend across all oxidizers, and, indeed, the following trend in the initiation temperature of the decomposition exotherm was observed with over half the oxidizers:

benzoic acid < cyclohexanol ~ hexatriacontane < charcoal < naphthalene
Interestingly, hexatriacontane and cyclododecanol, which had boiling points only one degree apart, produced DSC traces almost identical to each other, suggesting the reaction of cyclododecanol was that of a hydrocarbon rather than an alcohol. It was also observed that with fuels other than aluminum, ammonium perchlorate mixtures decomposed at lower temperatures than those with potassium perchlorate.

Aluminum, which has been used as a fuel in mixtures with ammonium nitrate and perchlorate, was used as the highest melting fuel. With two exceptions, the oxidizers decomposed long before the aluminum reacted, and aluminum did not react until over 800°C (Fig. 18, 19). In two cases (KClO₃, KNO₂) the exotherm appeared at a significantly lower temperature indicating that these oxidizers react readily with the aluminum (Fig. 20, 21). All the oxidizer/Al samples were examined by SDT, and a few were also examined by DSC. The low temperature exotherm observed for KIO₄ was its conversion into KIO₃. The low temperature (i.e. under 800°C) exotherms recorded for other oxidizers reflect the decomposition of the oxidizer.

![Fig. 18 KMnO₄ + 20 mass% Aluminum](image)
Fig. 19 KNO₃ + 20 mass% Aluminum

Fig. 20 KNO₂ + 20 mass% Aluminum

Fig. 21 KClO₃ + 20 mass% Aluminum
Summary

Neat oxidizers appeared to undergo decomposition roughly in line with their standard reduction potentials (Table 1) [4,5]. Most oxidizers produced some heat when decomposed without fuel, but it was a few hundred joules per gram compared to 1500 to 3000 Jg\(^{-1}\) when decomposed with fuel. The exceptions were the ammonium salts which produced 1000 to 1500 Jg\(^{-1}\) without fuel and double that with fuel. The oxides of chlorine released the most heat, in line with the general trend that the larger the electronegative difference between oxygen and the central element, the more stable the oxyhalide. When anions containing the same central atom are compared, the order of stability is attributed to the degree of pi-bonding in each species: ClO\(_4^-\) > ClO\(_3^-\) and NO\(_3^-\) > NO\(_2^-\) [46,47]. For the oxo-chlorine and oxo-nitrogen species, perchlorate and nitrate are more stable and less sensitive than the less highly oxidized chlorate and nitrite.

When fuels were added to the oxidizer, the phase changes of the individual oxidizers and fuels were often still observed. Most of the fuels were added at the 50 mass\% level, but thermograms of 20 mass\% sucrose were examined and shown to be very similar to 50 mass\% sucrose in terms of appearance and heat release. Variations in appearance and heat release (±25\%) were attributed to inhomogeneity in the samples and variations in particle size [48-51], although even neat ammonium nitrate exhibited 15\% variation in heat release. We suspect that with energetic materials it is difficult for the DSC thermocouples to accurately track the fast release of heat. Differences in DSC and SDT traces appeared to be related to the ability of reactants/products to vaporize in the open or lightly capped SDT containers.
We found that a phase change in the fuel or oxidizer or decomposition of the oxidizer typically was the trigger causing their reaction; therefore, we classified the reactions as fuel- or oxidizer-controlled. With the exception of charcoal and aluminum, all fuels used melted below 200°C. The melt or phase change of the sugars or sulfur triggered the reaction of most of the oxidizers, but in mixtures with the non-polyalcohol fuels, decomposition tended to occur at higher temperatures. Three oxidizers, KNO₃, KClO₄, and NH₄ClO₄, most often triggered their own reaction, and typically exhibited the highest reaction temperatures, i.e. above 400°C, regardless of the fuel.

The poorest oxidizer was clearly potassium dichromate, releasing barely 100 Jg⁻¹. The rest of the oxidizer/fuel mixtures released heat ranging from 1100 to 2200 Jg⁻¹ with an average of about 1500 Jg⁻¹ (Table 4). Oxidizers consistently releasing the most heat were KClO₃, AP, and AN. (The heat release values for potassium perchlorate may have been artificially low due to the fact they were only observable by SDT, which could allow material to escape prior to the exothermic event). The amount of heat released appeared dependent on the oxidizer rather than the fuel. No fuel stood out as clearly the ‘best’; they averaged 1500 Jg⁻¹ by DSC analysis.

Response to hot-wire ignition was assessed by the length of the burn and the light output. Table 1 orders the oxidizers left to right as highest oxidizing power to lowest in terms of electromotive potential; this roughly followed their thermal stability. Light output, when the fuel was aluminium, also roughly followed this trend.
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Thermal Stability Studies on IMX-101

(Dinitroanisole/Nitroguanidine/NTO)

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Abstract

The recent emphasis on the development of new insensitive munitions has resulted in the development of a number of new energetic formulations. Many of the formulations intended for use as replacements for 2,4,6-trinitrotoluene (TNT) contain 2,4-dinitroanisole (DNAN) as a major ingredient. An in-depth evaluation of the thermal stability of one of the new insensitive TNT replacements, IMX-101, which is a mixture of DNAN, nitroguanidine (NQ) and 3-nitro-1,2,4-triazol-5-one (NTO), has been conducted using both differential scanning calorimetry (DSC) and isothermal decomposition tests. The results of this investigation were compared to a similar formulation in which the DNAN was replaced with 2,4-dinitritoluene (DNT). DNAN was expected to show greater thermal stability than DNT, both neat and in combination with NTO and NQ. The isothermal studies showed that, as expected, neat DNAN was more stable than neat DNT. However, when mixed with either or both of the other components of the IMX-101 formulation, the thermal stability of both DNAN and DNT was decreased. The decomposition of both DNAN and DNT was significantly accelerated by the presence of NQ. NTO also enhanced the decomposition of both nitroarenes, but this compound had a significantly greater impact on DNAN than on DNT. An examination of the decomposition products from the various mixtures showed that 2,4-dinitroaniline (DNA) was produced from the decomposition of both DNAN and DNT with either of the two additives; DNA was not observed during the neat decompositions of the two arenes. It was thought that
ammonia, which has been detected in either gaseous form or as ammonium ions during decomposition studies on both NQ and NTO, might be one cause of the decreased stability imparted to the nitroarenes by the two additives. Heating DNAN and DNT in the presence of ammonia generated from ammonium carbonate produced dinitroaniline and had an accelerating effect on the decomposition of the two nitroarenes, with the greater impact, both in the acceleration level and the amount of dinitroaniline produced, on DNAN.

**Introduction**

In 2001 the United States Congress passed the ‘Insensitive Munitions Law’, which required that "the Secretary of Defense ensure, to the extent practicable, that insensitive munitions under development or procurement are safe throughout development and fielding when subject to unplanned stimuli” [1]. Many other nations also have initiatives to develop and use less sensitive munitions [2-4]. The mandate that explosive materials be safer is not easily met. An insensitive munitions formulation should have good explosive properties but should also be thermally stable and must not react violently when subjected to unplanned events [5]. In general, materials that have good explosive properties are not particularly thermally stable and tend to be sensitive to accidental ignition [4]. Finding materials that have acceptable explosive performance and low sensitivity has proven to be quite difficult, even after many years of research. In general, the quest for insensitive munitions has followed one of two approaches; either explosive materials are encased in less sensitive
polymeric materials to form polymer bonded explosives (PBXs), or entirely new explosive formulations are developed [5,6].

One of the early candidates for a TNT replacement was 2,4-dinitroanisole (DNAN), which, like TNT, is melt-castable but also toxic [7-10]. The use of DNAN is not new; it was used as part of the explosive formulation Amatol 40 during WWII, but this use was most likely due to a shortage of TNT rather than because of concerns about the sensitivity of munitions [7,11]. More recently, the improved sensitivity of DNAN based munitions has led to the development of numerous DNAN formulations, some of which have been qualified for use by the U.S. National Service Authority [11-18]. The TNT replacement IMX-101, which contains 43.5% DNAN, 19.7% 3-nitro-1,2,4-triazol-5-one (NTO), and 36.8% nitroguanidine (NQ), was certified for use in 2010 [16]. IMX-101 is listed as having a theoretical maximum density of 1.67 g/cc and a detonation velocity of 6900 m/s; it has passed the STANAG fast and slow heating tests 4240 and 4382, respectively [16,19]. However, while IMX-101 did pass the various ageing and stability tests to which it has been subjected, it has not always shown better results than TNT and RDX. In the vacuum thermal stability test at 100°C, IMX-101 evolved slightly more gas than TNT and RDX, and events occurred at lower temperatures than TNT in the Woods Metal bath and Henkin time to explosion tests, and at lower temperatures than both TNT and RDX in the 1-liter spherical cook-off test. IMX-101 did outperform both TNT and RDX in the small-scale ESD, ERL/Bruceton impact, and BAM friction tests [16]. This study examined the use of DNAN (mp 94-95°C) in insensitive munitions formulations versus 2,4-
dinitrotoluene (DNT), which, with a melting point of 70°C, would also be melt-castable. The structures of DNAN, DNT, NTO, and NQ are shown in Figure 1.

![Structures of DNAN, DNT, NTO, & NQ](image)

Figure 1: Structures of DNAN, DNT, NTO, & NQ

Experimental Setup

**Materials:** 2,4-Dinitroanisole (DNAN, 98%) and 2,4-dinitrotoluene (DNT, 95%) were purchased from Alfa Aesar and were ground in a mortar and pestle prior to mixing with other formulation components or weighing into glass capillaries. Solvents were Optima (for LC/MS) or HPLC (for LC/UV) grade purchased from Fisher Scientific. Nitroguanidine (NQ) and NTO were prepared in-house. High bulk density NQ was obtained by dissolving the low-density needles in 2,2-dimethylformamide, pouring the solution into acetone and cooling the mixture until small white crystals of NQ formed [20]. The synthesized NTO was a fine white powder, and used without recrystallization. (DSC traces of a small amount of recrystallized material showed little difference from the non-recrystallized NTO.) Mixtures of the four materials were prepared either by stirring them together in a ceramic dish using a wooden stick or by mixing them using an acoustic mixer.
(LabRAM) for two minutes at 30 to 50% intensity with the frequency set to automatic. Mixture sizes ranged from 40 mg to 1g.

**Differential Scanning Calorimetry (DSC):** DSC samples were prepared by measuring about 0.240-0.260 mg of material into a glass capillary, which was then placed on a liquid nitrogen cooled metal post and sealed with a small flame. Liquid nitrogen was used to cool the samples to insure that decomposition did not occur during the sample preparation process [21]. The sealed capillaries were weighed before and after DSC analysis to determine if any material had leaked during testing. Samples were run on a TA Instruments Q100 DSC from 30 to 500°C with a ramp rate of 20°C/min under a nitrogen flow, and results were analyzed via TA’s Universal Analysis software.

**Isothermal Kinetics:** Samples were prepared by measuring about 0.540 to 0.560 mg of material into half of a melting point capillary with one end sealed. The top of the capillary was then sealed with a small flame. The material was tapped to the bottom of the capillary prior to flame sealing to prevent it from being decomposed in the sealing process. Samples were placed in either a Woods metal or sand bath in an HP 5890 GC oven heated to the desired temperature in the range of 180 to 300°C. For the initial analysis of each mixture at a given temperature, samples were generally removed at 15, 30, 45, and 60 min. The results of these initial tests were then used to determine additional incubation times. Prior to being analyzed on the HPLC, the capillaries were placed in 50 mL glass vials, crushed under 20 mL of acetonitrile, sonicated for 45 minutes, and filtered through 13 mm Millex-FG syringe driven filter
units (Millipore). If samples were not going to be analyzed immediately, they were stored in a freezer. Samples run under an ammonia atmosphere were prepared in the same manner, except that ~0.2 mg ammonium carbonate (\(\text{NH}_4\text{H}_2\text{CO}_3\)) was added to the DNAN or DNT prior to flame sealing the capillaries. At the temperatures used for the decomposition of the nitroarenes, the ammonium carbonate decomposed to produce the desired molar excess of gaseous ammonia.

**HPLC Analysis:** A 10.0 μL aliquot of each sample was analyzed on a Hewlett Packard 1100 series HPLC system with a diode array detector set at 235 nm. The C-18 column (Hypersil BDS or Zorbax Eclipse XDB, Agilent) was held in a heated column compartment set to 38°C. The gradient elution, based on an HP Application Note, had a flow rate of 0.75 mL/min [22]. The initial eluent was 26% aqueous acetonitrile; the organic component was increased to 40% then 55% over two ten minute increments, and then raised to 100% over the next 14 minutes. The system was held at 100% acetonitrile for one minute before returning to the initial composition. Each set of samples was accompanied by combined DNAN and DNT standards covering the range from 0.5 to 100 μg/mL, and yielding \(R^2\) values that were generally 0.999 or better. New standards were made when the \(R^2\) values fell below this value. Chromatographic results were analyzed using the Agilent Chem Station software.

**Decomposition Products:** Samples, prepared as described above, were typically about 0.55 mg of sample in 20 mL methanol or acetonitrile (~27.5 ng/μL) which had been filtered through a 0.45 micron PTFE syringe filter. Injections of 10 μL (~275 ng)
were made onto the HPLC/MS system [Thermo Electron (Franklin, MA, USA) Exactive Orbitrap mass spectrometer affixed with an electrospray ionization (ESI) interface]. A mixture of DNAN, DNT, NTO and NQ [5 μg/mL in 50/50 (v/v) methanol/water] was infused to optimize conditions for analysis. Negative ions of m/z 103.0261 for NQ, m/z 129.0054 for NTO, m/z 181.0255 for DNT and m/z 197.0204 for DNAN were monitored for this optimization. The demethylated phenolic fragment of DNAN at m/z 183.0047 was many times more intense than the intact parent, but the detection of m/z 197.0204 was important since dinitrophenol is a known decomposition product of DNAN. Conditions were optimized as follows: spray voltage, 3200 V; capillary temperature, 200 °C; sheath gas (N₂), 30; auxiliary gas (N₂), 15; capillary voltage, -25 V; tube lens, -85 V; and skimmer, -25 V. Units for sheath and auxiliary gas flow are arbitrary. Injections of 10 μL of the same solution were separated on several different columns to optimize chromatographic conditions for the mixture. Liquid chromatography was performed using a Thermo Electron Accela quaternary pump with a CTC Analytics (Zwingen, Switzerland) HTS PAL autosampler. The HPLC system developed for optimum analysis of the four-component mixture employed an Analytical Sales and Service (Pompton Plains, NJ, USA) Echelon column (50 x 2.1 mm, 5 μm). With a flow rate of 300 μL/min, samples were introduced into an initial mobile phase of 98% solvent A (water) and 2% solvent B (acetonitrile). Following injection, this was held for 1 minute and then ramped linearly to 98% solvent B and 2% solvent A over 7 minutes. This was held for 1 minute before returning to initial conditions over 30 seconds and re-equilibrated for 2.5 minutes prior to the next injection (total run time of 12 minutes). Because the
polarities of these 4 components vary significantly, some compromise was required in this analysis. Normal phase methods retained NTO and NQ, but DNT and DNAN eluted close to the void. Other reverse phase columns retain DNT and DNAN very well, but peak shape, retention or resolution of NTO and NQ were unacceptable. The chosen method provided good peak shape for all compounds with reasonable resolution of all components; however, NTO did not retain acceptably. Since the intention of this analysis was to determine the decomposition products of these compound mixtures, this compromise was made because NTO decomposition is well documented. Compounds smaller than NTO that may elute earlier are not likely to be detected with this system. Data collection and analysis was performed with Thermo Xcalibur software version 2.2, SP 1.48.

**Results**

**Differential Scanning Calorimetry (DSC):** DSC scans obtained at a scan rate of 20°C/minute confirmed that DNAN was somewhat more stable than DNT. Both these nitroarenes are more thermally stable than NQ and NTO, and slightly more stable than TNT (see Figure 2).
Figure 2: DSC Traces of Individual Energetic Compounds scanned 20°C/min.
Figure 3: DNAN with NQ & NTO (50:50 & 80:20), DNT with NQ & NTO (50:50 & 80:20), and NTO with NQ
When DNT was mixed with NTO (80:20) the DSC trace contained two exotherms which could be attributed to NTO ~257°C and DNT ~344°C, with only a slight depression (15°C) of the NTO peak. When the loading of NTO was increased (50:50), the larger exotherm shifted to the earlier peak, and the two peaks were no longer fully resolved, with the first peak at a somewhat higher temperature (~267°C) and the second peak at a lower temperature (~326°C). Likewise, DNAN with NTO (80:20) showed peaks around 256°C and 340°C. While the former was readily assigned to NTO, the exotherm at 340°C was 30°C below where DNAN alone exhibited an exotherm. In the 50:50 DNAN:NTO mix, the peaks were again not fully resolved, and the second peak was shifted even lower, to ~311°C. When NQ was mixed 1-to-1 with either nitroarene the exotherms of both were significantly depressed, appearing immediately after the melt of NQ at 243°C. (See Figure 3)

To emulate IMX-101 a three-part mix of DNAN (43%), NTO (20%), and NQ (37%) and a similar one using DNT instead of DNAN were scanned by DSC (Figure 4 a & b). Both three-part mixtures showed a large broad exotherm immediately after an endotherm around 215°C, which was assumed to be the melt of nitroguanidine, though slightly depressed. The average total heat released by the DNAN three-part mixture was slightly more than that produced by the DNT three-part mixture (2900±250 J/g vs. 2100±230 J/g, respectively). It has been claimed that the DSC of the three-part mixture IMX 101 appears to be the superposition of the individual components; therefore, the decomposition of one does not affect the other [23]. This was not found to be the case. There was sufficient heat being generated at temperatures below the decomposition exotherm of neat DNAN or neat DNT that decomposition of the three-
part mixture was nearly complete by that temperature. The results from this study do agree with Cuddy’s findings that decomposition of the IMX-101 mixture begins below 200°C. To examine these observations in more detail, isothermal analyses were performed.

Figure 4: DNAN and DNT three part mixtures with NTO & NQ

**Kinetics:** DNAN and DNT were heated in sealed capillary tubes for up to five days to achieve approximately 50% decomposition. Decompositions appeared first-order out to 20-25% decomposition. Over the temperature range 200 to 300°C, DNT decomposed up to one order of magnitude faster than DNAN (Table 1, Figure 5).

| Neat | DNAN | DNT | TNT   |
|------|------|-----|-------|
| °C   |      |     |       |
| 180  | 4.0E-08 | 8.7E-07 | --   |
| 200  | 2.4E-06 | 7.6E-06 | 1.6E-05 |
| 240  | 1.3E-05 | 1.2E-04 | --   |
| 250  | 1.3E-05 | 4.7E-05 | --   |
| 270  | 2.4E-05 | 4.3E-04 | --   |
| 280  | 3.0E-04 | 1.1E-03 | 3.5E-03 |
| 300  | 5.4E-04 | 2.0E-03 | --   |
However, when DNAN was mixed with either NTO or NQ the decomposition rate was so enhanced that noticeable decomposition was observed within an hour at 200°C (Tables 2 & 3). The thermal stability of DNT was not greatly affected by the addition of NTO, but NQ greatly accelerated the decomposition of both nitroarenes. The three-part mixtures showed the same instability imparted by NQ. From the fraction remaining after one hour at 200°C, it was evident that the three-part mixture with DNAN was more seriously destabilized by the additives than was DNT. Because NQ has a similar acceleratory effect on the decomposition of both DNAN and DNT, this increased instability was likely due to the impact of NTO, which had a significantly larger destabilizing effect on DNAN than on DNT.

