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THERMAL STABILITY AND SENSITIVITY OF ENERGETIC FORMULATIONS

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**THERMAL STABILITY AND SENSITIVITY
OF ENERGETIC FORMULATIONS**

BY

MARIA A. DONNELLY

**A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF**

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DOCTORAL DISSERTATION IN CHEMISTRY
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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-terrorist 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, KNO_3 , KClO_4 , and NH_4ClO_4 , 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. KClO_4 /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⁻¹. Most of the mixtures released 1000 to 1500 Jg⁻¹, with potassium chlorate, ammonium perchlorate, and ammonium nitrate releasing significantly more heat, around 2000 Jg⁻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 polyalcohols, 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 (Jg^{-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 $23\ \mu\text{m}$) 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]:

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

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.

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

Oxidizer	KIO ₄	KMnO ₄	KBrO ₃	KClO ₃	K ₂ Cr ₂ O ₇	NH ₄ ClO ₄	KClO ₄	KIO ₃	KNO ₃	NH ₄ NO ₃	KNO ₂
anion potential 1M aq. H ₂ 0V	1.7-1.6	1.7-1.5	1.5-1.4	1.5	1.4-1.3		1.4-1.2	1.2-1.1	1.0-0.8		-0.46
mass % oxygen in oxidizer	28%	25%	29%	39%	16%	34%	46%	22%	40%	20%	28%
Decomp °C 8/2 oxidizer/sucrose	187	236	186	180	231	484	540	182	396	176	212
Jg ⁻¹ heat released	1681	1741	1511	3195	157	1342	735	939	1108	2084	1777
Burn Test 8:2 Oxidizer:Al	KIO ₄	KMnO ₄	KBrO ₃	KClO ₃	K ₂ Cr ₂ O ₇	NH ₄ ClO ₄	KClO ₄	KIO ₃	KNO ₃	NH ₄ NO ₃	KNO ₂
Ave Burn Time by Eye (s)	too fast	too fast	too fast	too fast	too fast	4.3	too fast	7.5	3.8	18.2	2.5
Std. Dev	too fast	too fast	too fast	too fast	too fast	1.0	too fast	2.1	0.7	1.6	0.6
Ave Peak Light Signal Thor Lab (mV)	2564	2360	1113	1129	140	144	2736	—	—	—	—
Std. Dev	232	297	437	286	54	73	11	—	—	—	—
Notes	bright flash	bright flash	bright flash	bright flash	bright flash	bright flash, strobes	bright flash	bubbled	bubbled	bubbled	bubbled
Burn Test 8:2 Oxidizer:Sucrose	KIO ₄	KMnO ₄	KBrO ₃	KClO ₃	K ₂ Cr ₂ O ₇	NH ₄ ClO ₄	KClO ₄	KIO ₃	KNO ₃	NH ₄ NO ₃	KNO ₂
Ave Burn Time by Eye (s)	too fast	1.9	too fast	1.0	4.9	4.6	2.5	1.6	2.5	18.1	1.3
Std. Dev	too fast	0.2	too fast	0.4	1.7	0.8	0.3	0.4	0.7	2.7	0.3
Ave Peak Light Signal Thor Lab (mV)	56	25	346	104	—	3	11	—	—	—	32
Std. Dev	25	6	98	45	—	1	3	—	—	—	12
Notes	purple flickering	orange flame	purple flame	purple flame	charing, no flame	yellow flame	purple flame	charing, no flame	charing, no flame	dim yellow flame	yellow flame
Burn Test 5:5 Oxidizer:Sucrose	KIO ₄	KMnO ₄	KBrO ₃	KClO ₃	K ₂ Cr ₂ O ₇	NH ₄ ClO ₄	KClO ₄	KIO ₃	KNO ₃	NH ₄ NO ₃	KNO ₂
Ave Burn Time by Eye (s)	3.1	10.4	too fast	2.6	15.9	9.2	8.1	9.0	0.9	21.4	2.6
Std. Dev	0.5	2.1	too fast	0.8	1.7	1.2	1.1	4.2	0.1	4.8	1.1
Ave Peak Light Signal Thor Lab (mV)	—	8	430	128	—	10	58	—	43	—	43
Std. Dev	—	7	163	41	—	2	13	—	13	—	13
Notes	no light, black snake	dim yellow flame	purple flame	purple flame	dim yellow flame	dim yellow flame	dim yellow flame	dim yellow flame	dim yellow flame	no light, black snake	dim yellow flame
Burn Test 8:2 Oxidizer:Benzoic Acid	KIO ₄	KMnO ₄	KBrO ₃	KClO ₃	K ₂ Cr ₂ O ₇	NH ₄ ClO ₄	KClO ₄	KIO ₃	KNO ₃	NH ₄ NO ₃	KNO ₂
Ave Burn Time by Eye (s)	1.6	3.0	too fast	4.4	16.0	6.3	4.5	4.9	4.5	28.7	2.1
Std. Dev	0.5	0.8	too fast	1.7	1.6	1.0	0.6	1.2	1.8	6.2	0.5
Ave Peak Light Signal Thor Lab (mV)	1413	147	2228	762	26	226	737	221	91	14	160
Std. Dev	331	22	228	104	8	45	304	35	33	4	88
Notes	bright flash	orange flame	bright flash	bright yellow flame	yellow flame	bright yellow flame	white flame	white flickering	orange flame	yellow flickering	orange flame

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 Jg⁻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, K₂O, and KI were

observed, and the DSC traces showed the decomposition of periodate to iodate around 330°C (eq 3); thereafter, their thermograms were identical [12-17].