Because ammonia is a likely decomposition product of both NQ and NTO, the rate of decomposition of DNAN and DNT under ammonia was examined at 200°C. Figure 6 shows that while ammonia has an accelerating effect on the decomposition of both nitroarenes, the impact on DNAN is much larger.
Table 2: Relative Stabilities: DNAN and DNT Mixtures Exemplified by Half-Life at 200°C

| Formulation       | Fraction Remaining | Time          |
|-------------------|--------------------|---------------|
| DNAN              | 0.47               | 5 days 4 hours|
| DNT               | 0.41               | 4 days        |
| DNAN/NQ/NTO       | 0.49               | 15 min        |
| DNT/NQ/NTO        | 0.54               | 60 min        |
| DNAN/NQ (50:50)   | 0.46               | 30 min        |
| DNT/NQ (50:50)    | 0.51               | 30 min        |
| DNAN/NTO (80:20)  | 0.51               | 4 hrs         |
| DNT/NTO (80:20)   | 0.47               | 2 days        |
| DNAN/NTO (50:50)  | 0.48               | 90 min        |
| DNT/NTO (50:50)   | 0.42               | 20 hrs        |

Table 3: First-Order Rate Constants for Components of Mixtures

| Temperature | DNAN | DNT | NQ  | NTO |
|-------------|------|-----|-----|-----|
| 200°C       |      |     |     |     |
| DNAN/NQ/NTO | 3.7E-04 | -- | 4.3E-04 | 1.8E-03 |
| DNT/NQ/NTO  | -- | 2.6E-04 | 7.5E-04 | 6.5E-04 |
| DNAN/NQ     | 4.5E-04 | -- | 4.2E-04 | -- |
| DNT/NQ      | -- | 4.6E-04 | 6.5E-04 | -- |
| DNAN/NTO (80:20) | 3.9E-05 | -- | -- | 1.9E-04 |
| DNT/NTO (80:20) | -- | 6.8E-06 | -- | 3.6E-04 |
| DNAN/NTO (50:50) | 2.3E-04 | -- | -- | 3.7E-04 |
| DNT/NTO (50:50) | -- | 1.6E-05 | -- | 8.3E-05 |
| 180°C       | DNAN | DNT | NQ  | NTO |
| DNAN/NQ/NTO | 1.4E-04 | -- | 9.6E-05 | 6.1E-04 |
| DNT/NQ/NTO  | -- | 5.2E-05 | 1.7E-04 | 2.8E-04 |

Figure 6: Impact of ammonia on the decomposition of DNAN and DNT
Decomposition Products

Both DNT and DNAN can undergo oxidation of the methyl or methoxy group, reduction of the nitro groups, Meisenheimer complex formation and various oligomerization reactions [11-36]. DNT has been shown to experience elimination of a nitro group to form p- and o-nitrotoluene and, under aerobic conditions, to eventually yield nitrite and catechols [35,37]. Anaerobic reduction and biotransformation of DNT produces nitroso-, amino-, aminonitro-, and diaminotoluenes, as well as azoxy compounds [29,34,35]. For DNAN, loss of the methoxy group to yield 2,4 dinitrophenol has been reported under various different reaction conditions, such as mammalian metabolism and reactions with piperidines and sodium hydroxide [11,38-40]. The methoxy group has also been shown to undergo aromatic and aliphatic nucleophilic substitution reactions resulting in the replacement of either the methyl or the entire methoxy group by amines or other nucleophiles [11,39]. As with DNT, the nitro groups of DNAN can be reduced microbially to form amino- and aminonitroanisole [12,29-32]; arylnitroso and arylhydroxylamino intermediates, azoxy- and azo-dimers, demethylated and acetylated products, and ring cleavage have also been reported [33,41].

Under our experimental conditions, in which DNT and DNAN were heated in glass capillaries at 200°C for four and five days, respectively, to achieve approximately 50% decomposition, numerous products were observed (Figures 7 and 8). Assignment of chemical formulas was based on the high-resolution mass spectrometry results where compositions could be determined within 5 ppm of their calculated mass. Masses associated with proposed structures here, and throughout the
paper, are those obtained from the LC/MS for the M-1 adducts detected in negative ion mode. (Table 4):

Figure 7: Proposed structures for decomposition products observed in neat DNAN.

Figure 8: Proposed structures for decomposition products observed in neat DNT.
| Observed Mass** (min) | RT | Compound/ formula** | DNAN | DNAN/ NO | DNAN/ NTO | DNAN/ NTO/ NO | DNT | DNT/ NO | DNT/ NTO | DNT/ NTO/ NO |
|-----------------------|----|---------------------|------|----------|----------|--------------|-----|---------|-----------|---------------|
| 103.0254 | 0.79 | NQ (CH4O2N4) | 1.3E+06 | 2.5E+06 | 2.4E+06 | 1.2E+04 |     |         |           |               |
| 129.0051 | 0.57 | NTO (C2H2O3N4) | 9.7E+04 | 3.8E+04 | 1.4E+05 |     |         |           |               |
| 143.0097 | 0.66 | C3H3O3N4 | 1.3E+05 | 2.5E+04 |     |     |         |           |               |
| 162.0308 | 6.09 | C7H4O2N3 | 3.2E+05 |     | 3.5E+05 | 2.3E+05 |     |         |           |               |
| 166.0137 | 0.85 | CH4O4N | 3.7E+06 | 3.1E+05 | 1.2E+04 |     |         |           |               |
| 178.0250 | 5.28 | C7H4O3N3 | 7.7E+03 | 3.2E+04 | 1.2E+05 |     |         |           |               |
| 181.0256 | 0.66 | DNT isomer | 2.2E+05 | 3.3E+04 | 1.2E+05 |     |         |           |               |
| 181.0256 | 4.92 | DNT isomer | 4.3E+04 |     |     |     |         |           |               |
| 181.0256 | 7.16 | DNT (C7H5O4N2) | 7.1E+05 | 9.0E+05 | 2.6E+05 | 1.2E+06 |     |         |           |               |
| 182.0096 | 0.73 | C7H4O5N | 2.4E+05 | 8.0E+04 |     |     |         |           |               |
| 182.0208 | 6.51 | DNA (C6H4O4N3) | 5.6E+06 | 3.0E+04 | 2.7E+05 |     |         |           |               |
| 183.0040 | 7.61 | C6H5O4N2 | 7.3E+04 | 2.9E+05 | 3.1E+06 | 5.3E+06 |     |         |           |               |
| 183.0048 | 1.11 | C6H5O5N2 | 4.5E+06 | 1.7E+05 |     |     |         |           |               |
| 197.0193 | 6.65 | DNAN (C6H3O5N2) | 4.2E+06 | 2.9E+06 | 3.1E+06 | 2.5E+06 |     |         |           |               |
| 199.0762 | 6.56 | C13H11O2 | 9.6E+04 |     |     |     |         |           |               |
| 205.0371 | 5.22 | C8H5O4N | 4.5E+04 | 1.7E+05 |     |     |         |           |               |
| 207.9995 | 4.53 | C8H5O3N3 | 7.2E+04 |     |     |     |         |           |               |
| 224.0431 | 5.66 | C7H6O4N3 | 2.5E+04 |     |     |     |         |           |               |
| 227.9895 | 4.65 | C6H2O7N3 | 1.4E+05 |     |     |     |         |           |               |
| 233.0636 | 5.43 | C7H11O3N2 | 1.1E+05 |     |     |     |         |           |               |
| 244.0597 | 5.71 | C10H9O5N3 | 8.0E+04 |     |     |     |         |           |               |
| 247.0595 | 6.35 | C9H7O3N2 | 5.4E+04 | 7.3E+04 |     |     |         |           |               |
| 249.0367 | 5.85 | C9H5O4N4 | 5.8E+04 | 1.5E+04 |     |     |         |           |               |
| 279.0496 | 5.99 | C9H7O5N6 | 4.5E+04 | 1.6E+04 |     |     |         |           |               |
| 280.0377 | 7.63 | C8H6O6N5 | 3.1E+04 |     |     |     |         |           |               |
| 291.0409 | 6.12 | C9H7O5N6 | 6.4E+04 | 1.5E+04 |     |     |         |           |               |
| 294.0520 | 5.34 | C10H5O5N6 | 2.5E+04 |     |     |     |         |           |               |
| 302.0416 | 5.19 | C11H9O4N2 | 2.5E+04 |     |     |     |         |           |               |
| 308.0385 | 5.51 | C10H5O6N2 | 2.4E+04 |     |     |     |         |           |               |
| 311.0429 | 7 | C14H7O5N4 | 9.5E+04 |     |     |     |         |           |               |
| 326.0547 | 8.13 | C14H8O5N5 | 8.7E+04 | 2.8E+04 |     |     |         |           |               |
| 329.0528 | 7.8 | C14H9O6N4 | 2.1E+05 |     |     |     |         |           |               |
| 330.0367 | 5.22 | C14H8O6N5 | 1.4E+05 |     |     |     |         |           |               |
| 333.0417 | 7.88 | C14H9O7N4 | 9.8E+04 |     |     |     |         |           |               |
| 334.0319 | 5.3 | C13H8O6N4 | 1.0E+05 | 4.3E+04 |     |     |         |           |               |
| 334.0319 | 7.58 | C13H8O6N4 | 1.2E+05 | 2.1E+04 |     |     |         |           |               |
| 345.0113 | 5.42 | C13H8O6N4 | 5.9E+04 |     |     |     |         |           |               |
| 345.0476 | 5.25 | C14H9O7N4 | 6.9E+04 | 6.2E+04 |     |     |         |           |               |
| 345.0491 | 7.42 | C14H9O7N4 | 1.9E+05 | 5.7E+04 | 7.7E+04 |     |     |         |           |               |
| 346.0317 | 5.38 | C14H8O6N5 | 5.5E+04 |     |     |     |         |           |               |
| 348.0236 | 7.75 | C12H8O6N5 | 5.2E+03 | 2.6E+05 | 1.4E+05 | 5.0E+04 |     |         |           |               |
| 356.0274 | 6.03 | C14H9O7N5 | 5.3E+04 |     |     |     |         |           |               |
| 356.0274 | 6.03 | C14H9O7N5 | 5.3E+04 |     |     |     |         |           |               |
| 363.0220 | 5.36 | C13H7O9N4 | 1.2E+05 |     |     |     |         |           |               |
| 372.0285 | 5.12 | C7H10O13N5 | 4.0E+04 |     |     |     |         |           |               |
| 373.0139 | 5.47 | C7H9O4N4 | 1.1E+05 | 2.1E+04 |     |     |         |           |               |
| 375.0218 | 5.22 | C7H9O4N4 | 1.1E+05 |     |     |     |         |           |               |
| 375.0235 | 5.02 | C7H9O4N4 | 1.2E+05 |     |     |     |         |           |               |
| 408.0683 | 7.73 | C9H12O9N4 | 3.4E+04 |     |     |     |         |           |               |
| 427.0533 | 8.13 | C7H9O5N7 | 1.9E+05 |     |     |     |         |           |               |
| 490.0752 | 6.93 | C21H12O9N6 | 1.3E+04 |     |     |     |         |           |               |

* MS run in negative ion mode; thus formulii provided are M-H. ring coupling substituted with NQ or NTO Oxidized Species
Nitroguanidine is reported to exist in two tautomeric forms (Figure 9) with A being predominant under all but extremely basic conditions [42,43].

\[
\begin{align*}
\text{(A)} & \quad \text{H}_2\text{N} & \quad \text{C} & \quad \text{N} & \quad \text{NO}_2 \\
\text{(B)} & \quad \text{H}_2\text{N} & \quad \text{N} & \quad \text{C} & \quad \text{H} & \quad \text{NO}_2
\end{align*}
\]

Figure 9: NQ tautomers

The thermal decomposition of NQ has been observed to produce numerous gaseous products, including NH₃, NO₂, N₂O, CO₂, HNCO, H₂O, N₂, NO, and HCN [44-46]. In addition to these gases, the thermolysis of NQ yields small molecules such as cyanogen (CN)₂, cyanimide (H₂NCN), urea (CO(NH₂)₂), and cyanic acid (CNOH), as well as cyclic materials such as melamine, ammeline, ammelide, cyanuric acid, melem, melam, melon, and paracyanogen [45-46]. Structures of some of these cyclic compounds are shown in Figure 10. It has been proposed that the nitramide and cyanimide formed from the decomposition of the nitroguanidine combine to form melamine, which then undergoes hydrolysis reactions to yield ammeline, ammelide, and cyanuric acid [45]. Gases such as NH₃, N₂O, and CO₂ have also been detected in base hydrolysis reactions of NQ [42-43,47]. Ammonia, nitrite, nitrate, nitrosoguanidine, hydroxyguanidine, cyanoguanidine, guanidine, cyanimide, cyanoguanidine, melamine, and guanidine have been reported as products of biotransformation processes, and many have also been observed after and photolysis in water [43,48-50]. Kaplan noted that urea and cyclic species such as ammeline, ammelide, and cyanuric acid were not produced through biodegradation [49].
The majority of products created through the decomposition of NTO are gases, including CO₂, CO, HCN, N₂, H₂O, NO₂, N₂O, NO, and H₂ [51-59]. Other reported products include 1,2,4-triazol-3-one (TO) from thermal decomposition [54-56], nitroso-TO from laser induced decomposition [53], amino-TO from bioremediation [60], a ring coupled dimer of NTO molecules from electroreduction [61], nitrate and ammonium ions from electrochemical oxidation [59] and an insoluble polymeric material from thermal decomposition [55-57]. In addition to the production of ammonium ions through electrochemical reduction, Fan also noted the creation of ammonia, in the form of ammonium ions, via thermal decomposition [54]. When NTO was thermally decomposed with TNT, the products observed, which included TO, triazole, 2,4-DNT, 2,6-DNT, trinitrobenzene (TNB), and aminodinitrobenzoic acid, were similar to the products observed when TNT and NTO were decomposed alone [55]. A number of studies have reported the decomposition kinetics of NTO.
[52,62], and labeling studies have been used to elucidate the decomposition mechanisms [54]. A number of routes have been proposed, including bond homolysis with or without hydrogen transfer, mono- or bi-molecular nitro-nitrite rearrangement, or a combination of both [51,54,63-65]. These may be manifest by the evolution first of NO₂, HONO, or CO₂, but in all cases a polymeric residue results. Various proposed decomposition mechanisms, as summarized by Smith, are shown in Figure 11 [62].

Figure 11: Summary of proposed decomposition mechanisms for NTO taken from ref 61. Clockwise from top left: Homolysis of C-NO₂ bond; Nitro group rearrangement; Ring rupture (mono & bi-molecular pathways); Nitro-nitrite rearrangement.

Under the LC/MS conditions used in this study, no peaks were observed in the chromatogram of an extract of NQ thermolyzed at 200°C for 2 days, and an analysis
of an extract of NTO incubated at 200°C for the same amount of time showed only the molecular ion (m/z 129). When NTO and NQ were heated together, only the molecular ion peak of both was observed (m/z 129 and 103 respectively). However, when either NTO or NQ was heated with DNAN or DNT, numerous decomposition products could be detected in addition to the parent ions. When NTO was heated with DNAN, one of the decomposition products was a methylated form of NTO (m/z 143); all other decomposition products that were identified in the mixtures contained some form of the phenyl ring from the nitroarene.

When DNAN or DNT was heated at 200°C with NQ, most of the decomposition products appeared to be related to NQ addition to the nitroarene; however, formation of dinitrophenol from DNAN and oxidation processes (e.g. conversion of the methyl group in DNT to a carboxyl group) had also occurred (Table 4, Figures 12 & 13).

Figure 12: Proposed structures of products observed during the decomposition of DNAN with NQ that were not detected during the decomposition of neat DNAN or neat NQ.
Figure 13: Proposed structures of products observed during the decomposition of DNT with NQ that were not detected during the decomposition of neat DNT or neat NQ.

While products identified from our thermolysis conditions indicated the replacement of the methyl or methoxy substituent by an amino group to form 2,4-dinitroaniline (DNA), no mono- or diaminoanisole or mono- or diaminotoluene, which might be expected under reducing conditions, were identified. When NQ and DNAN were combined, the reaction appeared to begin with replacement of the methoxy substituent with an amino group. This species underwent further reactions as depicted in Scheme I.

Scheme I  DNAN heated with NQ
In a situation similar to that with NQ, products observed from the decomposition of the two-part mixtures of DNAN or DNT with NTO that were not also present in the decomposition of the neat materials were primarily the result of the attachment of NTO or an NTO fragment to the arene ring. Many of the observed decomposition products of the DNT/NTO mixture also showed the oxidation of the DNT methyl group. Dinitroaniline was observed in the decomposition of both DNAN and DNT with NTO, but more dinitroaniline was observed in the reactions between DNAN and NQ or NTO than in the reactions of DNT with either of the two additives (Figures 14 & 15).

Figure 14: Proposed structures of products observed during the decomposition of DNAN with NTO that were not also detected during the decomposition of neat DNAN or neat NTO.

Figure 15: Proposed structures of products observed during the decomposition of DNT with NTO that were not detected during the decomposition of neat DNT or neat NTO.
There were few products seen in the decomposition of the three-part mixtures that were not also observed in either the neat materials or the two-part mixtures. Proposed structures are shown in Figures 16 & 17.

![Proposed structures](image)

Figure 16: Proposed structures of products observed during the decomposition of DNAN with NQ and NTO that were not detected during the decomposition of the neat materials or the two part mixtures.

![Proposed structure](image)

Figure 17: Proposed structure of product observed during the decomposition of DNT with NQ and NTO that were not detected during the decomposition of the neat materials or the two part mixtures.

**Discussion**

Dinitrophenol and dinitroaniline were observed in the decomposition of DNAN with either NQ or NTO. While dinitrophenol was also observed in the thermolysis of neat DNAN, dinitroaniline was only observed when NQ or NTO was
present. Though dinitroaniline was also detected as a product when DNT was decomposed with either NQ or NTO, the formation of DNA was two orders of magnitude greater for DNAN than for DNT with either species. This is likely due to the ease with which the methoxy group is lost from DNAN as compared to methyl loss from DNT. Dinitroaniline could be formed from DNAN if, after loss of methoxy, NQ added to the ring and then was subsequently lost. However, NTO would have no such route available to it. NQ and NTO have been observed to generate ammonia or ammonium ions [42-47,50,54,59], which may replace the methoxy group with amine via a substitution reaction. Multiple studies have demonstrated DNAN’s ability to undergo nucleophilic substitution reactions, and amines were the nucleophiles in some of those experiments. [11,39]. Dinitroaniline was also formed when DNT was heated in the presence of NQ or NTO, but at significantly lower levels than were observed with DNAN. Again we attribute this to the reaction of the DNT with ammonia generated from the thermolysis of NQ or NTO.

In order to examine the impact of ammonia on the decomposition of DNAN and DNT, each nitroarene was heated at 200°C in the presence of excess ammonium carbonate. The results of this test showed that the decomposition rates of both DNAN and DNT were significantly enhanced by the ammonia generated; however, as with NTO, the impact on DNAN was far greater than the impact on DNT. While approximately 50% decomposition of DNAN was achieved by heating for five minutes at 200°C in the presence of ammonium carbonate, DNT, under the same conditions, took about 12.5 hours to reach the same level of decomposition. After three hours at 200°C, no DNAN could be detected in the reaction mixtures containing
ammonium carbonate. The two products detected by LC/MS were dinitrophenol and dinitroaniline. When DNT was heated for three hours under the same conditions, little decomposition was observed, and only trace amounts of DNA were detected. Previous studies have shown that ammonia has an acceleratory effect on the decomposition of TNT [55], and ammonia has been detected as a decomposition product of mixtures of TNT and NQ [66].