Ammonium perchlorate (AP, NH_4ClO_4) did not melt but exhibited an endotherm around 245°C ($\sim 70 \text{ Jg}^{-1}$) 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 ($\sim 1300 \text{ Jg}^{-1}$). The SDT results appeared quite different. Immediately after the 245°C phase change, a small exotherm ($\sim 360 \text{ Jg}^{-1}$) at $\sim 318^\circ\text{C}$ 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.

Fig. 1 Ammonium Perchlorate DSC (1a) vs SDT (1b)

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)

		KIO ₄						KMnO ₄						KBrO ₃						KClO ₃						K ₂ Cr ₂ O ₇					
						exo max °C	Jg ⁻¹	#					exo max °C	Jg ⁻¹	#					exo max °C	Jg ⁻¹	#					exo max °C	Jg ⁻¹	#		
		endo	exo	endo	onset				endo	onset						endo	onset						endo	onset							
phase change																															
melt				543				3S	lit							415			3D	358			6D	402					3D		
melt KX				675				3S	540							731			3S	766			13S								
decompose					348	355	94	3D		296	305	142	3D			435	456	217	3D		517	580	465	3D							
Sucrose		185, 238	258 433 (air)	674	155	167	2054	2D 3S	183	225	236	1064	4D	173, 730	186	206	1110	6D 13S	767	170	175	2037	3D 3S	191, 391	231	241	127	3D 13S			
Sucrose 20%				160, 675	170	183	1805	4D3 S	191, 893	232	237	1798	2D 3S	176, 770	176, 364	207, 368	1718, 694	4D 13S	766	191, 331	240, 342	2091, 165	5D 3S	193, 391	231	244	102	3D			
Fructose		129	254	115, 676	126	138	1620	3D 13S	99	177	200	1222	4D	116, 730	180	196	1317	2D 3S	111, 766	133	166	2,296	13S		105, 174	109, 190	80, 115	3D 12S			
Lactose		153, 208	279																151	183	197	1597	3D								
Glucose		165, 233	285																149	205	243	2688	9D								
penta- erythritol		190, 263, 359												190, 732	223	246	1427	12D 13S	191, 767	251	267	2058	7D 4S	193, 399, 800	385	390	129	3D 2S			
erythritol		122, 297 bp		115, 601, 665	118	145	1140	3S	108	140, 325	161, 358	1702, 204	4D						119	235	258	2272	5D								
Hexatriaco ntane		79		296, 422	308, 437	274, 411		3D											75, 363	NR<500			13D								
Cyclodode canol		78		197, 286, 354	212, 314, 366	19, 237, 496		3D	72	314	320	768	2D	72	398	408	876	3D	74, 357	436	470	1129	3D	77	360	384	256	3D			
sulfur		107- 119- 135	341 (air)	114, 577	242	300	2353	4D 3S	116, 581	298	309	2360	3D 3S	116, 186	213	320	815	2D	116, 316, 438	171	183	723	4D								
naphthale ne		80		292, 450	317, 481	~350 (ends after 500)		3D	80	287	303	931	3D	81	423	433	1779	2D	81, 351	437	461	ended past 500	4D	81, 396	468	471	68	2D			
benzoic acid 20%		121		284, 404	299, 415	959, 544		3D	120	124, 288	159, 311	909, 430	3D	124	368	369	835	3D	124	325	344	3648	3D	119	385	387	138	3D			
charcoal		416 (air)		350, 444	356, 447	116, 240		4D		294	310	792	3D							329	333	1585	4D	395	397, 672	400, 702	74, 82	3D 3S			
Al 20%		541, 654, 676		347	356	76		2D 1S	653	789	819	726	1S	654, 733	421	430	149	4D 1S	654, 769	364	477	1499	3D 1S								
		KIO ₄						KMnO ₄						KBrO ₃						KClO ₃						K ₂ Cr ₂ O ₇					

Table 2 con't. Temperature Endotherms & Exotherms DSC & SDT (20°/min, Heat Release/ Jg⁻¹)