A comparison of the effects of NQ and NTO on the nitroarenes indicates that, while NQ has a similar impact on the thermal stability of both DNAN and DNT, NTO, like ammonia, has a much greater acceleratory effect on the rate of decomposition of DNAN than it does on DNT. The observation that NTO has more of a destabilizing affect on DNAN than on DNT may be related to the fact that the principle way NTO affects DNT is not via replacement of the methyl group, which is a much poorer leaving group than a methoxy, but via hydrogen transfer. We, as well as Menapace, have reported the decomposition of TNT with NTO over the temperature range 220-280°C [55,67]. In those studies, NTO accelerated the decomposition of TNT 10-fold, while TNT accelerated the decomposition of NTO 100-fold. Using deuterated analogs, Menapace found that the NH group of NTO favored reaction with the nitro groups of TNT via a process involving hydrogen abstraction, and that a similar hydrogen abstraction process also occurred between the nitro group on NTO and the methyl hydrogens on TNT. Hydrogen abstraction from TNT did not result in a loss of the methyl group, but instead produced aryl hydroxyl nitroxide radical adducts, such as that shown in Figure 18, which are similar to some products observed in our thermolysis of DNT.
In addition to dinitroanisole and dinitrophenol, a number of other decomposition products were detected in the DNAN mixtures that were not present in the decomposition of neat DNAN. In general, the decomposition products observed in the mixtures of NTO and/or NQ with DNAN appeared to be the arene ring with one or more NQ or NTO moieties attached at the position of the methoxy group (m/z 224, 225, 249, 291, 292, 280, 308), with occasional attachment at the site of a nitro group (m/z 279). In addition to methylated NTO, the DNAN/NTO thermolyzed mixture showed unique decomposition products at m/z 279 and 280; m/z 279 appears to be NTO attached to DNAN via one of its former nitro groups, while m/z 280 has an NTO moiety attached to the methoxy group. All of the unique decomposition products from the DNAN/NQ mixture had the methoxy group replaced by a nitrogen substituent; in most cases the nitrogen was part of a cyclic structure formed from the decomposition products of NQ.

The decomposition of neat DNT yielded primarily molecules containing oxidized forms of the methyl group and species best described as linked DNT molecules. When DNT was thermolyzed with NTO and/or NQ, most products that were not present in the decomposition of neat DNT were again derived from NTO, NQ or combinations/fragments of these materials attached to the arene ring. The site of attachment was often the location of the methyl group (m/z 178, 190, 205, 244, 246,
247), but the location of the adjacent nitro group was involved more frequently than in decompositions involving DNAN (m/z 178, 190, 205, 244, 246, 247, 326, 375). In many cases, bicyclic structures were formed that involved both the site of the methyl group and the site of the adjacent nitro group (m/z 178, 190, 205, 244, 246, 247).

**Conclusion**

The addition of NQ accelerated the decomposition of both DNAN and DNT by approximately two-orders of magnitude. A similar acceleratory effect was seen when DNAN was decomposed with NTO; however, NTO only increased the decomposition of DNT by one-order of magnitude. As would be expected from the results of the two part mixtures, both nitroarenes decomposed faster in the NTO/NQ mixture; however, DNT was not as severely accelerated as DNAN. NTO decomposed a little slower in the 50:50 DNT/NTO mixture than in the corresponding DNAN/NTO mix. In contrast, NQ decomposed a little faster in DNT/NQ than in DNAN/NQ.

An IMX 101 mixture using 2,4-dinitrotoluene rather than 2,4-dinitroanisole would be more thermally stable although not as energetic. Some evidence suggests that DNAN might be more toxic than TNT [7-8]; thus, using DNT might provide a less toxic mix. Furthermore, 2,4-DNT is a widely used chemical since it is an intermediate in the production of toluene diisocyanate (TDI) used in polyurethane production. As a result it is relatively inexpensive and widely available. Despite these apparent advantages of DNT over DNAN, the 20°C higher melting point of DNAN may continue to favor it, and improvements to the formulation may come from removing NQ entirely.
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Appendix I: Representative DSC & SDT Traces from the FOX Project

Figure 1. Potassium chlorate, DSC

Figure 2. Potassium Chlorate, SDT
Figure 3. 50:50 Sucrose:Potassium chlorate, DSC

Figure 4. 50:50 Sucrose:Potassium chlorate, SDT
Figure 5. 20:80 Sucrose:Potassium chlorate, DSC

Figure 6. 20:80 Sucrose:Potassium chlorate, SDT
Figure 7. 50:50 Lactose:Potassium chlorate, DSC

Figure 8. 50:50 Fructose:Potassium chlorate, DSC
Figure 9. 50:50 Fructose:Potassium chlorate, SDT

Figure 10. 50:50 Glucose:Potassium chlorate, DSC
Figure 11. 50:50 Pentaerythritol:Potassium chlorate, DSC

Figure 12: 50:50 Pentaerythritol:Potassium chlorate, SDT
Figure 13. 50:50 Erythritol:Potassium chlorate, DSC

Figure 14. 50:50 Charcoal:Potassium chlorate, DSC
Figure 15. 50:50 Sulfur:Potassium chlorate, DSC

Figure 16. 50:50 Cyclododecanol:Potassium chlorate, DSC
Figure 17. 50:50 Hexatriacontane:Potassium chlorate, DSC

Figure 18. 50:50 Naphthalene:Potassium chlorate, DSC
Figure 19. 20:80 Benzoic acid:Potassium chlorate, DSC

Figure 20. 20:80 Aluminum:Potassium chlorate, DSC
Figure 21. Potassium perchlorate, DSC

Figure 22. Potassium perchlorate, SDT
Figure 23. 50:50 Sucrose:Potassium perchlorate, DSC

Figure 24. 50:50 Sucrose:Potassium perchlorate, SDT

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Figure 25. 20:80 Sucrose:Potassium perchlorate, SDT

Figure 26. 50:50 Fructose:Potassium perchlorate, DSC
Figure 27. 50:50 Fructose:Potassium perchlorate, SDT

Figure 28. 50:50 Erythritol:Potassium perchlorate, DSC
Figure 29. 50:50 Erythritol:Potassium perchlorate, SDT

Figure 30. 50:50 Charcoal:Potassium perchlorate, DSC
Figure 31. 50:50 Charcoal:Potassium perchlorate, SDT

Figure 32. 50:50 Sulfur:Potassium perchlorate, DSC
Figure 33. 50:50 Sulfur:Potassium perchlorate, SDT

Figure 34. 50:50 Cyclododecanol:Potassium perchlorate, DSC
Figure 35. 50:50 Hexatriacontane:Potassium perchlorate, DSC

Figure 36. 50:50 Naphthalene:Potassium perchlorate, DSC
Figure 37. 20:80 Benzoic acid:Potassium perchlorate, DSC

Figure 38. Potassium iodate, DSC
Figure 39. Potassium iodate, SDT

Figure 40. 50:50 Sucrose:Potassium iodate, DSC
Figure 41. 50:50 Sucrose:Potassium iodate, SDT

Figure 42. 20:80 Sucrose:Potassium iodate, DSC
Figure 43. 20:80 Sucrose:Potassium iodate, SDT

Figure 44. 50:50 Fructose:Potassium iodate, DSC
Figure 45. 50:50 Fructose:Potassium iodate, SDT

Figure 46. 50:50 Erythritol:Potassium iodate, DSC
Figure 47. 50:50 Erythritol:Potassium iodate, SDT

Figure 48. 50:50 Charcoal:Potassium iodate, DSC
Figure 49. 50:50 Charcoal:Potassium iodate, SDT

Figure 50. 50:50 Sulfur:Potassium iodate, DSC
Figure 51. 50:50 Sulfur:Potassium iodate, SDT

Figure 52. 50:50 Cyclododecanol:Potassium iodate, DSC
Figure 53. 50:50 Hexatriacontane:Potassium iodate, DSC

Figure 54. 50:50 Naphthalene:Potassium iodate, DSC
Figure 55. 20:80 Benzoic acid:Potassium iodate, DSC

Figure 56. Potassium periodate, DSC
Figure 57. Potassium periodate, SDT

Figure 58. 50:50 Sucrose:Potassium periodate, DSC
Figure 59. 50:50 Sucrose:Potassium periodate, SDT

Figure 60. 20:80 Sucrose:Potassium periodate, DSC
Figure 61. 20:80 Sucrose:Potassium periodate, SDT

Figure 62. 50:50 Fructose:Potassium periodate
Figure 63. 50:50 Fructose:Potassium periodate, SDT

Figure 64. 50:50 Erythritol:Potassium periodate, SDT
Figure 65. 50:50 Charcoal:Potassium periodate, DSC

Figure 66. 50:50 Sulfur:Potassium periodate, DSC
Figure 67. 50:50 Sulfur:Potassium periodate, SDT

Figure 68. 50:50 Cyclododecanol:Potassium periodate, DSC
Figure 69. 50:50 Hexatriacontane:Potassium periodate, DSC

Figure 70. 50:50 Naphthalene:Potassium periodate, DSC
Figure 71. 20:80 Benzoic acid:Potassium periodate, DSC

Figure 72. 20:80 Aluminum:Potassium periodate, DSC
Figure 73. Potassium bromate, DSC

Figure 74. Potassium bromate, SDT
Figure 75. 50:50 Sucrose:Potassium bromate, DSC

Figure 76. 50:50 Sucrose:Potassium bromate, SDT
Figure 77. 20:80 Sucrose:Potassium bromate, DSC

Figure 78. 20:80 Sucrose:Potassium bromate, SDT
Figure 79. 50:50 Fructose:Potassium bromate, DSC

Figure 80. 50:50 Fructose:Potassium bromate, SDT
Figure 81. 50:50 Pentaerythritol:Potassium bromate, DSC

Figure 82. 50:50 Pentaerythritol:Potassium bromate, SDT
Figure 83. 50:50 Sulfur:Potassium bromate, DSC

Figure 84. 50:50 Cyclododecanol:Potassium bromate, DSC
Figure 85. 50:50 Naphthalene:Potassium bromate, DSC

Figure 86. 20:80 Benzoic acid:Potassium bromate, DSC
Figure 87. 20:80 Aluminum:Potassium bromate, DSC

Figure 88. Potassium nitrate, DSC
Figure 89. Potassium nitrate, SDT

Figure 90. 50:50 Sucrose:Potassium nitrate, DSC
Figure 91. 20:80 Sucrose:Potassium nitrate, DSC

Figure 92. 20:80 Sucrose:Potassium nitrate, SDT
Figure 93. 50:50 Lactose:Potassium nitrate, DSC

Figure 94. 50:50 Fructose:Potassium nitrate, DSC
Figure 95. 50:50 Glucose:Potassium nitrate, DSC

Figure 96. 50:50 Pentaerythritol:Potassium nitrate, DSC
Figure 97. 50:50 Pentaerythritol:Potassium nitrate, SDT

Figure 98. 50:50 Erythritol:Potassium nitrate, DSC
Figure 99. 50:50 Charcoal:Potassium nitrate, DSC

Figure 100. 50:50 Charcoal:Potassium nitrate, SDT
Figure 101. 50:50 Sulfur:Potassium nitrate, DSC

Figure 102. 50:50 Cyclododecanol:Potassium nitrate, DSC
Figure 103. 50:50 Hexatriacontane:Potassium nitrate, DSC

Figure 104. 50:50 Naphthalene:Potassium nitrate, DSC
Figure 105. 20:80 Benzoic acid:Potassium nitrate, DSC

Figure 106. 20:80 Aluminum:Potassium nitrate, DSC
Figure 107. Potassium nitrite, DSC

Figure 108. Potassium nitrite, SDT
Figure 109. 50:50 Sucrose:Potassium nitrite, DSC

Figure 110. 20:80 Sucrose:Potassium nitrite, DSC
Figure 111. 20:80 Sucrose:Potassium nitrite, SDT

Figure 112. 50:50 Fructose:Potassium nitrite, DSC
Figure 113. 50:50 Erythritol:Potassium nitrite, DSC

Figure 114. 50:50 Charcoal:Potassium nitrite, DSC
Figure 115. 50:50 Sulfur:Potassium nitrite, DSC

Figure 116. 50:50 Sulfur:Potassium nitrite, SDT
Figure 117. 20:80 Benzoic acid:Potassium nitrite, DSC

Figure 118. Potassium permanganate, DSC
Figure 119. Potassium permanganate, SDT

Figure 120. 50:50 Sucrose:Potassium permanganate, DSC
Figure 121. 20:80 Sucrose:Potassium permanganate, DSC

Figure 122. 20:80 Sucrose:Potassium permanganate, SDT
Figure 123. 50:50 Fructose:Potassium permanganate, DSC

Figure 124. 50:50 Erythritol:Potassium permanganate, DSC
Figure 125. 50:50 Charcoal:Potassium permanganate, DSC

Figure 126. 50:50 Sulfur:Potassium permanganate, DSC
Figure 127. 50:50 Sulfur:Potassium permanganate, SDT

Figure 128. 50:50 Cyclododecanol:Potassium permanganate, DSC
Figure 129. 50:50 Naphthalene:Potassium permanganate, DSC

Figure 130. 20:80 Benzoic acid:Potassium permanganate, DSC
Figure 131. Potassium dichromate, DSC

Figure 132. 50:50 Sucrose:Potassium dichromate, DSC
Figure 133. 50:50 Sucrose:Potassium dichromate, SDT

Figure 134. 20:80 Sucrose:Potassium dichromate, DSC
Figure 135. 50:50 Fructose:Potassium dichromate, DSC

Figure 136. 50:50 Fructose:Potassium dichromate, SDT
Figure 137. 50:50 Pentaerythritol:Potassium dichromate, DSC

Figure 138. 50:50 Pentaerythritol:Potassium dichromate, SDT
Figure 139. 50:50 Charcoal:Potassium dichromate, DSC

Figure 140. 50:50 Charcoal:Potassium dichromate, SDT
Figure 141. 50:50 Cyclododecanol:Potassium dichromate, DSC

Figure 142. 50:50 Naphthalene:Potassium dichromate, DSC
Figure 143. 20:80 Benzoic acid:Potassium dichromate, DSC

Figure 144. Ammonium perchlorate, DSC
Figure 145. Ammonium perchlorate, SDT

Figure 146. 50:50 Sucrose:Ammonium perchlorate, DSC
Figure 147. 50:50 Sucrose:Ammonium perchlorate, SDT

Figure 148. 20:80 Sucrose:Ammonium perchlorate, DSC
Figure 149. 20:80 Sucrose:Ammonium perchlorate, SDT

Figure 150. 50:50 Fructose:Ammonium perchlorate, DSC
Figure 151. 50:50 Fructose:Ammonium perchlorate, SDT

Figure 152. 50:50 Erythritol:Ammonium perchlorate, DSC
Figure 153. 50:50 Charcoal:Ammonium perchlorate, DSC

Figure 154. 50:50 Charcoal:Ammonium perchlorate, SDT
Figure 155. 50:50 Sulfur:Ammonium perchlorate, DSC

Figure 156. 50:50 Sulfur:Ammonium perchlorate, SDT
Figure 157. 50:50 Cyclododecanol:Ammonium perchlorate, DSC

Figure 158. 50:50 Hexatriacontane:Ammonium perchlorate, DSC
Figure 159. 50:50 Naphthalene:Ammonium perchlorate, DSC

Figure 160. 50:50 Naphthalene:Ammonium perchlorate, DSC
Figure 161. 20:80 Benzoic acid:Ammonium perchlorate, DSC

Figure 162. 20:80 Aluminum:Ammonium perchlorate, DSC
Figure 163. Ammonium nitrate, DSC

Figure 164. Ammonium nitrate, SDT
Figure 165. 50:50 Sucrose:Ammonium nitrate, DSC

Figure 166. 20:80 Sucrose:Ammonium nitrate, DSC
Figure 167. 20:80 Sucrose:Ammonium nitrate, SDT

Figure 168. 50:50 Lactose:Ammonium nitrate, DSC
Figure 169. 50:50 Fructose:Ammonium nitrate, DSC

Figure 170. 50:50 Glucose:Ammonium nitrate, DSC
Figure 171. 50:50 Pentaerythritol:Ammonium nitrate, DSC

Figure 172. 50:50 Erythritol:Ammonium nitrate, DSC
Figure 173. 50:50 Charcoal:Ammonium nitrate, DSC

Figure 174. 50:50 Sulfur:Ammonium nitrate, DSC
Figure 175. 50:50 Hexatriacontane:Ammonium nitrate, DSC

Figure 176. 50:50 Naphthalene:Ammonium nitrate, DSC
Figure 177. 20:80 Benzoic acid:Ammonium nitrate, DSC

Figure 178. 20:80 Aluminum:Ammonium nitrate, DSC
Figure 179. Benzoic acid, DSC

Figure 180. Charcoal, DSC
Figure 181. Charcoal, SDT under nitrogen

Figure 182. Charcoal, SDT run under air
Figure 183. Cyclododecanol, DSC

Figure 184. Erythritol, DSC
Figure 185. Erythritol, SDT

Figure 186. Fructose, DSC
Figure 187. Fructose, SDT

Figure 188. Glucose, DSC
Figure 189. Hexatriacontane, DSC

Figure 190. Lactose, DSC
Figure 191. Naphthalene, DSC

Figure 192. Pentaerythritol, DSC
Figure 193. Pentaerythritol, SDT

Figure 194. Sucrose, DSC
Figure 195. Sucrose, SDT run under nitrogen

Figure 196. Sucrose, SDT run under air
Figure 197. Sulfur, DSC

Figure 198. Sulfur, SDT run under nitrogen
Figure 199. Sulfur, SDT run under air
## Appendix II: Summary of Averaged FOX DSC & SDT Data

### Table 1. Oxidizer endotherms

| Sample                  | # | Start Endo (°C) | End Endo (°C) | Start Tang. (°C) | End Tang. (°C) | Start Dev. Endo Temp Min. | End Dev. Endo Temp Max. | Start Dev. Tang. Temp Min. | End Dev. Tang. Temp Max. | DSC/SDT | Heated Abs. (mg) | Heated Abs. (mg) | Oxidizer endotherms (%) | DSC/SDT | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) | Heated Abs. (mg) |
|-------------------------|---|-----------------|---------------|------------------|---------------|---------------------------|--------------------------|---------------------------|---------------------------|---------|-----------------|-----------------|--------------------------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ammonium Nitrate (AN)   | 3 | 53              | 65            | 53               | 54            | 20                        | 5                        | 114                       | 144                       | 122              | 128          | 2              | 52              | 287                        | 327            | 338                        | 329            | 332            | 12              | 51              | 15              |
| Ammonium Nitrate (AN) SDT | 3 | 88              | 122           | 89               | 94            | 0.9                       | 23                       | 0.7                       | 121                       | 153            | 123            | 128.5           | 45              | 1              | 153            | 199            | 160            | 167            | 0.2             | 36              | 1              | 211            | 360            | 255            | 261            | 1              | 1049            | 149            | 523            | 653            | 531            | 579            | 13              | 90              | 37              |
| Ammonium Perchlorate (AP)| 3 | 244             | 259           | 245              | 248           | 1                         | 71                       | 10                        | 377                       | 463            | 385            | 433             | 266             | 13             | 722            | 771            | 752            | 758             | 0.3             | 19              | 1              |
| Ammonium Perchlorate (AP) SDT | 3 | 235             | 277           | 237              | 242           | 0.6                       | 71                       | 7                         | 377                       | 463            | 385            | 433             | 266             | 13             | 722            | 771            | 752            | 758             | 0.3             | 19              | 1              |
| Potassium Bromate       | 3 | 378             | 431           | 407              | 415           | 1                         | 77                       | 90                        | 75                        | 716            | 749            | 728             | 731             | 1               | 75             | 12              |
| Potassium Bromate SDT   | 3 | 390             | 428           | 406              | 413           | 1                         | 75                        | 13                        | 716                       | 749            | 728            | 731             | 75              | 12              |
| Potassium Chlorate      | 3 | 361             | 376           | 353              | 358           | 1                         | 341                       | 17                        | 754                       | 790            | 762            | 766             | 180             | 4              |
| Potassium Chlorate SDT  | 3 | 308             | 358           | 355              | 358           | 0.4                       | 158                       | 13                        | 754                       | 790            | 762            | 766             | 180             | 4              |
| Potassium Dichromate    | 3 | 389             | 409           | 398              | 402           | 2                         | 156                       | 66                        |                           |                |                |                 |                  |                 |                |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| Potassium Iodate        | 3 | 531             | 632           | 549              | 555           | 2                         | 380                       | 696                       | 671                       | 705            | 677            | 680             | 0.6             | 85             | 12             | 813            | 916            | 840            | 900             | 23              | 234            | 42              |
| Potassium Iodate SDT    | 3 | 585             | 647           | 417              | 424           | 0.5                       | 391                       | 99                        | 667                       | 757            | 688            | 731             | 16              | 30             | 39              |
| Potassium Nitrate       | 4 | 125             | 147           | 129              | 132           | 1                         | 58                        | 12                        | 321                       | 341            | 326            | 331             | 43              | 35             |
| Potassium Nitrate SDT   | 3 | 125             | 173           | 126              | 131           | 0.8                       | 92                        | 4                         | 285                       | 368            | 312            | 325             | 0.9             | 72             | 13             | 614            | 763            | 670            | 703             | 8               | 606            | 169            | 607            | 859            | 838            | 31             | 88             | 65              |
| Potassium Nitrate       | 4 | 41              | 63            | 44               | 45            | 0.6                       | 20                        | 14                        | 399                       | 430            | 414            | 419             | 6               | 110            |
| Potassium Nitrate SDT   | 5 | 390             | 476           | 417              | 424           | 0.5                       | 391                       | 99                        | 667                       | 757            | 688            | 731             | 16              | 30             | 39              |
| Potassium Perchlorate   | 3 | 302             | 318           | 304              | 307           | 0.8                       | 78                        | 10                        |                           |                |                |                 |                  |                 |                |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| Potassium Perchlorate SDT | 3 | 238             | 365           | 330              | 308           | 1                         | 91                        | 3                         | 587                       | 639            | 699            | 613             | 2               | 121            | 7              | 747            | 860            | 765            | 769             | 0.5             | 178            | 19              |
| Potassium Perchlorate   | 3 | 306             | 613           | 334              | 543           | 2                         | 379                       | 398                       | 668                       | 693            | 672            | 675             | 0.2             | 50             | 4              | 708            | 741            | 710            | 727             | 6               | 8              | 3               |
| Potassium Perchlorate SDT | 3 | 409             | 574           | 494              | 540           | 2                         | 63                        | 5                         |                           |                |                |                 |                  |                 |                |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |

Note: The table provides a summary of the averaged FOX DSC & SDT data for various oxidizer endotherms, including the sample name, number, and specific endothermic reactions observed.
| Sample                                | # | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. |
|---------------------------------------|---|----------------|--------------|-----------------|-------------------|-----------------------|-----------------------------------------------------|---------------------|-----------------|----------------|--------------|----------------|-------------------|-------------------|-----------------------------------------------------|---------------------|-----------------|
Table 3. Endotherms from Benzoic acid mixtures

| Sample | Start Endo (°C) | Endo Endo (°C) | Onset Temp. (°C) | Endo Temp. Min. | Std Dev. Endo Temp. Min. | Additional Mins & Shoulders (%C) seen in some traces | Heat Abs. (J/g) | Std Dev. Heat Abs. | Start Endo (°C) | Endo Endo (°C) | Onset Temp. (°C) | Endo Temp. Min. | Std Dev. Endo Temp. Min. | Additional Mins & Shoulders (%C) seen in some traces | Heat Abs. (J/g) | Std Dev. Heat Abs. | Start Endo (°C) | Endo Endo (°C) | Onset Temp. (°C) | Endo Temp. Min. | Std Dev. Endo Temp. Min. | Additional Mins & Shoulders (%C) seen in some traces | Heat Abs. (J/g) | Std Dev. Heat Abs. |
|--------|----------------|----------------|-----------------|-----------------|------------------------|------------------------------------------------------|---------------|------------------|----------------|----------------|-----------------|----------------|------------------------|------------------------------------------------------|---------------|------------------|----------------|----------------|-----------------|----------------|------------------------|------------------------------------------------------|---------------|------------------|
| Benzoic Acid | 3 118 134 119 121 | 0.9 | 157 | 3 |
| Mix 111: 20% Benzoic Acid/80% AN | 2 50 60 52 53 | 0.4 | 19 | 0.7 | 119 134 122 127 | 121 | 75 | 7 | 157 175 162 166 | 20 | 57 | 0.3 |
| Mix 112: 20% Benzoic Acid/80% AP | 2 121 135 123 125 | 0.09 | 36 | 5 | 243 257 243 246 | 0.5 | 251 48 | 2 |
| Mix 113: 20% Benzoic Acid/80% KBrO3 | 3 121 135 122 124 | 0.3 | 50 | 18 |
| Mix 103: 20% Benzoic Acid/80% KClO3 | 3 121 137 122 124 | 1 | 47 | 16 |
| Mix 110: 20% Benzoic Acid/80% KClO3 | 3 114 133 116 119 | 9 | 47 | 16 |
| Mix 107: 20% Benzoic Acid/80% KClO3 | 2 121 143 122 124 | 1 | 129 | 37 | 11 |
| Mix 105: 20% Benzoic Acid/80% KNO3 | 3 122 142 127 129 | 3 | 124, 133 | 66 | 20 | 311 325 314 318 | 2 | 47 | 12 |
| Mix 106: 20% Benzoic Acid/80% KNO3 | no DSC runs showed exotherms or endotherms though mixture did turn brown; may have already decomposed (smell was noted during sample prep) |
| Mix 104: 20% Benzoic Acid/80% KClO3 | 3 121 137 122 125 | 2 | 41 | 10 | 301 317 304 306 | 2 | 51 | 18 |
| Mix 108: 20% Benzoic Acid/80% KIO4 | 3 118 130 119 121 | 0.5 | 27 | 12 |
| Mix 109: 20% Benzoic Acid/80% KMnO4 | 3 116 123 118 120 | 0.5 | 45 | 23 |
Table 4. Exotherms from Benzoic acid mixtures

| Sample                                | # | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Std Dev Exo Temp Max | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Std Dev Exo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Std Dev Exo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. |
|----------------------------------------|---|----------------|--------------|-----------------|-------------------|---------------------|----------------------|----------------|--------------|-----------------|-------------------|---------------------|---------------------|-----------------------------|------------------|----------------|----------------|----------------|----------------|-------------------|---------------------|-----------------------------|------------------|----------------|----------------|----------------|----------------|-------------------|
| Benzoic Acid                          | 3 | no exotherms   |              |                 |                   |                     |                      |                |              |                 |                   |                     |                      |                             |                  |                |                |                |                |                    |                      |                             |                  |                |
| Mix 111: 20% Benzoic Acid/80% AN      | 2 | 267            | 364          | 313             | 335               | 5                   | 359                  | 1879           | 8            |                 |                   |                     |                      |                             |                  |                |                |                |                |                    |                      |                             |                  |                |
| Mix 112: 20% Benzoic Acid/80% AP      | 2 | 316            | 359          | 323             | 337               | 4                   | 421                  | 203            | 393          | 482            | 446               | 457                 | 5                   | 1926                        | 445              |                |                |                |                |                    |                      |                             |                  |                |
| Mix 113: 20% Benzoic Acid/80% KBrO₃   | 3 | 355            | 381          | 368             | 369               | 3                   | 835                  | 698            |              |                 |                   |                     |                      |                             |                  |                |                |                |                |                    |                      |                             |                  |                |
| Mix 103: 20% Benzoic Acid/80% KClO₃   | 3 | 189            | 381          | 325             | 344               | 14                  | 307, 340             | 3648           | 472          |                 |                   |                     |                      |                             |                  |                |                |                |                |                    |                      |                             |                  |                |
| Mix 110: 20% Benzoic Acid/80% KCr₂O₇  | 3 | 371            | 381          | 374             | 376               | 6                   | 24                   | 17             | 381          | 401            | 385               | 387                 | 3                   | 138                         | 118              |                |                |                |                |                    |                      |                             |                  |                |
| Mix 107: 20% Benzoic Acid/80% KIO₃    | 2 | 395            | 403          | 395             | 398               | 0.9                 | 16                   | 2              | 403          | 454            | 418               | 426                 | 2                   | 476                         | 268              |                |                |                |                |                    |                      |                             |                  |                |
| Mix 105: 20% Benzoic Acid/80% KNO₃    | 3 | no exotherms   |              |                 |                   |                     |                      |                  |              |                 |                   |                     |                      |                             |                  |                |                |                |                |                    |                      |                             |                  |                |
| Mix 106: 20% Benzoic Acid/80% KNO₂    |             | no DSC runs showed exotherms or endotherms though mixture did turn brown; may have already decomposed |
| Mix 104: 20% Benzoic Acid/80% KClO₄   | 3 | 395            |              |                 |                   |                     |                      |                  |              |                 |                   |                     |                      |                             |                  |                |                |                |                |                    |                      |                             |                  |                |
| Mix 108: 20% Benzoic Acid/80% KIO₄    | 3 | 259            | 369          | 284             | 299               | 3                   | 333, 347             | 959            | 163          | 385            | 433               | 404                 | 415                 | 5                           | 544              | 62             |                |                |                |                    |                      |                             |                  |                |
| Mix 109: 20% Benzoic Acid/80% KMnO₄   | 3 | 123            | 244          | 124             | 159               | 48                  | 150, 182, 202, 234   | 909            | 403          | 274            | 341               | 288                 | 311                 | 0.5                         | 430              | 47             |                |                |                |                    |                      |                             |                  |                |
### Table 5. Endotherms from Charcoal mixtures

| Sample | FOX (fuel/oxidizer) Mixtures, DSC & SDT runs. | # | Start Endo (°C) | Endo Endo (°C) | Onset Temp (°C) | Endo Temp Min. (°C) | Std Dev Endo Temp Min | Additional Mins & Shoulders (°C) seen in some traces | Heat Abs. (J/g) | Std Dev Heat Abs. | Start Endo (°C) | Endo Endo (°C) | Onset Temp (°C) | Endo Temp Min. (°C) | Std Dev Endo Temp Min | Additional Mins & Shoulders (°C) seen in some traces | Heat Abs. (J/g) | Std Dev Heat Abs. |
|--------|---------------------------------------------|---|----------------|----------------|----------------|---------------------|-----------------------|----------------------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------------|----------------------------------------------------|----------------|----------------|----------------|----------------|
| Charcoal | no DSC or SDT (under N₂) runs showed exotherms or endotherms | | | | | | | | | | | | | | | | | | | | | |
| Charcoal in air SDT | 2 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 41: 50% Charcoal/ 50% AN | 4 | 51 | 67 | 52 | 54 | 1 | 7 | 3 | 114 | 133 | 119 | 124 | 4 | 12 | 7 |
| Mix 69: 50% Charcoal/ 50% AP SDT | 4 | 237 | 259 | 239 | 244 | 1 | 19 | 19 |
| Mix 42: 50% Charcoal/ 50% KClO₃ | 4 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 98: 50% Charcoal/ 50% K₂Cr₂O₇ | 3 | 392 | 397 | 393 | 395 | 1 | 13 | 10 |
| Mix 98: 50% Charcoal/ 50% K₂Cr₂O₇ | 3 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 99: 50% Charcoal/ 50% KI | 3 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 99: 50% Charcoal/ 50% KIO₃ | 1 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 43: 50% Charcoal/ 50% KNO₃ | 5 | 127 | 136 | 127 | 129 | 0.6 | 20 | 6 | 318 | 330 | 320 | 324 | 7 | 25 | 9 |
| Mix 43a: 50% Charcoal/ 50% KNO₃ SDT | 3 | 124 | 171 | 126 | 129 | 0.2 | 18 | 8 | 324 | 361 | 327 | 332 | 0.5 | 40 | 7 |
| Mix 102: 50% Charcoal/ 50% KNO₃ | 3 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 54: 50% Charcoal/ 50% KClO₄ | 3 | 302 | 318 | 305 | 307 | 0.5 | 51 | 14 |
| Mix 54/70 Charcoal/ 50% KClO₄ SDT | 7 | 298 | 328 | 299 | 304 | 1 | 26 | 9 | 757 | 774 | 761 | 765 | 2 | 14 | 6 |
| Mix 100: 50% Charcoal/ 50% KIO₄ | 4 | no endotherms | | | | | | | | | | | | | | | | | | | | |
| Mix 101: 50% Charcoal/ 50% KMnO₄ | 3 | no endotherms | | | | | | | | | | | | | | | | | | | | |
Table 6. Exotherms from Charcoal mixtures

| FOX (fuel/oxidizer) Mixtures, DSC & SDT runs. |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | # | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev | Endo Temp Max. (°C) | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max. | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. |
| Charcoal in air SDT | 2 | 202 | 579 | 416 | 522 | 6 | 433 |  | 20821 | 483 | 203 | 241 | 222 | 223 | 2 | 1607 | 399 |
| Mix 41: 50% Charcoal/ 50% AN | 4 | 353 | 465 | 447 | 451 | 9 | 1718 | 229 | 359 | 408 | 312 | 338 | 10 | 1738 | 469 |
| Mix 69: 50% Charcoal/ 50% AP | 3 | 300 | 361 | 329 | 333 | 5 | 312, 328, 333 |  | 1585 | 183 |  |  |  |  |  |  |  |  |
| Mix 42: 50% Charcoal/ 50% KClO₃ | 4 | 397 | 417 | 397 | 400 | 1 | 74 | 20 | 389 | 477 | 391 | 397 | 1 | 239 | 265 | 670 | 745 | 672 | 702 | 4 | 82 | 57 |
| Mix 98: 50% Charcoal/ 50% K₂Cr₂O₇ | 3 | 436 | 456 | 443 | 448 | 7 | 300 | 162 | 425 | 510 | 444 | 454 | 492 | 139 |  |  |  |  |  |  |  |
| Mix 43: 50% Charcoal/ 50% KNO₃ | 5 | 409 | 486 | 461 | 474 | 11 | 462 | 1361 | 413 |  |  |  |  |  |  |  |  |  |  |  |  |
| Mix 43a: 50% Charcoal/ 50% KNO₃, SDT | 3 | 423 | 730 | 459 | 461 | 2 | 1920 | 353 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mix 102: 50% Charcoal/ 50% KNO₃ | 3 | 346 | 407 | 358 | 381 | 2 | 625 | 179 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mix 54: 50% Charcoal/ 50% KClO₄ | 3 | 462 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mix 54/70: Charcoal/ 50% KClO₄, SDT | 7 | 470 | 557 | 510 | 525 | 8 | 512 | 1172 | 475 |  |  |  |  |  |  |  |  |  |  |  |  |
| Mix 100: 50% Charcoal/ 50% KIO₄ | 4 | 344 | 364 | 350 | 356 | 1 | 116 | 81 | 343 | 456 | 444 | 447 | 9 | 240 | 173 |  |  |  |  |  |
| Mix 101: 50% Charcoal/ 50% KMnO₄ | 3 | 277 | 344 | 294 | 310 | 2 | 792 | 269 |  |  |  |  |  |  |  |  |  |  |  |  |  |
Table 7. Endotherms from Cyclododecanol mixtures

| FOX (fuel/oxidizer) Mixtures, DSC & SDT runs. |  |
|---|---|
| **Sample** | **#** | **Start Endo (°C)** | **End Endo (°C)** | **Onset Temp (°C)** | **Endo Temp Min. (°C)** | **Std Dev Endo Temp Min.** | **Additional Mins & Shoulders (°C) seen in some traces** | **Heat Abs. (J/g)** | **Std Dev Heat Abs.** | **Start Endo (°C)** | **End Endo (°C)** | **Onset Temp (°C)** | **Endo Temp Min. (°C)** | **Std Dev Endo Temp Min.** | **Additional Mins & Shoulders (°C) seen in some traces** | **Heat Abs. (J/g)** | **Std Dev Heat Abs.** | **Start Endo (°C)** | **End Endo (°C)** | **Onset Temp (°C)** | **Endo Temp Min. (°C)** | **Std Dev Endo Temp Min.** | **Additional Mins & Shoulders (°C) seen in some traces** | **Heat Abs. (J/g)** | **Std Dev Heat Abs.** |
| Cyclododecanol | 4 | 57 | 94 | 72 | 78 | 1 | 72 | 172 | 11 |
| Mix 128: 50% Cyclododecanol/50% AP | 2 | 66 | 88 | 70 | 76 | 2 | 71 | 69 | 12 | 242 | 257 | 243 | 249 | 3 | 30 | 10 |
| Mix 130: 50% Cyclododecanol/50% KBrO₃ | 3 | 63 | 84 | 68 | 72 | 0.5 | 65 | 8 |
| Mix 48: 50% Cyclododecanol/50% KClO₃ | 3 | 65 | 86 | 70 | 74 | 3 | 71, 76 | 69 | 11 | 339 | 362 | 351 | 357 | 0.4 | 339 | 94 | 8 |
| Mix 126: 50% Cyclododecanol/50% K₂CrO₇ | 3 | 63 | 94 | 70 | 77 | 0.5 | 72 | 94 |
| Mix 127: 50% Cyclododecanol/50% KIO₃ | 3 | 65 | 85 | 69 | 75 | 3 | 72 | 7 |
| Mix 47: 50% Cyclododecanol/50% KNO₃ | 4 | 61 | 85 | 69 | 73 | 0.9 | 87 | 12 | 126 | 139 | 127 | 129 | 2 | 17 | 5 | 313 | 336 | 320 | 326 | 3 | 22 | 11 |
| Mix 123: 50% Cyclododecanol/50% KClO₄ | 2 | 65 | 88 | 69 | 77 | 2 | 72 | 64 | 11 | 303 | 314 | 304 | 307 | 0.3 | 34 | 1 |
| Mix 129: 50% Cyclododecanol/50% KIO₃ | 3 | 64 | 90 | 70 | 77 | 0.8 | 71 | 74 | 5 |
| Mix 124: 50% Cyclododecanol/50% KMnO₄ | 2 | 63 | 87 | 69 | 72 | 0.08 | 77 | 19 |
Table 8. Exotherms from Cyclododecanol mixtures

| FOX (fuel/oxidizer) Mixtures, DSC & SDT runs. | Sample | # | Start (°C) | End (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev | Start (°C) | End (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Additional Max & Shoulders (°C) seen in some traces | Std Dev | Heat Released (J/g) | Start (°C) | End (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev | Additional Max & Shoulders (°C) seen in some traces | Std Dev | Heat Released (J/g) |
|---------------------------------------------|--------|---|------------|---------|----------------|------------------|--------|------------|---------|----------------|------------------|--------|-----------------------------------------------|-----------------|-----------------------------------------------|--------|-----------------|------------|---------|----------------|------------------|--------|-----------------------------------------------|--------|-----------------|
| Cyclododecanol                             | 4      | no exotherms               |          |          |                |                  |        |            |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 128: 50% Cyclododecanol/50% AP         | 2      | 323 | 454        | 361     | 404            | 3                | 1877  | 392               |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 130: 50% Cyclododecanol/50% KBrO₃     | 3      | 379 | 429        | 398     | 408            | 1                | 386   | 194               |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 46: 50% Cyclododecanol/50% KCIO₃       | 3      | 397 | 494        | 436     | 470            | 11               | 483   | 432               |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 126: 50% Cyclododecanol/50% K₂CrO₇     | 3      | 321 | 435        | 360     | 384            | 9                | 354, 268, 390 | 256   | 93               |         |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 127: 50% Cyclododecanol/50% KIO₃       | 3      | 414 | 468        | 444     | 452            | 2                | 354   | 16                |         |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 47: 50% Cyclododecanol/50% KNO₂        |        | no exotherms               |          |          |                |                  |        |            |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 123: 50% Cyclododecanol/50% KClO₃      | 2      | no exotherms               |          |          |                |                  |        |            |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 129: 50% Cyclododecanol/50% KClO₄      | 3      | 185 | 234        | 197     | 212            | 2                | 19    | 5.1              |         |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
| Mix 124: 50% Cyclododecanol/50% KMnO₄      | 2      | 198 | 357        | 314     | 320            | 0.04             | 340   | 768              | 313     |                |                  |        |                                               |                 |                                               |        |                |            |        |              |                   |        |                                               |        |                |
Table 9. Endotherms from Erythritol mixtures