NH ₄ ClO ₄					KClO ₄					KIO ₃					KNO ₃					NH ₄ NO ₃					KNO ₂					
endo	onset	exo max °C	Jg ⁻¹	#	endo	onset	exo max °C	Jg ⁻¹	#	endo	onset	exo max °C	Jg ⁻¹	#	endo	onset	exo max °C	Jg ⁻¹	#	endo	onset	exo max °C	Jg ⁻¹	#	endo	onset	exo max °C	Jg ⁻¹	#	
248				3D	307				3D	nothing in D					132				4D	128				3D	45				4D	phase chg
					613				3S	555d				3S	331				4D	167				3S	419				4D	melt
758				3S	769				3S	680				3S										3S	731				4S	melt KX
	398	402	1233	3D		645	654	293	3S						703				3S		282	311	1407	3D	903	512	519	2	4S	decompos
164, 245, 756	176, 268	184, 341	199, 2253	5D 3S	183, 306, 766	249, 497	281, 501	138, 1125	3D 3S	154, 678	165	187	1243	4D 4S	133, 178	238, 391	262, 397	242, 1016	4D	55, 128	152	172	2092	3D		225	248	1281	3D	Sucrose
172, 246, 758	476	477	1357	3D 3S	186, 304, 768	506, 602	538, 622	869, 217	4S	160, 670	169	185	838	5D 3S	133, 179, 331	377	386	681	3D	55, 130	163, 324	182, 334	1793, 839	4D 3S	171, 407, 878	180	210	1689	2D 3S	Sucrose 20%
122, 244, 756	173, 277	181, 338	222, 1638	7D 3S	125, 309, 767	506	508	993	4D 3S	124, 678	143	156	1442	3D 4S	154	227, 396	248, 404	205, 391	3D	55, 120	155	169	2652	5D		148	168	987	2D	Fructose
															152, 212	253, 389	271, 393	276, 696	3D	55, 105	170	182	1480	4D						Lactose
															133, 164	258, 394	285, 398	299, 363	3D	55, 114	166	186	2277	3D						Glucose
															131, 187, 351	450	469	1638	7D 3S	55, 130, 171	263	267	2118	4D						penta-erythritol
112, 246	362	404	3822	4D	119, 305, 768	324, 450, 627	348, 477, 642	397, >500, 176	4D 4D 3S	121, 608, 666	156	181	871	3D 4S	115, 132	397	413	2438	3D	90	265	267	1758	3D	109	288	315	1009	3D	erythritol
78	406	412	1414	3D	77, 308	NR<500			3D	77	443	451	209	3D	132, 334	NR<500			3D	54, 77, 128, 167	339	349	794	3D						Hexatriacontane
76, 249	361	404	1877	2D	77, 307	NR<500			2D	75	444	452	354	3D	129, 326	NR<500			4D											Cyclododecanol
116, 249, 670	416	422	1747	3D 3S	116, 306, 765	458	468	1612	3D 3S	116, 195, 581	324	350	2299	3D 3S	117, 190	324	336	1,054	6D	54, 116	204	213	2328	3D	120, 169	255	300	2094	2D	sulfur
81, 247	435	470	1527	3D	82, 308	NR<500			2D	81	NR<500			3D	81, 131, 334	NR<500			3D	82, 129	305	328	829	3D						naphthalene
125, 246	446	457	2347	2D	125, 306	395	>500		3D	124	418	426	476	2D	129, 318	NR<500			3D	127, 166	313	335	1879	2D		NR				benzoic acid 20%
246	447	451	1718	3D 4S	307, 765	510	525	1172	3D 7S		443	448	300	3D	129, 324	461	474	1361	6D 3S	54, 124	222	223	1607	4D	102	358	381	625	3D	charcoal
247, 654	439, 872	479, 902	1887, 1279	4D 1S	303, 654, 769	594	626	796	1S	555, 654, 676	581	590	45	1S	331, 572, 653	795	857	1377	3D 1S	171, 277, 654	320, 864	331, 883	825, 216	2D 1S	423, 654	695	762	2597	1S	20% or 30% Al
NH ₄ ClO ₄					KClO ₄					KIO ₃					KNO ₃					NH ₄ NO ₃					KNO ₂					

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 (KIO_4 , KMnO_4 , KBrO_3 , KClO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , AN, KNO_2) reacted with the sugars immediately after their melt, and a large exotherm was observed, as can be seen in Figure 2 (DSC thermogram of KIO_4 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
KBrO_3	propan-2-ol	acetone	35
KClO_3	sucrose	KCl , CO_2 , H_2O	38
KClO_3	lactose	KCl , CO_2 , H_2O , CO , H_2 , C , CH_4	36,37
KClO_4	sucrose	KCl , CO_2 , H_2O	38
KIO_4	pea cannery waste	cleaved sugars, KIO_3	27
KIO_4	diacetyl, diisobutyl, benzil, camphorquinone	iodate, carboxylic acid	28
KMnO_4	fructose, glucose, galactose, maltose, sucrose	formic acid & lower sugars	39
NaIO_4	dextran (an anhydroglucose polymer)	formic acid	29
NaIO_4	salicyl alcohol	dimer of intermediate via Diels-Alder	30
NaIO_4	glucose	HCO_3H , HCHO , IO_3^-	25
NaIO_4	crystalline cellulose	dialdehyde	31
NaIO_4	glucose, ethylene glycol	formaldehyde	32
NaIO_4	cellulose	dialdehyde	33
NaIO_4	catechol	<i>o</i> -benzoquinone	34

Fig. 2 KIO_4 + 50 mass% Sucrose

Fig. 3 KClO_3 + 50 mass% disaccharide: Sucrose (3a) & Lactose (3b)

Fig. 4 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

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).

Fig. 6 KNO₃ + 50 mass% disaccharide: Sucrose (6a) & Lactose (6b)

Fig. 7 KNO₃ + 50 mass% monosaccharide: Glucose (7a) & Fructose (7b)

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).

Fig. 8 KNO₂ + 50 mass% Sucrose (8a) + 20 mass% Sucrose (8b)

Fig. 9 AP + 50 mass% Sucrose (9a) & 20 mass% Sucrose (9b)

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).