| Sample                                    | # | Start Endo (°C) | End Endo (°C) | Onset Temp (°C) | Endo Temp Min (°C) | Std Dev Endo Temp Min | Heat Abs. (J/g) | Std Dev Heat Abs. | Start Endo (°C) | End Endo (°C) | Onset Temp (°C) | Endo Temp Min (°C) | Std Dev Endo Temp Min | Heat Abs. (J/g) | Std Dev Heat Abs. | Start Endo (°C) | End Endo (°C) | Onset Temp (°C) | Endo Temp Min (°C) | Std Dev Endo Temp Min | Heat Abs. (J/g) | Std Dev Heat Abs. | Start Endo (°C) | End Endo (°C) | Onset Temp (°C) | Endo Temp Min (°C) | Std Dev Endo Temp Min | Heat Abs. (J/g) | Std Dev Heat Abs. |
|-------------------------------------------|---|-----------------|---------------|-----------------|-------------------|---------------------|-----------------|------------------|-----------------|---------------|-----------------|-------------------|---------------------|-----------------|------------------|-----------------|---------------|-----------------|-------------------|---------------------|-----------------|------------------|-----------------|---------------|-----------------|-------------------|---------------------|-----------------|------------------|-----------------|---------------|-----------------|-------------------|---------------------|-----------------|------------------|
Table 10. Exotherms from Erythritol mixtures

| Sample | #  | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Exo | Endo Temp Max. (°C) | Std Dev Endo | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Exo | Endo Temp Max. (°C) | Std Dev Endo | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. |
|--------|----|----------------|--------------|-----------------|-------------------|-------------|-------------------|-------------|------------------------------------------------|-------------------|---------------|----------------|--------------|--------------|----------------|-------------------|-------------|-------------------|-------------|------------------------------------------------|-------------------|---------------|
| Erythritol | 4  | no exotherms   |              |                 |                   |             |                   |             |                                                 |                   |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Erythritol SDT | 2  | no exotherms   |              |                 |                   |             |                   |             |                                                 |                   |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 35: 50% Erythritol/ 50% AN | 3  | 260 | 281 | 265 | 267 | 8 | 1758 | 244 |                                     |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 44: 50% Erythritol/ 50% AP | 4  | 258 | 449 | 362 | 404 | 74 | 291, 337 | 3822 | 861 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 30b: 50% Erythritol/ 50% KClO₃ | 5  | 192 | 281 | 235 | 258 | 8 | 215 | 2272 | 390 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 64: 50% Erythritol/ 50% KIO₃ | 3  | 141 | 219 | 156 | 181 | 6 | 183 | 871 | 304 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 64: 50% Erythritol/ 50% KIO₃ SDT | 4  | 148 | 268 | 159 | 179 | 3 | 892 | 79 | 285 | 358 | 294 | 317 | 4 | 36 | 30 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 34: 50% Erythritol/ 50% KNO₃ | 3  | 352 | 461 | 397 | 413 | 2 | 2438 | 336 |                                     |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 57: 50% Erythritol/ 50% KNO₂ | 3  | 261 | 356 | 288 | 315 | 2 | 1009 | 30 |                                     |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 45: 50% Erythritol/ 50% KClO₄ | 4  | 313 | 386 | 324 | 348 | 19 | 319 | 397 | 187 | 450 | 477 | 11 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 45: 50% Erythritol/ 50% KClO₄ SDT | 3  | 509 | 593 | 524 | 575 | 6 | 50 | 9 | 593 | 669 | 627 | 642 | 2 | 609, 626 | 176 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 67a: 50% Erythritol/ 50% KIO₃ SDT | 3  | 119 | 286 | 118 | 145 | 7 | 183, 243 | 1140 | 452 | 129 | 363 | 332 | 343 | 14 | 10 | 7 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
| Mix 46: 50% Erythritol/ 50% KMnO₄ | 4  | 112 | 230 | 140 | 161 | 2 | 115, 125 | 1702 | 270 | 312 | 395 | 325 | 358 | 9 | 204 | 63 |                               |                  |               |               |              |              |               |                   |             |                   |             |                                                 |                   |               |
### Table 11. Endotherms from Fructose mixtures

| Sample | FOX (fuel/oxidizer) Mixtures, DSC & SDT runs. | Start Endo (°C) | Endo | Onset Temp (°C) | Endo Temp Min. (°C) | Std Dev Endo Temp Min | Additional Mints & Shoulders (°C) seen in some traces | Heat Abs. (J/g) | Std Dev Heat Abs. Start Endo (°C) | Endo | Onset Temp (°C) | Endo Temp Min. (°C) | Std Dev Endo Temp Min | Additional Mints & Shoulders (°C) seen in some traces | Heat Abs. (J/g) | Std Dev Heat Abs. |
|--------|----------------------------------------------|----------------|------|----------------|---------------------|-----------------------|------------------------------------------------------|----------------|-----------------------------------|------|----------------|---------------------|-----------------------|------------------------------------------------------|----------------|------------------|
| Fructose |                                             | 90            | 145  | 104            | 129                | 2                    | 185                                                | 47             |                                   |      |                |                     |                       |                                                      |                |                  |
| Mix 25a: 50% Fructose/ 50% AN |                                             | 88            | 167  | 103            | 124                | 2                    | 283                                                | 50             | 177                                              | 306 | 180            | 226                 | 35                     | 203                                              | 274            | 114              |
| Mix 29: 50% Fructose/ 50% AP Mix 29: 50% Fructose/ 50% AP SDT |                                             | 95            | 143  | 106            | 122                | 12                   | 90                                                | 34             | 242                                              | 252 | 243            | 244                 | 1                     | 19                                               | 8              |                  |
| Mix 29: 50% Fructose/ 50% AP SDT |                                             | 96            | 203  | 110            | 128                | 2                    | 167                                                | 378            | 150                                              | 724 | 807            | 734                 | 756                    | 2                                               | 54             | 59               |
| Mix 92: 50% Fructose/ 50% KBrO₃ |                                             | 99            | 130  | 103            | 116                | 2                    | 100                                                | 27             |                                   |      |                |                     |                       |                                                      |                |                  |
| Mix 92: 50% Fructose/ 50% KBrO₃ SDT |                                             | 98            | 136  | 105            | 123                | 3                    | 71                                                | 32             | 726                                              | 741 | 728            | 730                 | 0.6                    | 13                                               | 2              |                  |
| Mix 17: 50% Fructose/ 50% KClO₃ |                                             | 93            | 116  | 101            | 111                | 10                   | 94, 103                                            | 25             | 13                                               |      |                |                     |                       |                                                      |                |                  |
| Mix 17: 50% Fructose/ 50% KClO₃ SDT |                                             | 93            | 130  | 103            | 121                | 0.4                  | 96                                                | 40             | 758                                              | 776 | 763            | 766                 | 0.2                    | 19                                               | 10             |                  |
| Mix 16: 50% Fructose/ 50% K₂CrO₃ |                                             | 97            | 136  | 102            | 111                | 9                    | 105                                                | 14             | 13                                               |      |                |                     |                       |                                                      |                |                  |
| Mix 96: 50% Fructose/ 50% K₂CrO₃ |                                             | 115           | 129  | 119            | 124                | 1                    | 30                                                | 2              |                                   |      |                |                     |                       |                                                      |                |                  |
| Mix 96: 50% Fructose/ 50% K₂CrO₃ |                                             | 102           | 132  | 104            | 122                | 0.6                  | 41                                                | 12             | 673                                              | 689 | 675            | 678                 | 0.4                    | 8                                               | 1              |                  |
| Mix 96: 50% Fructose/ 50% KNO₃ |                                             | 98            | 146  | 105            | 154                | 50                   | 136                                                | 73             | 28                                               |      |                |                     |                       |                                                      |                |                  |
| Mix 96: 50% Fructose/ 50% KNO₃ |                                             | 99            | 146  | 102            | 125                | 4                    | 43                                                | 30             | 303                                              | 323 | 305            | 309                 | 1                     | 59                                               | 14             |                  |
| Mix 7: 50% Fructose/ 50% KClO₄ |                                             | 88            | 122  | 96             | 115                | 0.1                  | 36                                                | 4              | 660                                              | 695 | 670            | 676                 | 0.2                    | 27                                               | 6              |                  |
| Mix 7: 50% Fructose/ 50% KClO₄ |                                             | 79            | 125  | 98             | 99                 | 12                   | 84                                                | 48             |                                   |      |                |                     |                       |                                                      |                |                  |
Table 12. Exotherms from Fructose mixtures

| FOXY (fuel/oxidizer) | Mixtures, DSC & SDT runs. |  |  |  |  |  |  |  |  |  |  |  |  |
|----------------------|---------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Sample              | #  | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev Exo | End Exo | Std Dev Endo | Temp Max | Std Dev | Additional Max & Shoulders (°C) seen in some traces | Std Dev Exo | Heat Released (J/g) | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev Exo | End Exo | Std Dev Endo | Temp Max | Std Dev | Additional Max & Shoulders (°C) seen in some traces | Std Dev Exo | Heat Released (J/g) | Std Dev Heat Rel. |
| Fructose             | 4  | 248  | 318  | 254  | 270  | 2   | 204 | 63   |          |          |          |          |          |          |          |
| Mix 25a: 50% Fructose/50% AN | 5  | 149  | 228  | 155  | 169  | 0.4 | 199 | 2652 | # #      |          |          |          |          |          |          |
| Mix 29: 50% Fructose/50% AP | 7  | 167  | 208  | 173  | 181  | 2   | 222 | 89   |          |          |          |          |          |          |          |
| Mix 29: 50% Fructose/50% AP SDT | 3  | 203  | 448  | 273  | 337  | 33  | 327, 367 |          |          |          |          |          |          |          |
| Mix 92: 50% Fructose/50% KBrO₃ | 2  | 149  | 222  | 180  | 196  | 2   | 1317 | 147  |          |          |          |          |          |          |
| Mix 92: 50% Fructose/50% KBrO₃ SDT | 3  | 136  | 189  | 138  | 150  | 2   | 161  | 29   | 365  | 472  | 371  | 373  | 0.7       | 417  | 47   |
| Mix 17: 50% Fructose/50% KClO₃ | 10 | 116  | 255  | 133  | 166  | 25  | 128, 173, 191, 204, 250 | 2296 | 991   |          |          |          |          |          |
| Mix 17: 50% Fructose/50% KClO₃ SDT | 3  | 130  | 255  | 129  | 154  | 26  | 140, 183 | 466  | 265  | 318  | 441  | 325  | 328  | 1          | 388  | 165  |
| Mix 96: 50% Fructose/50% K₂CrO₄ | 3  | 102  | 123  | 105  | 109  | 2   | 80  | 72   |          |          |          |          |          |          |          |
| Mix 96: 50% Fructose/50% K₂CrO₄ SDT | 2  | 387  | 511  | 389  | 394  | 0.5 |          | 272  | 75   |          |          |          |          |          |
| Mix 63: 50% Fructose/50% KIO₃ | 3  | 129  | 189  | 143  | 156  | 0.5 |          | 1442 | 118  |          |          |          |          |          |
| Mix 63: 50% Fructose/50% KIO₃ SDT | 4  | 132  | 201  | 133  | 145  | 1   | 282  | 56   | 423  | 456  | 425  | 427  | 2          |          |          |
| Mix 21: 50% Fructose/50% KN0₃ | 3  | 217  | 357  | 227  | 248  | 1   | 297  | 205  | 46   | 379  | 437  | 396  | 404  | 10         | 391  | 144  |
| Mix 56: 50% Fructose/50% KNO₃ | 2  | 126  | 231  | 148  | 168  | 4   | 160  | 987  | 61   |          |          |          |          |          |
| Mix 27: 50% Fructose/50% KClO₄ | 4  | 414  | 140  | 140  | 140  | 0.4 |          | 631  | 55   | 335  | 384  | 341  | 349  | 0.2        | 33   | 5      |
| Mix 66: 50% Fructose/50% KIO₃ | 3  | 115  | 210  | 126  | 138  | 2   | 190  | 1620 | 371  |          |          |          |          |          |
| Mix 66: 50% Fructose/50% KIO₃ SDT | 3  | 122  | 202  | 130  | 133  | 0.4 |          | 631  | 55   | 335  | 384  | 341  | 349  | 0.2        | 33   | 5      |
| Mix 37: 50% Fructose/50% KMnO₄ | 4  | 130  | 282  | 177  | 200  | 37  | 235, 263 | 1222 | 348  |          |          |          |          |          |
**Table 13. Endotherms from Glucose & Lactose mixtures**

| Sample | # | Start Exo (ºC) | End Exo (ºC) | Onset Temp (ºC) | Endo Temp Min (ºC) | Std Dev Exo Temp Max | Std Dev Endo Temp Min | Additional Min & Shoulders (ºC) seen in some traces | Std Dev Heat Abs | Std Dev Heat Rel | Start Endo (ºC) | Endo Endo (ºC) | Onset Temp Min (ºC) | Endo Temp Min (ºC) | Std Dev Exo Temp Max | Std Dev Endo Temp Min | Additional Min & Shoulders (ºC) seen in some traces | Std Dev Heat Abs | Std Dev Heat Rel |
|--------|---|----------------|--------------|------------------|---------------------|----------------------|-----------------------|------------------------------------------------|----------------|----------------|----------------|----------------|----------------------|----------------------|----------------------|-----------------------|----------------|----------------|
| Glucose | 3 | 143            | 179          | 153              | 165                 | 0.7                  | 217                   | 201 251 206 233 0.1 | 62 15         |                 |                |                |                      |                      |                      |                       |                      |                 |
| Mix 24: 50% Glucose/ 50% AN | 3 | 53             | 69           | 54               | 55                  | 0.7                  | 17 6                  | 95 130 110 114 13 | 68 24         |                 |                |                |                      |                      |                      |                       |                      |                 |
| Mix 16: 50% Glucose/ 50% KClO₃ | 9 | 132           | 153          | 140              | 149                 | 8                    | 41                    | 142 173 155 164 0.6 | 112 15         |                 |                |                |                      |                      |                      |                       |                      |                 |
| Mix 20: 50% Glucose/ 50% KNO₃ | 3 | 130           | 141          | 131              | 133                 | 0.7                  | 5 1                   | 145 177 148 152 0.8 | 59 8          | 206            | 219            | 209            | 212 0.9            |                      |                      |                       |                      |                 |
| Lactose (galactose + glucose) | 4 | 145           | 172          | 148              | 153                 | 8                    | 115                   | 183 219 180 208 2 | 92 69         |                 |                |                |                      |                      |                      |                       |                      |                 |
| Mix 23: 50% Lactose/ 50% AN | 4 | 52             | 67           | 53               | 55                  | 0.9                  | 9 2                   | 93 133 96 105 2   | 84 14         |                 |                |                |                      |                      |                      |                       |                      |                 |
| Mix 15: 50% Lactose/ 50% KClO₃ | 3 | 145           | 165          | 147              | 151                 | 0.8                  | 63                    | 145 177 148 152 0.8 | 59 8          | 206            | 219            | 209            | 212 0.9            |                      |                      |                       |                      |                 |
| Mix 19: 50% Lactose/ 50% KNO₃ | 3 | 130           | 139          | 131              | 133                 | 0.7                  | 10 4                  | 145 177 148 152 0.8 | 59 8          | 206            | 219            | 209            | 212 0.9            |                      |                      |                       |                      |                 |

**Table 14. Exotherms from Glucose & Lactose mixtures**

| Sample | # | Start Exo (ºC) | End Exo (ºC) | Onset Temp (ºC) | Exo Temp Max (ºC) | Std Dev Exo Temp Max | Std Dev Endo Temp Max | Additional Max & Shoulders (ºC) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel | Start Exo (ºC) | End Exo (ºC) | Onset Temp (ºC) | Exo Temp Max (ºC) | Std Dev Exo Temp Max | Std Dev Endo Temp Max | Additional Max & Shoulders (ºC) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel |
|--------|---|----------------|--------------|------------------|---------------------|----------------------|-----------------------|------------------------------------------------|---------------------|----------------|----------------|----------------|----------------|----------------------|----------------------|----------------------|-----------------------|----------------|
| Glucose | 3 | 273            | 339          | 285              | 306                 | 4                    | 345                   | 250 348 291 328 28 482 353 | 315 294 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Mix 24: 50% Glucose/ 50% AN | 3 | 149           | 232          | 166              | 186                 | 5                    | 158                   | 2277 414 250 348 291 328 28 482 353 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Mix 16: 50% Glucose/ 50% KClO₃ | 9 | 151           | 290          | 205              | 243                 | 5                    | 168                   | 2668 762 | 372 422 394 398 5 392 363 62 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Mix 20: 50% Glucose/ 50% KNO₃ | 3 | 223           | 337          | 258              | 285                 | 18                   | 307 273 299 64 372 422 394 398 5 392 363 62 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Lactose (galactose + glucose) | 4 | 258           | 368          | 279              | 304                 | 3                    | 478                   | 255 333 273 302 25 187 174 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Mix 22: 50% Lactose/ 50% AN | 4 | 161           | 243          | 170              | 182                 | 1                    | 208                   | 1489 447 255 333 273 302 25 187 174 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Mix 15: 50% Lactose/ 50% KClO₃ | 3 | 174           | 289          | 183              | 197                 | 5                    | 256                   | 1597 102 | 237 348 363 396 58 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
| Mix 19: 50% Lactose/ 50% KNO₃ | 3 | 239           | 326          | 253              | 271                 | 0.8                  | 276                   | 366 426 389 393 0.6 696 78 | 237 348 363 396 58 |                 |                |                |                |                      |                      |                      |                       |                      |                 |
### Table 15. Endotherms from Hexatriacontane mixtures

| Sample                  | Start | End | Start Temp | End Temp | Std Dev | Mins & Shoulders | Host Abs (%) | Std Dev | Mins & Shoulders | Host Abs (%) | Std Dev | Mins & Shoulders | Host Abs (%) | Std Dev | Mins & Shoulders | Host Abs (%) | Std Dev | Mins & Shoulders | Host Abs (%) | Std Dev | Mins & Shoulders | Host Abs (%) |
|-------------------------|------|-----|------------|---------|--------|------------------|--------------|--------|------------------|--------------|--------|------------------|--------------|--------|------------------|--------------|--------|------------------|--------------|--------|------------------|--------------|--------|------------------|--------------|
| Hexatriacontane         | 3    | 69  | 100        | 75      | 79     | 2                | 201          | 8.8    |                   |              |        |                   |              |        |                   |              |        |                   |              |
| Mix 137: 50% Hexatriacontane/50% AN | 3    | 52  | 65         | 53      | 54     | 0.8              | 12           | 3      | 71                | 98           | 75     | 77               | 0.9          | 128    | 28               |              | 125    | 139              | 127          | 0.3    | 23               | 3            | 156    | 176              | 160          | 167    | 1                | 30 10        |
| Mix 134: 50% Hexatriacontane/50% AP | 3    | 72  | 87         | 76      | 78     | 0.7              | 81           | 22     |                   |              |        |                   |              |        |                   |              |        |                   |              |        |                   |              |        |                   |              |
| Mix 138: 50% Hexatriacontane/50% KClO₃ | 3    | 70  | 92         | 75      | 77     | 0.5              | 215          | 33     |                   |              |        |                   |              |        |                   |              |        |                   |              |        |                   |              |
| Mix 136: 50% Hexatriacontane/50% KNO₃ | 3    | 69  | 90         | 74      | 77     | 0.3              | 114          | 20     |                   |              |        |                   |              |        |                   |              |        |                   |              |        |                   |              |
| Mix 133: 50% Hexatriacontane/50% KClO₃ | 3    | 60  | 96         | 75      | 77     | 0.6              | 160          | 17     | 129               | 144          | 130    | 132              | 2            | 14     | 6                |              | 327    | 341              | 332          | 334    | 1                | 16 9         |
| Mix 132: 50% Hexatriacontane/50% KNO₃ | 3    | 71  | 93         | 75      | 77     | 1                | 125          | 14     | 303               | 316          | 305    | 308              | 1            | 39     | 5                |              |        |                   |              |        |                   |              |
| Mix 135: 50% Hexatriacontane/50% KClO₃ | 3    | 70  | 87         | 75      | 76     | 0.6              | 103          | 17     |                   |              |        |                   |              |        |                   |              |        |                   |              |