Fig. 10 AN + 50 mass% Sucrose (10a) & 20 mass% Sucrose (10b)

The heat released from the oxidizers with 20 mass% sucrose was comparable ($\sim 1400 \text{ Jg}^{-1}$) to the heat released with 50 mass% sucrose (Table 4). There was a large deviation in observed heat released ($\pm 25\%$) run to run which we have attributed to the slow response of the DSC thermocouples. $\text{K}_2\text{Cr}_2\text{O}_7$ 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⁻¹ below 500°C from Oxidizer/Fuel Mixes

	KIO ₄	KMnO ₄	KBrO ₃	KClO ₃	K ₂ Cr ₂ O ₇	AP	KClO ₄	KIO ₃	KNO ₃	AN	KNO ₂
exotherm Jg ⁻¹	94	142	217	465		1233	293			1407	SDT
Sucrose	2054	1064	1110	2037	127	2253	1125	1243	1016	2092	1281
Sucrose 20%	1805	1798	1718	2091	102	1357	869	838	681	1793	1689
Fructose	1620	1222	1317	2296	115	1638	993	1442	596	2652	987
Lactose				1597					696	1480	
Glucose				2688					697	2277	
Pentaerythritol			1427	2058					1638	2118	
Erythritol	1140	1702		2272	129	3822	573	871	2438	1758	1009
Cyclododecanol	790	768	876	1129	256	1877	not seen	354	not seen		
surfur	2353	2360	815	723		1747	1612	2299	1054	2328	2094
naphthalene	1205	931	1779	ended past 500	68	1527	not seen		not seen	829	
benzoic acid 20%	1500	1339	835	3648	138	2400	not seen	476	not seen	1879	not seen
charcoal	600	792		1585	156	1718	1172	300	1361	1607	625
Aluminum 20% all SDT	170	726	454	38, 1499 DSC		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 (KMnO₄ and KIO₄) 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. KClO₃ and KBrO₃, which had been labeled "sugar-controlled", remained triggered by the fuel, while KNO₃ 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 KMnO_4 + 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, KClO_4 and KNO_3 , 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). Occasionally 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 .

Fig. 13 Ammonium nitrate DSC (13a) vs. SDT (13b)

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).

Fig. 14 KMnO_4 + 50 mass% Sulfur

Fig. 15 KClO_4 + 50 mass% Sulfur

Table 5 records the temperature at which the exotherms were first observed to rise above the baseline (ramp rate of $20^\circ\text{C}/\text{min}$). 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 KBrO_3 is mixed with naphthalene (Fig. 16), the difference between the onset and first deviation from baseline is not large ($\sim 30^\circ\text{C}$), but for KIO_3 and sulfur (Fig. 17) the difference between the calculated onset and the deviation from baseline is huge ($\sim 160^\circ\text{C}$). (Note that this trace of oxidizer and sulfur is typical for sulfur mixtures.)

Fig 16 KBrO_3 + 50 mass% 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 (KClO_3 , KNO_2) 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 KIO_4 was its conversion into KIO_3 . The low temperature (i.e. under 800°C) exotherms recorded for other oxidizers reflect the decomposition of the oxidizer.

Fig. 18 KMnO_4 + 20 mass% Aluminum

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: ClO₄⁻ > ClO₃⁻ and NO₃⁻ > NO₂⁻ [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 ($\pm 25\%$) 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, KNO_3 , KClO_4 , and NH_4ClO_4 , 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 KClO_3 , 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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Manuscript 2

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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-dinitrotoluene (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.

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 $(\text{NH}_4)_2\text{CO}_3$ 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 $\mu\text{g/mL}$, 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 (N_2), 30; auxiliary gas (N_2), 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 $\sim 257^{\circ}\text{C}$ and DNT $\sim 344^{\circ}\text{C}$, 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 ($\sim 267^{\circ}\text{C}$) and the second peak at a lower temperature ($\sim 326^{\circ}\text{C}$). 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 $\sim 311^{\circ}\text{C}$. 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).

Table 1: First Order Rate Constants of Neat Materials

Neat			
°C	DNAN	DNT	TNT
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	--

Figure 5: Arrhenius Plot for DNAN & DNT

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

200°C	DNAN	DNT	NQ	NTO
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.

Table 4: Species detected by LC/MS in negative ion mode

Observed Mass**	RT (min)	Compound/ formula**	Compound Relative Peak Height				DNT	DNT/NQ	DNT/ NTO	DNT/ NTO /NQ
			DNAN	DNAN/ NQ	DNAN/ NTO	DNAN/ NTO/NQ				
103.0254	0.79	NQ (CH4O2N4)		1.3E+06		2.5E+06		2.4E+06		1.2E+04
129.0051	0.57	NTQ (C2H2O3N4)			9.7E+04	3.8E+04				1.4E+05
143.0207	0.65	C3H3O3N4			1.3E+05	2.5E+04				
162.0308	6.09	C7H4O2N3							8.8E+04	2.3E+05
166.0137	0.85	C7H4O4N					3.2E+05			3.5E+04
178.0250	5.28	C7H4O3N3						7.7E+03		3.2E+04
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
182.0096	1.26	C7H4O5N					4.0E+05		9.7E+04	
182.0208	6.51	DNA (C6H4O4N3)		5.6E+06	1.2E+06	1.8E+06		5.6E+04	3.0E+04	2.7E+05
183.0040	7.61	C6H3O5N2				4.0E+05				
183.0048	1.11	C6H3O5N2			7.3E+05					
183.0049	0.77	DN-OH (C6H3O5N2)	4.2E+06	2.9E+06	3.1E+06	2.5E+06				
190.0260	5.38	C8H4O3N3							5.8E+04	
197.0193	6.85	DNAN (C6H5O5N2)	1.1E+07	1.1E+06	1.9E+06	5.3E+06				
199.0758	6.56	C13H11O2								9.9E+04
205.0371	5.22	C8H5O3N4						4.5E+04		1.7E+05
207.9995	4.53	C7H2O5N3				7.2E+04				
224.0431	5.66	C7H6O4N5		2.5E+04						
225.0261	6.04	C7H5O5N4				1.3E+04				
227.9895	4.65	C6H2O7N3				1.4E+05				
233.0636	5.43	C7H11O6N3								1.1E+05
241.0099	4.55	C8H5O7N2/C11H3O4N3	8.0E+04							
244.0597	5.71	C9H6O2N7						1.1E+04		
246.0754	5.95	C9H8O2N7						3.6E+04		
247.0595	6.35	C9H7O3N6							5.4E+04	7.3E+04
249.0387	5.85	C8H5O4N6		5.8E+04		1.5E+04				
279.0496	5.99	C9H7O5N6			4.5E+04	1.6E+04				
280.0337	7.63	C9H6O6N5			3.1E+04					
291.0609	6.12	C9H7O4N8		8.4E+04		3.5E+03				
292.0450	5.34	C9H6O5N7		2.5E+04						
302.04187	5.19	C13H8O6N3					2.5E+04			
308.0385	5.51	C9H6O6N7				2.4E+04				
311.04239	7	C14H7O5N4					9.5E+04			
326.0547	8.13	C14H8O5N5							8.7E+04	2.8E+04
329.0528	7.8	C14H9O6N4	2.1E+05							
330.03687	5.22	C14H8O N3					1.4E+05			
333.04767	7.88	C13H9O7N4	9.8E+04							
334.0319	5.3	C13H8O8N3	1.0E+05			4.3E+04				
334.0319	7.58	C13H8O8N3	1.2E+05			2.1E+04				
345.0113	5.42	C13H5O8N4	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
346.03171	5.38	C14H8O8N3					5.5E+04			
348.0236	7.75	C12H6O8N5	5.2E+03	2.6E+05	1.4E+05	5.0E+04				
356.0274	6.03	C14H6O7N5					5.3E+04			
363.0220	5.36	C13H7O9N4	1.2E+05							
372.02805	5.12	C7H10O13N5					4.0E+04			
373.0139	5.47	C7H9O14N4					1.1E+05		2.1E+04	
375.02182	5.22	C14H7O9N4					1.1E+05			
375.0235	5.02	C14H7O9N4						1.2E+04		
408.0683	7.73	C14H12O9N6	3.4E+04							
457.0628	8.13	C15H9O8N10		1.9E+05						
490.07523	6.93	C21H12O8N7					1.3E+04			

* MS run in negative ion mode; thus formula 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].

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].

Figure 10: Some of the cyclic products reportedly obtained from the decomposition of NQ.

The majority of products created through the decomposition of NTO are gases, including CO_2 , CO , HCN , N_2 , H_2O , NO_2 , N_2O , NO , and H_2 [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 diaminoanisoole 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 the 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.

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.

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.

Figure 18: Radical adduct produced via hydrogen abstraction from TNT [66]

In addition to dinitroaniline 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

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

Figure183. 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

[illegible]

Table 2. Oxidizer exotherms

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	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.
Ammonium Nitrate (AN)	3	254	327	282	311	7		1407	240								
Ammonium Nitrate (AN) SDT	3	no exotherms															
Ammonium Perchlorate (AP)	3	359	414	398	402	2		1233	155								
Ammonium Perchlorate (AP) SDT	3	277	377	294	319	0.7		332	23	463	536		481	3		56	20
Potassium Bromate	3	no exotherms															
Potassium Bromate SDT	3	428	507	435	456	10		217	18								
Potassium Chlorate	6	no exotherms															
Potassium Chlorate SDT	3	474	650	517	580	6	617	465	35								
Potassium Dichromate	3																
Potassium Iodate		no exotherms															
Potassium Iodate SDT	5	no exotherms															
Potassium Nitrate	4	no exotherms															
Potassium Nitrate SDT	3	no exotherms															
Potassium Nitrite	4	no exotherms															
Potassium Nitrite SDT	5	510	536	512	519	8		2	0.1	883			922	29	879, 944, 918, 978		
Potassium Perchlorate	3	no exotherms															
Potassium Perchlorate SDT	3	630	691	645	654	3		293	25								
Potassium Periodate	3	330	366	348	355	0.5		94	9.4								
Potassium Periodate SDT	3	308	400	334	351	0.2		86	13								
Potassium Permanganate	3	277	328	296	305	0.1		142	22								
Potassium Permanganate SDT	2	257	378	293	301	0.3		112	32								

Table 3. Endotherms from Benzoic acid mixtures

[illegible]

Table 4. Exotherms from Benzoic acid 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	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.
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% KBrO ₃	3	355	381	368	369	3		835	698								
Mix 103: 20% Benzoic Acid/80% KClO ₃	3	189	381	325	344	14	307, 340	3648	472								
Mix 110: 20% Benzoic Acid/80% KCr ₂ O ₇	3	371	381	374	376	6		24	17	381	401	385	387	3		138	118
Mix 107: 20% Benzoic Acid/80% KIO ₃	2	395	403	395	398	0.9		16	2	403	454	418	426	2		476	268
Mix 105: 20% Benzoic Acid/80% KNO ₃	3	no exotherms															
Mix 106: 20% Benzoic Acid/80% KNO ₂		no DSC runs showed exotherms or endotherms though mixture did turn brown; may have already decomposed															
Mix 104: 20% Benzoic Acid/80% KClO ₄	3	395															
Mix 108: 20% Benzoic Acid/80% KIO ₄	3	259	369	284	299	3	333, 347 150, 182,	959	163	385	433	404	415	6		544	62
Mix 109: 20% Benzoic Acid/80% KMnO ₄	3	123	244	124	159	48	202, 234	909	403	274	341	288	311	0.5		430	47