### Table 16. Exotherms from Hexatriacontane mixtures

| Sample                  | Start | End | Start Temp | End Temp | Std Dev | Max & Shoulders | Heat Released (J/g) | Std Dev | Heat Rel. | Start | End | Start Temp | End Temp | Std Dev | Max & Shoulders | Heat Released (J/g) | Std Dev | Heat Rel. | Start | End | Start Temp | End Temp | Std Dev | Max & Shoulders | Heat Released (J/g) | Std Dev | Heat Rel. |
|-------------------------|------|-----|------------|---------|--------|-----------------|---------------------|--------|-----------|------|-----|------------|---------|--------|-----------------|---------------------|--------|-----------|------|-----|------------|---------|--------|-----------------|---------------------|--------|-----------|
| Hexatriacontane         | 3    |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |
| Mix 137: 50% Hexatriacontane/50% AN | 3    | 278 | 373        | 339    | 349    | 22              | 313                | 343    | 362       | 794 | 202 | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |
| Mix 134: 50% Hexatriacontane/50% AP | 3    | 367 | 435        | 406    | 412    | 8               | 1414              | 233    |           |      |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |
| Mix 138: 50% Hexatriacontane/50% KClO₃ | 3    |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |
| Mix 136: 50% Hexatriacontane/50% KNO₃ | 3    | 418 | 469        | 443    | 451    | 3               | 209               | 46     |           |      |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |
| Mix 133: 50% Hexatriacontane/50% KClO₃ | 3    |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |
| Mix 135: 50% Hexatriacontane/50% KNO₃ | 3    | 210 | 234        | 221    | 224    | 3               | 18                | 1      | 287       | 341 | 296 | 308        | 24      | 274    | 88               | 373                | 447    | 422               | 437 2        | 411    | 57               |           |        |                 |                     |        |           |      |     | no exotherms |         |        |                 |                     |        |           |

FOX (fuel/oxidizer) Mixtures, DSC & SDT runs.
## Table 17. Endotherms from Naphthalene mixtures

| Sample                  | # | Start (°C) | End (°C) | Endo Temp (°C) | std Dev Endo Temp Min | Heat Abs. (J/g) | std Dev Heat Abs. | Start (°C) | End (°C) | Onset Temp (°C) | std Dev Onset Temp Min | Heat Abs. (J/g) | std Dev Heat Abs. | Start (°C) | End (°C) | Onset Temp (°C) | std Dev Onset Temp Min | Heat Abs. (J/g) | std Dev Heat Abs. | Start (°C) | End (°C) | Onset Temp (°C) | std Dev Onset Temp Min | Heat Abs. (J/g) | std Dev Heat Abs. |
|-------------------------|---|------------|----------|----------------|-----------------------|-----------------|------------------|------------|----------|----------------|----------------------|-----------------|------------------|------------|----------|----------------|----------------------|-----------------|------------------|------------|----------|----------------|----------------------|-----------------|------------------|
| Naphthalene             | 3 | 76         | 95       | 77             | 80                    | 1               | 177              | 11         |         |                |                      |                 |                  |            |          |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 117: 50% Naphthalene/50% AN | 3 | 77         | 93       | 79             | 82                    | 1               | 74              | 23         | 125      | 137             | 126                   | 129             | 0.5              | 18         | 13       |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 118: 50% Naphthalene/50% AP | 4 | 77         | 90       | 78             | 81                    | 0.6             | 97              | 4          | 242      | 254             | 246                   | 247             | 0.7              | 35         | 3        |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 120: 50% Naphthalene/50% KBrO₃ | 2 | 77         | 90       | 79             | 81                    | 2               | 62              | 1          | 242      | 254             | 246                   | 247             | 0.7              | 35         | 3        |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 114: 50% Naphthalene/50% KClO₃ | 4 | 77         | 93       | 78             | 81                    | 0.9             | 77              | 15         | 336      | 359             | 347                   | 351             | 9                | 58         | 32       |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 122: 50% Naphthalene/50% K₂Cr₂O₇ | 3 | 76         | 93       | 79             | 81                    | 0.7             | 31              | 15         | 388      | 403             | 393                   | 396             | 2                | 71         | 22       |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 119: 50% Naphthalene/50% KIO₃ | 3 | 76         | 95       | 78             | 81                    | 1               | 59              | 10         | 336      | 341             | 333                   | 334             | 2                | 13         | 5        |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 116: 50% Naphthalene/50% KNO₃ | 3 | 78         | 97       | 79             | 81                    | 0.2             | 131             | 24         | 128      | 139             | 128                   | 131             | 2                | 6          | 5        |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 115: 50% Naphthalene/50% KClO₃ | 2 | 78         | 93       | 79             | 82                    | 0.2             | 77              | 7          | 303      | 313             | 305                   | 308             | 0.8              | 35         | 5        |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 113: 50% Naphthalene/50% KIO₃ | 2 | 76         | 92       | 78             | 81                    | 1               | 65              | 1          | 336      | 341             | 333                   | 334             | 2                | 13         | 5        |                |                      |                 |                  |            |          |                |                      |                 |                  |
| Mix 121: 50% Naphthalene/50% KMnO₄ | 3 | 76         | 90       | 78             | 80                    | 0.7             | 92              | 11         | 242      | 254             | 246                   | 247             | 0.7              | 35         | 3        |                |                      |                 |                  |            |          |                |                      |                 |                  |
Table 18. Exotherms from Naphthalene mixtures

| Sample                        | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev Exo Endo | Std Dev Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev Exo Endo | Std Dev Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. |
|-------------------------------|----------------|--------------|-----------------|-------------------|-------------------|-----------------|-----------------------------------------------|-------------------|----------------|----------------|--------------|----------------|----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|----------------|
| Naphthalene                   |                |              |                 |                   |                   |                 |                                              |                   |                |                |              |                |                |                 |                |                |                 |                |                |                |
| Mix 117: 50% Naphthalene/50% AN | 279            | 343          | 305             | 328               | 4                 | 317             | 829              | 525               |                   |                |                |                |                |                 |                 |                |                |                 |                |
| Mix 118: 50% Naphthalene/50% AP | 356            | 490          | 435             | 470               | 21                | 347             | 358              | 463              | 477               | 1527           | 722            |                |                |                 |                 |                |                |                 |                |
| Mix 120: 50% Naphthalene/50% KBrO₃ | 391            | 482          | 423             | 433               | 2                 | 408             | 1779             | 596               |                   |                |                |                |                |                 |                 |                |                |                 |                |
| Mix 114: 50% Naphthalene/50% KClO₃ | 397            | 477          | 437             | 461               | 35                | 456             | 773              | 176               |                   |                |                |                |                |                 |                 |                |                |                 |                |
| Mix 122: 50% Naphthalene/50% K₂Cr₂O₇ | 3              | no exotherms |                 |                   |                   |                 |                                              |                   |                |                |              |                |                |                 |                |                |                 |                |
| Mix 119: 50% Naphthalene/50% KIO₃ | 3              | no exotherms |                 |                   |                   |                 |                                              |                   |                |                |              |                |                |                 |                |                |                 |                |
| Mix 116: 50% Naphthalene/50% KNO₃ | 3              | no exotherms |                 |                   |                   |                 |                                              |                   |                |                |              |                |                |                 |                |                |                 |                |
| Mix 115: 50% Naphthalene/50% KClO₃ | 2              | no exotherms |                 |                   |                   |                 |                                              |                   |                |                |              |                |                |                 |                |                |                 |                |
| Mix 131: 50% Naphthalene/50% KIO₃ | 255            | 391          | 292             | 317               | 1                 | 759             | 6                | 404              | 450              | 421            | 432           | 0.6            | 83             | 12             | 450           | x              | x              | 481            | 19             | off scale     |
| Mix 121: 50% Naphthalene/50% KMnO₄ | 265            | 356          | 287             | 303               | 0.5               | 931             | 207              |                  |                  |                |                |                |                |                 |                |                |                |                |                |                |
Table 19. Endotherms from Pentaerythritol mixtures

| Sample | 1  | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|--------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|
| FOX (Fuel/Oxidizer) Mixtures, DSC & DIL runs. | | | | | | | | | | | | | | | | | | | |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |
| Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst | Start | End | Cryst |

- 1: Pentaerythritol
- 2: 5% Pentaerythritol
- 3: 10% Pentaerythritol
- 4: 15% Pentaerythritol
- 5: 20% Pentaerythritol
- 6: 25% Pentaerythritol
- 7: 30% Pentaerythritol
- 8: 35% Pentaerythritol
- 9: 40% Pentaerythritol
- 10: 45% Pentaerythritol
- 11: 50% Pentaerythritol
- 12: 55% Pentaerythritol
- 13: 60% Pentaerythritol
- 14: 65% Pentaerythritol
- 15: 70% Pentaerythritol
- 16: 75% Pentaerythritol
- 17: 80% Pentaerythritol
- 18: 85% Pentaerythritol
- 19: 90% Pentaerythritol
- 20: 95% Pentaerythritol

**Notes:**
- FOX: Fuel/Oxidizer
- DSC: Differential Scanning Calorimetry
- DIL: Differential Scanning Calorimetry
- Start: Start temperature of the endotherm
- End: End temperature of the endotherm
- Cryst: Crystal temperature of the endotherm
- Min: Minimum temperature of the endotherm
- Max: Maximum temperature of the endotherm
- Start time: Start time of the endotherm
- End time: End time of the endotherm
- Duration: Duration of the endotherm
- Energy: Energy released during the endotherm
- %: Percentage of the endotherm
- Std Dev: Standard deviation of the endotherm
- Additional: Additional information about the endotherm
- Shrinkage: Shrinkage during the endotherm
- heated at: Heated at a specific temperature
- at: At a specific temperature
- in: In a specific temperature
- same: Same as previous measurement
- DTA: Differential Thermal Analysis
- TGA: Thermogravimetric Analysis
- MS: Mass Spectrometry
- TEM: Transmission Electron Microscopy
- IR: Infrared Spectroscopy
- UV: Ultraviolet Spectroscopy
- HPLC: High-Performance Liquid Chromatography
- GC: Gas Chromatography
- MS/MS: Mass Spectrometry/Mass Spectrometry
Table 20. Exotherms from Penterythritol mixtures

| Sample | FOX (fuel/oxidizer) Mixtures, DSC & SDT runs. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Std Dev Heat Rel. | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max. (°C) | Std Dev Endo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) |
|--------|---------------------------------------------|----------------|-------------|----------------|-------------------|----------------------|-----------------------------------------------|-----------------|----------------|-------------|----------------|----------------|-------------------|-----------------------------------------------|----------------|----------------|
| Pentaerythritol | 3 no exotherms | 242 | 332 | 263 | 267 | 2 | 343 | 2118 | 475 |
| Pentaerythritol SDT | 3 no exotherms | 4 | 211 | 299 | 223 | 246 | 10 | 224, 269 | 1427 | 78 |
| Mix 33: 50% Pentaerythritol/50% AN | 2 | 210 | 338 | 211 | 236 | 6 | 805 | 240 | 368 | 450 | 377 | 379 | 0.6 | 361 | 82 |
| Mix 93: 50% Pentaerythritol/50% KBrO₃ | 7 | 209 | 303 | 251 | 267 | 21 | 238, 273 | 290 | 2058 | 892 |
| Mix 93: 50% Pentaerythritol/50% KBrO₃ SDT | 4 | 221 | 377 | 278 | 297 | 62 | 248, 435 | 963 | 879 | 545 | 623 | 559 | 600 | 19 | 84 | 83 |
| Mix 31: 50% Pentaerythritol/50% KClO₃ | 4 | 383 | 411 | 385 | 390 | 26 | 129 | 87 |
| Mix 31: 50% Pentaerythritol/50% KClO₃ SDT | 3 | 333 | 392 | 350 | 386 | 2 | 308 | 500 | 378 | 406 | 308 | 500 | 378 | 406 | 274 |
| Mix 97: 50% Pentaerythritol/50% K₂Cr₂O₇ | 7 | 420 | 492 | 450 | 469 | 438, 442, 460 | 1638 | 229 |
| Mix 32: 50% Pentaerythritol/50% KNO₃ | 3 | 351 | 527 | 419 | 454 | 8 | 111 | 21 | 817 | 860 | 818 | 836 | 10 | 199 | 138 |
Table 21. Endotherms from Sucrose mixtures

| Sample          | #   | Start Ext. | End Ext. | Start Ext. | End Ext. | Start Ext. | End Ext. | Additional Heat & Shoulders | Heat max. | Std Dev. | Start Ext. | End Ext. | Start Ext. | End Ext. | Additional Heat & Shoulders | Heat max. | Std Dev. | Start Ext. | End Ext. | Start Ext. | End Ext. | Additional Heat & Shoulders | Heat max. | Std Dev. |
|-----------------|-----|------------|----------|------------|----------|------------|----------|-----------------------------|-----------|---------|------------|----------|------------|----------|-----------------------------|-----------|---------|------------|----------|------------|----------|-----------------------------|-----------|---------|
| (Fast/cool/rise) Mixtures, OSC & SRT runs. |     |            |          |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| Sucrose (glucose + fructose) | 4   | 189 202 177 185 7 | 186 185 125 19 | 224 252 224 238 2 | 16 8    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| Sucrose (glucose + fructose) | 3   | 183 326 185 191 1 | 190 191 125 19 | 224 252 224 238 2 | 16 8    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| Sucrose (glucose + fructose) | 5   | 148 172 152 164 5 | 148 164 125 19 | 242 257 244 245 1 | 21 13   |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| Sucrose (glucose + fructose) | 2   | 181 303 185 191 0 | 285 295 125 19 | 345 398 349 349 3 | 29 44   |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 6   | 161 179 162 173 6 | 162 173 125 19 | 323 360 329 329 3 | 29 44   |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 5   | 177 198 177 191 1 | 182 191 125 19 | 375 406 375 375 3 | 32 26   |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 4   | 104 147 104 147 0 | 104 147 125 19 | 275 323 275 275 2 | 16 8    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 3   | 176 184 176 181 0 | 176 181 125 19 | 363 393 363 363 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 2   | 172 179 173 173 0 | 172 173 125 19 | 366 393 366 366 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 1   | 172 179 173 173 0 | 172 173 125 19 | 366 393 366 366 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 0   | 167 186 172 183 4 | 167 183 125 19 | 358 378 358 358 3 | 16 8    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 9   | 52 61 54 55 1 | 52 61 125 19 | 177 202 177 177 1 | 22 14   |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 8   | 122 151 123 126 6 | 122 126 125 19 | 285 309 285 285 2 | 16 8    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 7   | 244 250 245 245 2 | 244 245 125 19 | 356 382 356 356 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 6   | 152 201 177 212 0 | 152 212 125 19 | 318 373 318 318 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 5   | 181 204 177 214 1 | 181 214 125 19 | 368 392 368 368 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 4   | 181 204 177 214 1 | 181 214 125 19 | 368 392 368 368 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 3   | 181 204 177 214 1 | 181 214 125 19 | 368 392 368 368 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 2   | 181 204 177 214 1 | 181 214 125 19 | 368 392 368 368 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 1   | 104 141 104 147 0 | 104 147 125 19 | 375 406 375 375 3 | 32 26   |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |
| KI@O2     | 0   | 202 250 203 246 2 | 202 246 125 19 | 348 382 348 348 3 | 21 4    |            |          |                             |           |         |            |          |            |          |                             |           |         |            |          |            |          |                             |           |         |

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Table 22. Exotherms from Sucrose mixtures

| Samples | Exotherm 1 (°C) | Exotherm 2 (°C) | Exotherm 3 (°C) | Exotherm 4 (°C) | Exotherm 5 (°C) | Exotherm 6 (°C) | Exotherm 7 (°C) | Exotherm 8 (°C) | Exotherm 9 (°C) | Exotherm 10 (°C) | Exotherm 11 (°C) | Exotherm 12 (°C) |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Sucrose (glucose + fructose) | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| KSO | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| KSB | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| KS | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| K | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| KSO | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| KSB | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| KS | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |
| K | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 | 201 | 292 |

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Table 23. Endotherms from Sulfur mixtures

| Sample          | #  | Start (°C) | End (°C) | Offset Temp (°C) | Net DTA Ends (°C) | Net DTA Ends (°C) seen in same traces | Additional Max & Shoulders (%) seen in same traces | Heat Abs (%) | Start (°C) | End (°C) | Offset Temp (°C) | Net DTA Ends (°C) | Net DTA Ends (°C) seen in same traces | Additional Max & Shoulders (%) seen in same traces | Heat Abs (%) | Start (°C) | End (°C) | Offset Temp (°C) | Net DTA Ends (°C) | Net DTA Ends (°C) seen in same traces | Additional Max & Shoulders (%) seen in same traces | Heat Abs (%) | Start (°C) | End (°C) |
|-----------------|----|------------|----------|------------------|-------------------|---------------------------------------|--------------------------------------------------|-------------|------------|----------|------------------|-------------------|---------------------------------------|--------------------------------------------------|-------------|------------|----------|------------------|-------------------|---------------------------------------|--------------------------------------------------|-------------|------------|----------|
Table 24. Exotherms from Sulfur mixtures

| Sample | # | Start Exo (°C) | End Exo (°C) | Onset Temp (°C) | Exo Temp Max (°C) | Std Dev Endo Temp Max | Additional Max & Shoulders (°C) seen in some traces | Heat Released (J/g) | Std Dev Heat Rel. |
|--------|---|----------------|-------------|----------------|------------------|------------------------|-----------------------------------------------|-------------------|------------------|
| Sulfur | 4 | no exotherms   |             |                |                  |                        |                                               |                   |                  |
| Sulfur SDT | 3 | no exotherms   |             |                |                  |                        |                                               |                   |                  |
| Sulfur SDT in air | 3 | 217  | 455  | 341  | 392  | 8 |                        | 6393             | 357              |
| Mix 39: 50% Sulfur/ 50% AN | 3 | 172  | 243  | 204  | 213  | 10 | 198, 232             | 2328             | 438              |
| Mix 85: 50% Sulfur/ 50% AP SDT | 3 | 391  | 434  | 416  | 422  | 5 | 389, 408             | 1747             | 896              |
| Mix 90: 50% Sulfur/ 50% KBrO₃ | 2 | 298  | 509  | 413  | 444  | 3 | 347                 | 817              | 69               |
| Mix 38: 50% Sulfur/ 50% KClO₃ | 4 | 193  | 382  | 213  | 320  | 15 |                        | 815              | 150              |
| Mix 88: 50% Sulfur/ 50% KIO₃ | 3 | 241  | 411  | 308  | 330  | 0.6 | 301, 358             | 526              | 125              |
| Mix 88: 50% Sulfur/ 50% KIO₃ SDT | 3 | 169  | 418  | 324  | 350  | 22 | 259, 354, 409        | 2299             | 280              |
| Mix 40: 50% Sulfur/ 50% KNO₃ | 6 | 294  | 438  | 324  | 336  | 12 | 305, 337, 354, 370   | 1054             | 258              |
| Mix 87: 50% Sulfur/ 50% KNO₂ | 3 | 189  | 430  | 255  | 300  | 13 | 248, 368             | 2094             | 199              |
| Mix 87: 50% Sulfur/ 50% KNO₂ SDT | 1 | 251  | 362  | 269  | 272  |                  |                                               |                   |                  |
| Mix 84: 50% Sulfur/ 50% KClO₄ | 3 | 428  | 482  | 458  | 468  | 8 | 456                 | 1612             | 279              |
| Mix 84: 50% Sulfur/ 50% KClO₄ SDT | 3 | 556  | 652  | 577  | 596  | 3 |                        | 157              | 5.9              |
| Mix 89: 50% Sulfur/ 50% KIO₄ | 4 | 182  | 376  | 242  | 300  | 6 | 264, 281, 301, 366   | 2353             | 571              |
| Mix 89: 50% Sulfur/ 50% KIO₄ SDT | 3 | 212  | 386  | 294  | 304  | 9 | 269, 300             | 1246             | 82               |
| Mix 86: 50% Sulfur/ 50% KMnO₄ | 3 | 189  | 397  | 298  | 309  | 0.3 | 332                 | 2360             | 251              |
| Mix 86: 50% Sulfur/ 50% KMnO₄ SDT | 3 | 252  | 401  | 293  | 315  | 0.6 | 304                 | 696              | 79               |
### Table 25. Endotherms for Aluminum mixtures

| Sample                  | Start Endo | Endo | Onset Temp | Start Dev | Endo Dev | Temp Min | Min | Std Dev | Heat Abs. | Std Dev | Heat Rel. |
|-------------------------|------------|------|------------|-----------|----------|----------|-----|---------|-----------|---------|-----------|
| 20% Aluminum/ 80% KBrO₃| 4          | no endotherms |             |           |          |          |     |         |           |         |           |
| 20% Aluminum/ 80% KClO₃| 3          | 341  | 351        | 357       | 1        | 340      | 96  | 26      |           |         |           |
| 20% Aluminum/ 80% KNO₃ | 2          | no endotherms |             |           |          |          |     |         |           |         |           |
| 20% Aluminum/ 80% KNO₃ | 3          | 126  | 137        | 130       | 2        | 35       | 10  | 323     | 339       | 325     | 331       |
| 20% Aluminum/ 80% AP   | 4          | 246  | 256        | 247       | 2        | 5        | 2   |         |           |         |           |
| 20% Aluminum/ 80% AN   | 2          | no endotherms |             |           |          |          |     |         |           |         |           |

### Table 26. Exotherms for Aluminum mixtures

| Sample                  | Start Exo | End Exo | Onset Temp | Start Dev | Endo Dev | Temp Max | Max | Std Dev | Additional Max & Shoulders | Heat Released | Std Dev | Heat Rel. |
|-------------------------|-----------|---------|------------|-----------|----------|----------|-----|---------|----------------------------|---------------|---------|-----------|
| 20% Aluminum/ 80% KBrO₃| 4         | 419     | 452        | 421       | 430      | 7        |     |         | no exotherms                | 149           | 90      |           |
| 20% Aluminum/ 80% KClO₃| 3         | no exotherms |             |           |          |          |     |         |                             |               |         |           |
| 20% Aluminum/ 80% KNO₃ | 2         | 339     | 362        | 347       | 356      | 1        |     |         | no exotherms                | 76            | 7       |           |
| 20% Aluminum/ 80% AN   | 3         | no exotherms |             |           |          |          |     |         |                             |               |         |           |
| 20% Aluminum/ 80% AP   | 4         | 435     | 489        | 439       | 479      | 17       |     |         |                             | 1051          | # #     |           |
| 20% Aluminum/ 80% AN   | 2         | 291     | 357        | 320       | 331      | 6        |     |         |                             | 825           | 922     |           |
# Appendix III: Summary of Averaged DSC & SDT Data from the Insensitive Munitions Project

## Table 1. Endotherms

| Sample                                                      | Sample | Start Endo (°C) | Endo Endo (°C) | Onset Temp Min. (°C) | Stdev min | Heat Absorbed (J/g) | Stdev heat abs | Start Endo (°C) | Endo Endo (°C) | Onset Temp Min. (°C) | Stdev min | Heat Absorbed (J/g) | Stdev heat abs |
|-------------------------------------------------------------|--------|-----------------|----------------|----------------------|-----------|---------------------|----------------|-----------------|----------------|----------------------|-----------|---------------------|----------------|
| 2,4-dinitroanisole (DNAN) avg                              |        | 4               | 91             | 108                  | 93        | 96                  | 0.8            | 91              | 23             |                      |           |                     |                |
| 2,4-dinitrotoluene avg                                     |        | 6               | 68             | 85                   | 70        | 74                  | 2              | 77              | 36             |                      |           |                     |                |
| 2,4,6-trinitrotoluene (TNT) avg                            |        | 4               | 75             | 92                   | 76        | 79                  | 0.7            | 121             | 16             |                      |           |                     |                |
| Nitroguanidine (NQ) avg                                    |        | 5               | 234            | 242                  | 239       | 241                 | 6              | 14              | 23             |                      |           |                     |                |
| Solvent recrystallized NQ (NQR) avg                        |        | 3               | 238            | 244                  | 241       | 243                 | 2              | 25              | 38             |                      |           |                     |                |
| 3-nitro-1,2,4-triazol-5-one (NTO) avg                       |        | 4               |                |                      |            | no endotherms       |                |                 |                |                      |           |                     |                |
| 3-nitro-1,2,4-triazol-5-one (NTO) (Devon) avg              |        | 3               |                |                      |            | no endotherms       |                |                 |                |                      |           |                     |                |
| 50% DNAN/50% NTO avg                                       |        | 3               | 91             | 106                  | 92        | 94                  | 0.3            | 50              | 5              |                      |           |                     |                |
| 80%DNAN/20%NTO (Mix3) avg                                  |        | 2               | 89             | 107                  | 90        | 93                  | 0.9            | 87              | 4              |                      |           |                     |                |
| 50% DNT/50% NTO avg                                        |        | 4               | 66             | 83                   | 67        | 69                  | 0.7            | 61              | 25             |                      |           |                     |                |
| 80%DNT/20%NTO (Mix4) avg                                   |        | 3               | 64             | 91                   | 68        | 73                  | 0.2            | 73              | 4              |                      |           |                     |                |
| 50%DNAN/50%NQ (I4) avg                                     |        | 3               | 89             | 109                  | 92        | 95                  | 0.4            | 64              | 231            | 248                  | 239       | 243                 | 0.4            | 79              | 10             |
| 50%DNT/50%NQ (I5) avg                                      |        | 4               | 64             | 83                   | 67        | 69                  | 1              | 71              | 21             | 236                  | 248       | 242                 | 246            | 0.4            | 70             | 26            |
| 50% NTO/50% NQ avg                                         |        | 3               | 219            | 228                  | 225       | 227                 | 3              | 36              | 14             |                      |           |                     |                |
| 43%DNAN/37%NQ/20%NTO (I1) avg                              |        | #               | 88             | 106                  | 90        | 93                  | 2              | 50              | 11             | 199                  | 219       | 209                 | 213            | 3              | 37             | 15            |
| 43%DNAN/37%NQ/20%NTO (I1) avg w/out earlier mix           |        | 9               | 89             | 104                  | 91        | 93                  | 2              | 54              | 9              | 199                  | 219       | 209                 | 213            | 3              | 37             | 15            |
| 43%DNT/37%NQ/20%NTO (I2) avg                               |        | 7               | 63             | 83                   | 66        | 70                  | 2              | 54              | 11             | 202                  | 218       | 207                 | 213            | 6              | 39             | 18            |
| 43%DNT/37%NQ/20%NTO (I2) avg w/out earlier mix            |        | 4               | 66             | 83                   | 68        | 70                  | 1              | 59              | 6              | 205                  | 222       | 213                 | 218            | 3              | 45             | 19            |
| 28%TNT/47%NQ/25%NTO (I3) avg                               |        | 3               | 76             | 89                   | 77        | 80                  | 0.9            | 46              | 7              | 211                  | 224       | 217                 | 220            | 2              | 56             | 6             |
| 44% TNT/37% NQ/19%NTO (I3a) avg                            |        | 4               | 75             | 89                   | 76        | 78                  | 1              | 45              | 10             | 204                  | 220       | 209                 | 214            | 7              | 61             | 13            |
Table 2. Exotherms

| Sample | # | Start Exo (°C) | End Exo (°C) | onset Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max | Start Exo (°C) | End Exo (°C) | onsent Temp (°C) | Stddev Max |
|--------|---|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|----------------|----------------|-----------------|-----------|
| 2,4-dinitromuslole (DNAN) avg | 4 | 331 | 415 | 367 | 380 | 0.9 | 2040 | 759 | 2,4-dinitrotoluene avg | 6 | 316 | 407 | 342 | 350 | 4 | 414 | 2107 | 758 | 2,4,6-trinitrotoluene (TNT) avg | 4 | 292 | 398 | 325 | 331 | 3 | 390 | 4798 | 963 | nitroguanidine (NQ) avg | 5 | 242 | 279 | 243 | 247 | 6 | 725 | 92 | Solvent recrystallized NQ (NQR) avg | 3 | 244 | 271 | 244 | 248 | 3 | 1174 | 410 | 3-nitro-1,2,4-triazol-5-one (NTO) avg | 4 | 248 | 290 | 271 | 272 | 0.7 | 1914 | 459 | 3-nitro-1,2,4-triazol-5-one (NTO) (Devon) avg | 3 | 257 | 292 | 275 | 277 | 0.1 | 2448 | 147 | 50% DNAN/50% NTO avg | 5 | 323 | 359 | 254 | 262 | 0.1 | 304 | 2925 | 89 | 80%DNAN/20%NTO (Mix3) avg | 2 | 145 | 213 | 151 | 182 | 0.7 | 157 | 234 | 21 | 219 | 266 | 226 | 242 | 0.4 | 103 | 41 | 277 | 413 | 312 | 342 | 2 | 2274 | 80 | 50% DNT/50% NTO avg | 4 | 242 | 368 | 260 | 266 | 1 | 330 | 2652 | 173 | 80%DNT/20%NTO (Mix4) avg | 3 | 231 | 294 | 244 | 258 | 2 | 251 | 37 | 297 | 447 | 324 | 345 | 1 | 419 | 1520 | 184 | 50%DNAN/50%NQ (14) avg | 3 | 248 | 396 | 249 | 292 | 20 | 269 | 356 | 2300 | 185 | 50%DNT/50%NQ (15) avg | 4 | 248 | 360 | 250 | 264 | 4 | 1927 | 490 | 50% NTO/50% NQ avg | 3 | 228 | 358 | 231 | 241 | 7 | 245 | 1951 | 385 | 43%DNAN/37%NQ/20%NTO (11) avg | 12 | 141 | 190 | 151 | 166 | 8 | 80 | 53 | 213 | 394 | 223 | 243 | 3 | 300 | 355 | 379 | 2486 | 755 | 43%DNAN/37%NQ/20%NTO (11) avg w/out earlier mix | 9 | 219 | 393 | 226 | 243 | 3 | 300 | 355 | 379 | 2877 | 261 | 43%DNAN/37%NQ/20%NTO (12) avg | 7 | 157 | 198 | 160 | 181 | 1 | 39 | 8 | 218 | 339 | 236 | 254 | 7 | 236, 266, 306 | 1744 | 472 | 43%DNAN/37%NQ/20%NTO (12) avg w/out earlier mix | 4 | 222 | 345 | 233 | 253 | 10 | 236, 274, 306 | 2072 | 233 | 28%TNT/47%NQ/25%NTO (13) avg | 3 | 224 | 352 | 234 | 244 | 3 | 264, 351 | 2916 | 527 | 44% TNT/37% NQ/19%NTO (13e) avg | 4 | 212 | 342 | 226 | 240 | 3 | 261, 342 | 2544 | 612 |
## Appendix IV: Data from the Insensitive Munitions Project Isothermal Studies

### Table 1. Averaged isothermal data for neat DNAN

| Incubation time | Fraction Remaining | St. Dev. | Ln Fraction Remaining | St. Dev. |
|-----------------|-------------------|----------|----------------------|----------|
| **180°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 0.97     | 0.02                 | -0.026   | 0.02    |
| 5 days          | 4200              | 0.92     | 0.1                  | -0.084   | 1.1     |
| 6 days          | 51800             | 0.99     | 0.07                 | -0.0099  | 0.07    |
| 7 days          | 60400             | 0.89     | 0.2                  | -0.11    | 6.2     |
| 8 days          | 69100             | 0.87     | 0.2                  | -0.14    | 6.2     |
| 9 days          | 77700             | 0.865    | 0.09                 | -0.15    | 0.1     |
| 10 days         | 86400             | 0.95     | 0.05                 | -0.055   | 0.05    |
| 11 days         | 95400             | 0.94     | 0.02                 | -0.078   | 0.2     |
| 12 days         | 1036800           | 0.94     | 0.007                | -0.058   | 0.007   |
| **200°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 1.00     | 0.06                 | 0.0017   | 0.06    |
| 1 day           | 86400             | 0.92     | 0.03                 | -0.085   | 0.04    |
| 2d 3h 40min     | 166000            | 0.91     | 0.005                | -0.091   | 0.006   |
| 3 days          | 239000            | 0.87     | 0.03                 | -0.14    | 0.04    |
| 4 days          | 345000            | 0.82     | 0.02                 | -0.20    | 0.02    |
| 5 days          | 432000            | 0.51     | 0.1                  | -0.66    | 0.3     |
| 5d 4h           | 446000            | 0.46     | 0.2                  | -0.77    | 0.5     |
| 5d 8h           | 460800            | 0.35     | 0.2                  | -1.0     | 0.6     |
| 5d 12h          | 475200            | 0.25     | 0.2                  | -1.4     | 0.6     |
| **240°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 0.99     | 0.05                 | -0.0081  | 0.05    |
| 15 min          | 900               | 0.98     | 0.07                 | -0.024   | 0.07    |
| 30 min          | 1800              | 0.98     | 0.03                 | -0.020   | 0.03    |
| 45 min          | 2700              | 0.93     | 0.2                  | -0.072   | 0.2     |
| 60 min          | 3600              | 0.92     | 0.1                  | -0.079   | 0.2     |
| 120 min         | 7200              | 0.92     | 0.009                | -0.087   | 0.009   |
| 180 min         | 10800             | 0.90     | 0.009                | -0.10    | 0.01    |
| 240 min         | 144000            | 0.77     | 0.3                  | -0.27    | 0.41    |
| 300 min         | 18000             | 0.86     | 0.03                 | -0.15    | 0.03    |
| 360 min         | 21600             | 0.82     | 0.04                 | -0.20    | 0.05    |
| 420 min         | 25200             | 0.81     | 0.02                 | -0.21    | 0.02    |
| 480 min         | 28800             | 0.71     | 0.06                 | -0.35    | 0.09    |
| 540 min         | 32400             | 0.66     | 0.08                 | -0.41    | 0.1     |
| 600 min         | 36000             | 0.58     | 0.1                  | -0.54    | 0.2     |
| 660 min         | 39600             | 0.56     | 0.1                  | -0.58    | 0.3     |
| 720 min         | 43200             | 0.56     | 0.4                  | -2.8     | 0.6     |
| **250°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 0.96     | 0.02                 | -0.046   | 0.02    |
| 15 min          | 900               | 0.95     | 0.05                 | -0.054   | 0.05    |
| 30 min          | 1800              | 0.93     | 0.04                 | -0.070   | 0.04    |
| 45 min          | 2700              | 0.93     | 0.05                 | -0.069   | 0.05    |
| 60 min          | 3600              | 0.91     | 0.07                 | -0.10    | 0.07    |
| **270°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 1.03     | 0.07                 | 0.029    | 0.07    |
| 15 min          | 900               | 1.1      | 0.04                 | 0.0018   | 0.04    |
| 30 min          | 1800              | 1.02     | 0.06                 | 0.022    | 0.06    |
| 45 min          | 2700              | 0.96     | 0.03                 | -0.043   | 0.03    |
| 60 min          | 3600              | 0.94     | 0.05                 | -0.058   | 0.05    |
| **280°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 1.02     | 0.2                  | 0.018    | 0.2     |
| 15 min          | 900               | 0.99     | 0.07                 | -0.0095  | 0.07    |
| 30 min          | 1800              | 0.89     | 0.2                  | -0.11    | 0.2     |
| 45 min          | 2700              | 0.82     | 0.3                  | -0.20    | 0.3     |
| 60 min          | 3600              | 0.75     | 0.2                  | -0.28    | 0.2     |
| 75 min          | 4500              | 0.66     | 0.08                 | -0.41    | 0.1     |
| 90 min          | 4800              | 0.57     | 0.09                 | -0.57    | 0.2     |
| 90 min          | 5400              | 0.50     | 0.08                 | -0.69    | 0.2     |
| 95 min          | 5700              | 0.20     | 0.06                 | -1.6     | 0.3     |
| 105 min         | 63300             | 0.38     | 0.05                 | -0.97    | 0.1     |
| 110 min         | 66000             | 0.053    | 0.07                 | -2.9     | 1.0     |
| **300°C**       |                   |          |                      |          |
| Room Temp       | 0                 | 1.03     | 0.07                 | 0.029    | 0.07    |
| 15 min          | 900               | 0.97     | 0.05                 | -0.030   | 0.06    |
| 30 min          | 1800              | 0.74     | 0.01                 | -0.30    | 0.01    |
| 45 min          | 2700              | 0.22     | 0.1                  | -1.52    | 0.5     |
Table 2. Averaged isothermal data for neat DNT

| Incubation time | Time (s)  | 180°C  |   |   | 200°C  |   |   | 240°C  |   |   | 250°C  |   |   | 270°C  |   |   | 280°C  |   |   | 300°C  |   |
|-----------------|-----------|--------|---|---|--------|---|---|--------|---|---|--------|---|---|--------|---|---|--------|---|---|--------|---|
| Room Temp       | Fraction Remaining (%) | St. Dev. | Ln Fraction Remaining (%) | St. Dev. | Fraction Remaining (%) | St. Dev. | Ln Fraction Remaining (%) | St. Dev. | Fraction Remaining (%) | St. Dev. | Ln Fraction Remaining (%) | St. Dev. | Fraction Remaining (%) | St. Dev. | Ln Fraction Remaining (%) | St. Dev. | Fraction Remaining (%) | St. Dev. | Ln Fraction Remaining (%) | St. Dev. | Fraction Remaining (%) | St. Dev. | Ln Fraction Remaining (%) | St. Dev. |
| 0.00             | 0.99       | 0.02   | -0.0080 | 0.02 | 0.99       | 0.02   | -0.0080 | 0.02 | 0.99       | 0.02   | -0.0080 | 0.02 | 0.99       | 0.02   | -0.0080 | 0.02 | 0.99       | 0.02   | -0.0080 | 0.02 | 0.99       | 0.02   | -0.0080 | 0.02 |
| 5 days           | 432000     | 0.98   | 0.03   | -0.016 | 0.03 | 0.98       | 0.03   | -0.016 | 0.03 | 0.98       | 0.03   | -0.016 | 0.03 | 0.98       | 0.03   | -0.016 | 0.03 | 0.98       | 0.03   | -0.016 | 0.03 | 0.98       | 0.03   | -0.016 | 0.03 |
| 7 days           | 604800     | 0.94   | 0.02   | -0.062 | 0.02 | 0.94       | 0.02   | -0.062 | 0.02 | 0.94       | 0.02   | -0.062 | 0.02 | 0.94       | 0.02   | -0.062 | 0.02 | 0.94       | 0.02   | -0.062 | 0.02 | 0.94       | 0.02   | -0.062 | 0.02 |
| 8 days           | 691200     | 0.93   | 0.01   | -0.075 | 0.01 | 0.93       | 0.01   | -0.075 | 0.01 | 0.93       | 0.01   | -0.075 | 0.01 | 0.93       | 0.01   | -0.075 | 0.01 | 0.93       | 0.01   | -0.075 | 0.01 | 0.93       | 0.01   | -0.075 | 0.01 |
| 9 days           | 777600     | 0.87   | 0.1    | -0.14  | 0.1  | 0.87       | 0.1    | -0.14  | 0.1  | 0.87       | 0.1    | -0.14  | 0.1  | 0.87       | 0.1    | -0.14  | 0.1  | 0.87       | 0.1    | -0.14  | 0.1  | 0.87       | 0.1    | -0.14  | 0.1  |
| 10 days          | 854400     | 0.62   | 0.2    | -0.48  | 0.3  | 0.62       | 0.2    | -0.48  | 0.3  | 0.62       | 0.2    | -0.48  | 0.3  | 0.62       | 0.2    | -0.48  | 0.3  | 0.62       | 0.2    | -0.48  | 0.3  | 0.62       | 0.2    | -0.48  | 0.3  |
| 11 days          | 950400     | 0.47   | 0.3    | -0.76  | 0.7  | 0.47       | 0.3    | -0.76  | 0.7  | 0.47       | 0.3    | -0.76  | 0.7  | 0.47       | 0.3    | -0.76  | 0.7  | 0.47       | 0.3    | -0.76  | 0.7  | 0.47       | 0.3    | -0.76  | 0.7  |
| 12 days          | 1036800    | 0.38   | 0.03   | -0.98  | 0.2  | 0.38       | 0.03   | -0.98  | 0.2  | 0.38       | 0.03   | -0.98  | 0.2  | 0.38       | 0.03   | -0.98  | 0.2  | 0.38       | 0.03   | -0.98  | 0.2  | 0.38       | 0.03   | -0.98  | 0.2  |