Table 5. Endotherms from Charcoal 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.
Charcoal		no DSC or SDT (under N ₂) 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	3	244	253	244	246	0.6		32	10								
Mix 69: 50% Charcoal/ 50% AP SDT	4	237	259	239	244	1		19	19								
Mix 42: 50% Charcoal/ 50% KClO ₃	4	no endotherms															
Mix 98: 50% Charcoal/ 50% K ₂ Cr ₂ O ₇	3	392	397	393	395	1		13	10								
Mix 98: 50% Charcoal/ 50% K ₂ Cr ₂ O ₇	3	no endotherms															
Mix 99: 50% Charcoal/ 50% KIO ₃	3	no endotherms															
Mix 99: 50% Charcoal/ 50% KIO ₃	1	no endotherms															
Mix 43: 50% Charcoal/ 50% KNO ₃	5	127	136	127	129	0.6		20	6	318	330	320	324	7		25	9
Mix 43a: 50% Charcoal/ 50% KNO ₃ SDT	3	124	171	126	129	0.2		18	8	324	361	327	332	0.5		40	7
Mix 102: 50% Charcoal/ 50% KNO ₂	3	no endotherms															
Mix 54: 50% Charcoal/ 50% KClO ₄	3	302	318	305	307	0.5		51	14								
Mix 54/70 Charcoal/ 50% KClO ₄ SDT	7	298	328	299	304	1		26	9	757	774	761	765	2		14	6
Mix 100: 50% Charcoal/ 50% KIO ₄	4	no endotherms															
Mix 101: 50% Charcoal/ 50% KMnO ₄	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	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		no DSC or SDT (under N ₂) runs showed exotherms or endotherms															
Charcoal in air SDT	2	202	579	416	522	6	433	20821	483								
Mix 41: 50% Charcoal/ 50% AN	4	203	241	222	223	2		1607	399								
Mix 69: 50% Charcoal/ 50% AP	3	353	465	447	451	9		1718	229								
Mix 69: 50% Charcoal/ 50% AP SDT	4	259	408	312	338	10		1738	469								
Mix 42: 50% Charcoal/ 50% KClO ₃	4	300	361	329	333	5	312, 328, 333	1585	183								
Mix 98: 50% Charcoal/ 50% K ₂ Cr ₂ O ₇	3	397	417	397	400	1		74	20								
Mix 98: 50% Charcoal/ 50% K ₂ Cr ₂ O ₇	3	389	477	391	397	1		239	265	670	745	672	702	4		82	57
Mix 99: 50% Charcoal/ 50% KIO ₃	3	436	456	443	448	7		300	162								
Mix 99: 50% Charcoal/ 50% KIO ₃	1	425	510	444	454		492	139									
Mix 43: 50% Charcoal/ 50% KNO ₃	5	409	486	461	474	11	462	1361	413								
Mix 43a: 50% Charcoal/ 50% KNO ₃ SDT	3	423	730	459	461	2		1920	353								
Mix 102: 50% Charcoal/ 50% KNO ₂	3	346	407	358	381	2		625	179								
Mix 54: 50% Charcoal/ 50% KClO ₄	3	462															
Mix 54/70: Charcoal/ 50% KClO ₄ SDT	7	470	557	510	525	8	512	1172	475								
Mix 100: 50% Charcoal/ 50% KIO ₄	4	344	364	350	356	1		116	81	438	456	444	447	9		240	173
Mix 101: 50% Charcoal/ 50% KMnO ₄	3	277	344	294	310	2		792	269								

Table 7. Endotherms from Cyclododecanol mixtures

[illegible]

Table 8. Exotherms from Cyclododecanol mixtures

[illegible]

Table 9. Endotherms from Erythritol mixtures

[illegible]

Table 10. Exotherms from Erythritol 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	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.
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% KClO ₃	5	192	281	235	258	8	215	2272	390								
Mix 64: 50% Erythritol/ 50% KIO ₃	3	141	219	156	181	6	183	871	304								
Mix 64: 50% Erythritol/ 50% KIO ₃ SDT	4	148	268	159	179	3		892	79	285	358	294	317	4		36	30
Mix 34: 50% Erythritol/ 50% KNO ₃	3	352	461	397	413	2		2438	336								
Mix 57: 50% Erythritol/ 50% KNO ₂	3	261	356	288	315	2		1009	30								
Mix 45: 50% Erythritol/ 50% KClO ₄	4	313	386	324	348	19	319	397	187	450			477	11			
Mix 45: 50% Erythritol/ 50% KClO ₄ SDT	3	509	593	524	575	6		50	9	593	669	627	642	2	609, 626	176	
Mix 67a: 50% Erythritol/ 50% KIO ₄ SDT	3	119	286	118	145	7	183, 243	1140	452	329	363	332	343	14		10	7
Mix 46: 50% Erythritol/ 50% KMnO ₄	4	112	230	140	161	2	115, 125	1702	270	312	395	325	358	9		204	63