- 180°C
- 200°C
- 240°C
- 250°C
- 270°C
- 280°C
- 300°C
Table 3. Averaged isothermal data for neat TNT

| Incubation time | Time (s) | Fraction Remaining | St. Dev. | Ln Fraction Remaining | St. Dev. |
|-----------------|---------|-------------------|----------|----------------------|----------|
| **200°C**       |         |                   |          |                      |          |
| Room Temp       | 0       | 1.00              | 0.02     | -0.00040             | 0.02     |
| 10 min          | 600     | 1.00              | 0.01     | -0.0026              | 0.01     |
| 15 min          | 900     | 0.98              | 0.03     | -0.020               | 0.03     |
| 25 min          | 1500    | 0.92              | 0.03     | -0.078               | 0.04     |
| 30 min          | 1800    | 0.94              | 0.1      | -0.065               | 0.1      |
| 45 min          | 2700    | 0.93              | 0.08     | -0.077               | 0.09     |
| 60 min          | 3600    | 0.97              | 0.05     | -0.035               | 0.05     |
| **270 °C**      |         |                   |          |                      |          |
| Room Temp       | 0       | 0.99              | 0.02     | -0.013               | 0.02     |
| 15 min          | 900     | 0.57              | 0.2      | -0.57                | 0.3      |
| 30 min          | 1800    | 0.065             | 0.1      | -2.7                 | 2        |
| **280°C**       |         |                   |          |                      |          |
| Room Temp       | 0       | 1.01              | 0.02     | 0.010                | 0.02     |
| 5 min           | 300     | 0.77              | 0.1      | -0.27                | 0.2      |
| 10 min          | 600     | 0.54              | 0.07     | -0.61                | 0.1      |
| 15 min          | 900     | 0.19              | 0.2      | -1.7                 | 1        |
| 17 min          | 1020    | 0.08              | 0.2      | -2.5                 | 2        |
| 20 min          | 1200    | 0.027             | 0.06     | -3.6                 | 2        |
| 25 min          | 1500    | 0.01              | 0.001    | -4.6                 | 0.1      |
| 30 min          | 1800    | 0.00              | 0.0008   | -5.8                 | 0.2      |
Table 4. Averaged isothermal data for the DNAN two-part mixes

| Incubation time | Time (s) | DNAN Fraction Remaining | St. Dev. | DNAN Ln Fraction Remaining | St. Dev. | NQ Fraction Remaining (approx) | NQ Ln Fraction Remaining |
|----------------|---------|------------------------|---------|---------------------------|---------|-------------------------------|--------------------------|
| **200°C 50:50 DNAN:NQ** |         |                        |         |                           |         |                               |                          |
| Room Temp      | 0       | 0.98                   | 0.1     | -0.024                    | 0.1     | 1                             | 0                        |
| 10 min         | 600     | 0.91                   | 0.1     | -0.090                    | 0.1     | 0.9                           | -0.11                    |
| 15 min         | 900     | 0.79                   | 0.1     | -0.24                     | 0.1     | 0.9                           | -0.11                    |
| 25 min         | 1500    | 0.68                   | 0.2     | -0.39                     | 0.3     | 0.6                           | -0.51                    |
| 30 min         | 1800    | 0.46                   | 0.1     | -0.78                     | 0.3     | 0.5                           | -0.69                    |
| 45 min         | 2700    | 0.30                   | 0.2     | -1.2                      | 0.6     | 0.3                           | -1.2                     |
| 60 min         | 3600    | 0.23                   | 0.2     | -1.5                      | 0.7     | 0.3                           | -1.2                     |
| **200°C 50:50 DNAN:NTO** |       |                        |         |                           |         |                               |                          |
| Room Temp      | 0       | 0.95                   | 0.2     | -0.051                    | 0.2     | 1                             | 0                        |
| 15 min         | 900     | 0.94                   | 0.1     | -0.067                    | 0.1     | 1                             | 0                        |
| 30 min         | 1800    | 0.99                   | 0.06    | -0.0058                   | 0.06    | 0.7                           | -0.36                    |
| 45 min         | 2700    | 1.05                   | 0.09    | 0.046                     | 2       | 0.7                           | -0.36                    |
| 60 min         | 3600    | 0.88                   | 0.2     | -0.12                     | 0.2     | 0.7                           | -0.36                    |
| 75 min         | 4500    | 0.72                   | 0.2     | -0.32                     | 0.2     | 0.6                           | -0.51                    |
| 90 min         | 5400    | 0.48                   | 0.2     | -0.74                     | 0.3     | 0.2                           | -1.6                     |
| 105 min        | 6300    | 0.32                   | 0.2     | -1.1                      | 0.6     | 0.1                           | -2.3                     |
| 2 hr           | 7200    | 0.16                   | 0.1     | -1.8                      | 0.7     | 0.07                          | -2.7                     |
| **200°C 80:20 DNAN:NTO** |       |                        |         |                           |         |                               |                          |
| Room Temp      | 0       | 0.95                   | 0.07    | -0.046                    | 0.08    | 1                             | 0                        |
| 15 min         | 900     | 0.94                   | 0.04    | -0.065                    | 0.04    | 0.8                           | -0.2                     |
| 30 min         | 1800    | 0.88                   | 0.2     | -0.13                     | 0.2     | 0.5                           | -0.7                     |
| 60 min         | 3600    | 0.88                   | 0.09    | -0.13                     | 0.1     | 0.5                           | -0.7                     |
| 4 hr           | 14400   | 0.51                   | 0.1     | -0.67                     | 0.3     |                               |                          |
| 6 hr           | 21600   | 0.32                   | 0.2     | -1.1                      | 0.7     |                               |                          |
| 8 hr           | 28800   | 0.37                   | 0.3     | -1.0                      | 0.7     |                               |                          |
Table 5. Averaged isothermal data for the DNT two-part mixes

| Incubation time | Time (s) | DNT Fraction Remaining | St. Dev. | DNT Ln Fraction Remaining | St. Dev. | NQ Fraction Remaining (approx) | NQ Ln Fraction Remaining |
|-----------------|----------|------------------------|----------|--------------------------|----------|-------------------------------|--------------------------|
| Room Temp       | 0        | 0.96                   | 0.2      | -0.045                   | 0.2      | 1                             | 0                        |
| 10 min          | 600      | 0.93                   | 0.2      | -0.076                   | 0.3      | 1                             | 0                        |
| 15 min          | 900      | 0.78                   | 0.1      | -0.25                    | 0.1      | 1                             | 0                        |
| 25 min          | 1500     | 0.71                   | 0.3      | -0.34                    | 0.5      | 0.6                           | -0.51                    |
| 30 min          | 1800     | 0.51                   | 0.3      | -0.67                    | 0.5      | 0.5                           | -0.69                    |
| 45 min          | 2700     | 0.36                   | 0.3      | -1.0                     | 0.9      | 0.2                           | -1.6                     |
| 60 min          | 3600     | 0.19                   | 0.3      | -1.7                     | 2        | 0.1                           | -2.3                     |

| Incubation time | Time (s) | DNT Fraction Remaining | St. Dev. | DNT Ln Fraction Remaining | St. Dev. | NTO Fraction Remaining (approx) | NTO Ln Fraction Remaining |
|-----------------|----------|------------------------|----------|--------------------------|----------|-------------------------------|--------------------------|
| Room Temp       | 0        | 1.13                   | 0.2      | 0.12                     | 0.2      | 1                             | 0                        |
| 15 min          | 900      | 1.04                   | 0.08     | 0.039                    | 0.08     | 1                             | 0                        |
| 30 min          | 1800     | 1.05                   | 0.3      | 0.051                    | 0.2      | 1                             | 0                        |
| 45 min          | 2700     | 1.10                   | 0.1      | 0.096                    | 0.1      | 0.9                           | -0.11                    |
| 60 min          | 3600     | 1.00                   | 0.2      | -0.00030                 | 0.2      | 1                             | 0                        |
| 4 hr            | 14400    | 0.78                   | 0.4      | -0.24                    | 0.5      | 0.4                           | -0.92                    |
| 8 hr            | 28800    | 0.72                   | 0.1      | -0.33                    | 0.2      | 0.1                           | -2.3                     |
| 16h 20m         | 58800    | 0.62                   | 0.06     | -0.48                    | 0.1      | 0.008                         | -4.8                     |
| 20 hr           | 72000    | 0.42                   | 0.2      | -0.86                    | 0.4      |                               |                          |
| 1d 4h           | 100800   | 0.25                   | 0.1      | -1.4                     | 0.4      |                               |                          |
| 1d 6h           | 108000   | 0.17                   | 0.1      | -1.8                     | 0.7      |                               |                          |
| 1d 12h 5m       | 129900   | 0.14                   | 0.06     | -2.0                     | 0.5      |                               |                          |
| 2d 30m          | 174600   | 0.051                  | 0.05     | -3.0                     | 1        |                               |                          |

| Incubation time | Time (s) | DNT Fraction Remaining | St. Dev. | DNT Ln Fraction Remaining | St. Dev. | NTO Fraction Remaining (approx) | NTO Ln Fraction Remaining |
|-----------------|----------|------------------------|----------|--------------------------|----------|-------------------------------|--------------------------|
| Room Temp       | 0        | 1.04                   | 0.06     | 0.043                    | 0.06     | 1                             | 0                        |
| 15 min          | 900      | 1.06                   | 0.06     | 0.059                    | 0.06     | 0.9                           | -0.11                    |
| 30 min          | 1800     | 1.04                   | 0.1      | 0.035                    | 0.1      | 0.5                           | -0.69                    |
| 60 min          | 3600     | 1.02                   | 0.1      | 0.022                    | 0.1      | 0.3                           | -1.2                     |
| 1 d             | 86400    | 0.67                   | 0.2      | -0.40                    | 0.3      |                               |                          |
| 1d 6h           | 115200   | 0.38                   | 0.2      | -0.96                    | 0.5      |                               |                          |
| 2 d             | 172800   | 0.47                   | 0.3      | -0.75                    | 0.6      |                               |                          |
| 2d 8h           | 201600   | 0.18                   | 0.04     | -1.7                     | 0.3      |                               |                          |
| 3 d             | 259200   | 0.20                   | 0.1      | -1.6                     | 0.6      |                               |                          |
| 4 d             | 345600   | 0.07                   | 0.05     | -2.7                     | 0.7      |                               |                          |
Table 6. Averaged isothermal data for the DNAN & DNT three-part mixes

| Incubation Temp | Time (s) | DNAN Fraction Remaining | St. Dev. | DNAN Ln Fraction Remaining | St. Dev. | NTO Fraction Remaining (approx) | NTO Ln Fraction Remaining | NQ Fraction Remaining (approx) | NQ Ln Fraction Remaining |
|-----------------|---------|-------------------------|---------|---------------------------|---------|-------------------------------|--------------------------|-------------------------------|---------------------------|
| Room Temp 0     | 1.02    | 0.2                     | 0.023   | 0.2                       | 1.0     | 0.04                          | 0.09                     | 1.0                          | 0.0                       |
| 15 min 900      | 0.96    | 0.1                     | -0.037  | 0.1                       | 1.0     | 0.04                          | 0.09                     | 1.0                          | 0.0                       |
| 30 min 1600     | 0.73    | 0.2                     | -0.32   | 0.2                       | 0.7     | -0.36                         | 1.0                      | 0.0                          | 0.0                       |
| 45 min 2700     | 0.71    | 0.2                     | -0.35   | 0.2                       | 0.3     | -1.2                          | 0.9                      | -0.11                        | 0.0                       |
| 60 min 3600     | 0.57    | 0.2                     | -0.55   | 0.3                       | 0.1     | -2.3                          | 0.8                      | -0.22                        | 0.0                       |
| 75 min 4500     | 0.64    | 0.2                     | -0.45   | 0.1                       | 0.06    | -2.8                          | 0.7                      | -0.36                        | 0.0                       |
| 90 min 5400     | 0.45    | 0.2                     | -0.80   | 0.4                       | 0.07    | -2.7                          | 0.6                      | -0.51                        | 0.0                       |

| Incubation Temp | Time (s) | DNT Fraction Remaining | St. Dev. | DNT Ln Fraction Remaining | St. Dev. | NTO Fraction Remaining (approx) | NTO Ln Fraction Remaining | NQ Fraction Remaining (approx) | NQ Ln Fraction Remaining |
|-----------------|---------|------------------------|---------|---------------------------|---------|-------------------------------|--------------------------|-------------------------------|---------------------------|
| Room Temp 0     | 1.03    | 0.2                    | 0.033   | 0.2                       | 1.0     | 1.0                           | 1.0                      | 1.0                          | 1.0                       |
| 15 min 900      | 0.95    | 0.1                    | -0.052  | 0.1                       | 1.0     | 0.0                          | 0.0                      | 0.0                          | 0.0                       |
| 30 min 1800     | 0.87    | 0.2                    | -0.14   | 0.2                       | 0.9     | -0.11                         | 0.9                      | -0.11                        | 0.0                       |
| 45 min 2700     | 0.02    | 0.1                    | -0.20   | 0.2                       | 0.8     | -0.22                         | 0.8                      | -0.22                        | 0.0                       |
| 60 min 3600     | 0.82    | 0.1                    | -0.20   | 0.2                       | 0.5     | -0.69                         | 0.8                      | -0.22                        | 0.0                       |
| 75 min 4500     | 0.84    | 0.1                    | -0.18   | 0.2                       | 0.3     | -1.2                          | 0.7                      | -0.36                        | 0.0                       |
| 90 min 5400     | 0.77    | 0.3                    | -0.26   | 0.4                       | 0.3     | -1.2                          | 0.6                      | -0.51                        | 0.0                       |
| 120 min 7200    | 0.71    | 0.3                    | -0.35   | 0.2                       | 0.2     | -1.6                          | 0.5                      | -0.69                        | 0.0                       |
| 150 min 8100    | 0.58    | 0.3                    | -0.55   | 0.5                       | 0.1     | -2.3                          | 0.3                      | -1.2                         | 0.0                       |
| 180 min 9000    | 0.63    | 0.2                    | -0.45   | 0.4                       | 0.1     | -2.3                          | 0.2                      | -1.6                         | 0.0                       |

| Incubation Temp | Time (s) | NTO Fraction Remaining (approx) | NTO Ln Fraction Remaining | NQ Fraction Remaining (approx) | NQ Ln Fraction Remaining |
|-----------------|---------|-------------------------------|--------------------------|-------------------------------|---------------------------|
| Room Temp 0     | 1.0     | 1.0                           | 1.0                      | 1.0                           | 1.0                       |
| 15 min 900      | 0.8     | 0.8                           | 0.8                      | 0.8                           | 0.8                       |
| 30 min 1800     | 0.6     | 0.6                           | 0.6                      | 0.6                           | 0.6                       |
| 45 min 2700     | 0.3     | 0.3                           | 0.3                      | 0.3                           | 0.3                       |
| 60 min 3600     | 0.5     | 0.5                           | 0.5                      | 0.5                           | 0.5                       |
| 75 min 4500     | 0.4     | 0.4                           | 0.4                      | 0.4                           | 0.4                       |
| 90 min 5400     | 0.3     | 0.3                           | 0.3                      | 0.3                           | 0.3                       |
| 120 min 7200    | 0.3     | 0.3                           | 0.3                      | 0.3                           | 0.3                       |
| 150 min 8100    | 0.2     | 0.2                           | 0.2                      | 0.2                           | 0.2                       |
| 180 min 9000    | 0.1     | 0.1                           | 0.1                      | 0.1                           | 0.1                       |

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Figure 1. Time vs. ln fraction remaining for DNAN & DNT at 300°C

Figure 2. Time vs. ln fraction remaining for DNAN & DNT at 280°C

Figure 3. Time vs. ln fraction remaining for DNAN & DNT at 270°C

Figure 4. Time vs. ln fraction remaining for DNAN & DNT at 250°C
Figure 5. Time vs. ln fraction remaining for DNAN & DNT at 240°C

Figure 6. Time vs. ln fraction remaining for DNAN & DNT at 200°C

Figure 7. Time vs. ln fraction remaining for DNAN & DNT at 180°C

Figure 8. Time vs. ln fraction remaining for TNT at 280°C
Figure 9. Time vs. In fraction remaining for TNT at 200°C

Figure 10. Time vs. In fraction remaining for DNAN & DNT in the 3-part mix at 200°C

Figure 11. Time vs. In fraction remaining for NTO in the DNAN or DNT 3-part mix at 200°C

Figure 12. Time vs. In fraction remaining for NQ in the DNAN or DNT 3-part mix at 200°C
Figure 13. Time vs. In fraction remaining for DNT, NTO, & NQ in the 3-part mix at 180°C

Figure 14. Time vs. In fraction remaining for DNAN, NTO, & NQ in the 3-part mix at 180°C

Figure 15. Time vs. In fraction remaining for DNAN or DNT with 20% NTO at 200°C

Figure 16. Time vs. In fraction remaining for 20% NTO with DNAN or DNT at 200°C
Figure 17. Time vs. In fraction remaining for DNAN or DNT with 50% NTO at 200°C

Figure 18. Time vs. In fraction remaining for 50% NTO with DNAN or DNT at 200°C

Figure 19. Time vs. In fraction remaining for DNAN or DNT with 50% NQ at 200°C

Figure 20. Time vs. In fraction remaining for 50% NQ with DNAN or DNT at 200°C
Table 7. Data for the calculation of activation energy for neat DNAN & DNT

| °C | DNAN | DNT | TNT | T (K) | 1/T(K) | ln (k) |
|----|------|-----|-----|-------|--------|--------|
| 180 | 4.0E-08 | 8.7E-07 | --  | 453   | 0.00221 | -17.04 |
| 200 | 2.4E-06 | 7.6E-06 | 1.6E-05 | 473   | 0.00211 | -12.94 |
| 240 | 1.3E-05 | 1.2E-04 | --  | 513   | 0.00195 | -11.25 |
| 250 | 1.3E-05 | 4.7E-05 | --  | 523   | 0.00191 | -11.27 |
| 270 | 2.4E-05 | 4.3E-04 | --  | 543   | 0.00184 | -10.63 |
| 280 | 3.0E-04 | 1.1E-03 | 3.5E-03 | 553   | 0.00181 | -9.13  |
| 300 | 5.4E-04 | 2.0E-03 | --  | 573   | 0.00175 | -7.53  |

Figure 21. Graph of the Natural Log of the Rate Constants vs. Inverse Temperature for neat DNAN & DNT

Table 8. Calculation of activation energy for neat DNAN & DNT

| ln k vs 1/T | Ea = -R* slope |
|-------------|----------------|
| DNAN        |                |
| 18128 x 1.98| 35893.44 36 kcal/mol |
| 18128 x 8.314| 150716.192 151 J/mol |
| DNT         |                |
| 16274 x 1.98| 32222.52 32 kcal/mol |
| 16274 x 8.314| 135302.036 135 J/mol |