Table 11. Endotherms from Fructose 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.
Fructose	4	90	145	104	129	2		185	47								
Fructose SDT	3	88	167	103	124	2		283	50	177	306	180	226	35	203, 274	188	40
Mix 25a: 50% Fructose/ 50% AN	5	53	67	54	55	1		13	5	83	138	91	120	9		114	59
Mix 29: 50% Fructose/ 50% AP	7	95	143	106	122	12		90	34	242	252	243	244	1		19	8
Mix 29: 50% Fructose/ 50% AP SDT	3	96	203	110	128	2	167	378	150	724	807	734	756	2		54	59
Mix 92: 50% Fructose/ 50% KBrO ₃	2	99	130	103	116	2		100	27								
Mix 92: 50% Fructose/ 50% KBrO ₃ SDT	3	98	136	105	123	3		71	32	726	741	728	730	0.6		13	2
Mix 17: 50% Fructose/ 50% KClO ₃	10	93	116	101	111	10	94, 103	25	13								
Mix 17: 50% Fructose/ 50% KClO ₃ SDT	3	93	130	103	121	0.4		96	40	758	776	763	766	0.2		19	10
Mix 96: 50% Fructose/ 50% K ₂ CrO ₇	3	no endotherms															
Mix 96: 50% Fructose/ 50% K ₂ CrO ₇ SDT	2	97	136	102	111	9	105	14	13								
Mix 63: 50% Fructose/ 50% KIO ₃	3	115	129	119	124	1		30	2								
Mix 63: 50% Fructose/ 50% KIO ₃ SDT	4	102	132	104	122	0.6		41	12	673	689	675	678	0.4		8	1
Mix 21: 50% Fructose/ 50% KNO ₃	3	98	146	105	154	50	136	73	28								
Mix 56: 50% Fructose/ 50% KNO ₂	2	no endotherms															
Mix 27: 50% Fructose/ 50% KClO ₄	4	99	146	102	125	4		43	30	303	323	305	309	1		59	14
Mix 66: 50% Fructose/ 50% KIO ₄	3	no endotherms															
Mix 66: 50% Fructose/ 50% KIO ₄ SDT	3	88	122	96	115	0.1		36	4	660	695	670	676	0.2		27	6
Mix 37: 50% Fructose/ 50% KMnO ₄	4	79	125	98	99	12		84	48								

Table 12. Exotherms from Fructose mixtures

[illegible]

Table 13. Endotherms from Glucose & Lactose mixtures

FOX (fuel/oxidizer) Mixtures, DSC & SDT runs.																									
Sample	#	Start Endo (°C)	End 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)	End 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)	End 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.
Glucose	3	143	179	153	165	0.7		217	39	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% KClO ₃	9	132	153	140	149	8		41	29																
Mix 20: 50% Glucose/ 50% KNO ₃	3	130	141	131	133	0.7		5	1	142	173	155	164	0.6		112	15								
Lactose (galactose + glucose)	4	145	172	148	153	2		115	17	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% KClO ₃	3	145	165	147	151	0.8		63	13																
Mix 19: 50% Lactose/ 50% KNO ₃	3	130	139	131	133	0.7		10	4	145	177	148	152	0.8		59	8	206	219	209	212	0.9		13	6

Table 14. Exotherms from Glucose & Lactose mixtures

FOX (fuel/oxidizer) Mixtures, DSC & SDT runs.																	
Sample	#	Start Exo (°C)	End Exo (°C)	Onset Temp (°C)	Exo Temp Max. (°C)	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 Temp Max	Additional Max & Shoulders (°C) seen in some traces	Heat Released (J/g)	Std Dev Heat Rel.
Glucose	3	273	339	285	306	4		345	126								
Mix 24: 50% Glucose/ 50% AN	3	149	232	166	186	5	158,	2277	414	250	348	291	328	28		482	353
Mix 16: 50% Glucose/ 50% KClO ₃	9	151	290	205	243	5	168, 255	2688	762								
Mix 20: 50% Glucose/ 50% KNO ₃	3	223	337	258	285	18	307, 273	299	64	372	422	394	398	5	392	363	62
Lactose (galactose + glucose)	4	258	368	279	304	3		478	58								
Mix 23: 50% Lactose/ 50% AN	4	161	243	170	182	1	208	1480	447	255	333	273	302	25		187	174
Mix 15: 50% Lactose/ 50% KClO ₃	3	174	289	183	197	5	218, 240, 256	1597	102								
Mix 19: 50% Lactose/ 50% KNO ₃	3	239	326	253	271	0.8		276	17	366	426	389	393	0.6		696	78

Table 15. Endotherms from Hexatriacontane 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.	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.
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	128	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% KClO ₃	3	70	92	75	77	0.5		215	33																								
Mix 136: 50% Hexatriacontane/50% KIO ₃	3	69	90	74	77	0.3		114	20																								
Mix 133: 50% Hexatriacontane/50% KNO ₃	3	69	96	75	77	0.6		168	17	129	144	130	132	2		14	6	327	341	332	334	1		16	9								
Mix 132: 50% Hexatriacontane/50% KClO ₄	3	71	93	75	77	1		125	14	303	316	305	308	1		39	5																
Mix 135: 50% Hexatriacontane/50% KIO ₄	3	70	87	75	76	0.6		103	17																								

Table 16. Exotherms from Hexatriacontane mixtures

FOX (fuel/oxidizer) Mixtures, DSC & SDT runs.																									
Sample	#	Start Exo (°C)	End Exo (°C)	Onset Temp (°C)	Exo Temp Max.	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.	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.	Std Dev Endo Temp Max	Additional Max & Shoulders (°C) seen in some traces	Heat Released (J/g)	Std Dev Heat Rel.
Hexatriacontane	3	no exotherms																							
Mix 137: 50% Hexatriacontane/ 50% AN	3	278	373	339	349	22	313, 343, 362	794	202																
Mix 134: 50% Hexatriacontane/ 50% AP	3	367	435	406	412	8		1414	233																
Mix 138: 50% Hexatriacontane/ 50% KClO ₃	3	no exotherms																							
Mix 136: 50% Hexatriacontane/ 50% KIO ₃	3	418	469	443	451	3		209	46																
Mix 133: 50% Hexatriacontane/ 50% KNO ₃	3	no exotherms																							
Mix 132: 50% Hexatriacontane/ 50% KClO ₄	3	no exotherms																							
Mix 135: 50% Hexatriacontane/ 50% KIO ₄	3	210	234	221	224	3		18	1	287	341	296	308	24		274	88	373	447	422	437	2		411	57

Table 17. Endotherms from Naphthalene mixtures

[illegible]

Table 18. Exotherms from Naphthalene mixtures

[illegible]

Table 19. Endotherms from Pentaerythritol mixtures

FOX (fuel/oxidizer) Mixtures, DSC & SDT runs.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
Sample	#	Start	End	Onset	Endo	Std Dev	Additional		Start	End	Onset	Endo	Std Dev	Additional		Start	End	Onset	Endo	Std Dev	Additional		Start	End	Onset	Endo	Std Dev	Additional		Start	End	Onset	Endo	Std Dev	Additional																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
		Endo (°C)	Endo (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Mins & Shoulders (°C) seen in some traces	Heat Abs. (J/g)	Std Dev Heat Abs.	Endo (°C)	Endo (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Mins & Shoulders (°C) seen in some traces	Heat Abs. (J/g)	Std Dev Heat Abs.	Endo (°C)	Endo (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Mins & Shoulders (°C) seen in some traces	Heat Abs. (J/g)	Std Dev Heat Abs.	Endo (°C)	Endo (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Mins & Shoulders (°C) seen in some traces	Heat Abs. (J/g)	Std Dev Heat Abs.	Endo (°C)	Endo (°C)	Temp (°C)	Temp (°C)	Temp (°C)	Mins & Shoulders (°C) seen in some traces	Heat Abs. (J/g)	Std Dev Heat Abs.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
Pentaerythritol	3	182	204	186	190	1		320	12	255	272	259	263	0.8		29	7	325	402	330	359	3		323	68																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				

Table 20. Exotherms from Penterythritol 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	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.
Pentaerythritol	3	no exotherms															
Pentaerythritol SDT	3	no exotherms															
Mix 33: 50% Pentaerythritol/ 50% AN	4	242	332	263	267	2	343	2118	475								
Mix 93: 50% Pentaerythritol/ 50% KBrO ₃	2	211	299	223	246	10	224, 269	1427	78								
Mix 93: 50% Pentaerythritol/ 50% KBrO ₃ SDT	3	210	338	211	236	6		805	240	368	450	377	379	0.6		361	82
Mix 31: 50% Pentaerythritol/ 50% KClO ₃	7	209	303	251	267	21	238, 273, 290	2058	892								
Mix 31: 50% Pentaerythritol/ 50% KClO ₃ SDT	4	221	377	278	297	62	248, 435	963	879	545	623	559	600	19		84	83
Mix 97: 50% Pentaerythritol/ 50% K ₂ Cr ₂ O ₇	3	383	411	385	390	26		129	87								
Mix 97: 50% Pentaerythritol/ 50% K ₂ Cr ₂ O ₇	1	333	392	350	386			60		392	506	393	427			424	
Mix 97: 50% Pentaerythritol/ 50% K ₂ Cr ₂ O ₇	2	308	500	378	406		387	274		308	500	378	406			274	
Mix 97: 50% Pentaerythritol/ 50% K ₂ Cr ₂ O ₇ SDT	2	320	446	364	396	14	387	167	151								
Mix 32: 50% Pentaerythritol/ 50% KNO ₃	7	420	492	450	469	5	438, 442, 460	1638	229								
Mix 32: 50% Pentaerythritol/ 50% KNO ₃ SDT	3	351	527	419	454	8		111	21	817	860	818	836	10		199	138

Table 21. Endotherms from Sucrose mixtures

[illegible]

Table 22. Exotherms from Sucrose mixtures

FOX (fuel/oxidizer) Mixtures, DSC & SDT runs.																									
Sample	#	Start Exo (°C)	End Exo (°C)	Onset Temp (°C)	Exo Temp Max	Std Dev Endo Temp	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	Std Dev Endo Temp	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	Std Dev Endo Temp	Additional Max & Shoulders (°C) seen in some traces	Heat Released (J/g)	Std Dev Heat Rel.
Sucrose (glucose + fructose)	4	250	338	258	299	1		372	78																
Sucrose (glucose + fructose)	3																								
SDT	3																								
Sucrose (glucose + fructose)	2	269	637	433	565	31	371	6948	396																
SDT in air	3	142	229	152	172	3	204	2092	#	242	331	262	294	9		263	221								
Mix 22: 50% Sucrose/ 50% AN	5	172	230	176	184	1	208	199	61	263	413	268	341	22	278, 420	2253	680								
Mix 28: 50% Sucrose/ 50% AP	3	202	535	281	347	26	234, 273, 321	2091	190																
SDT	3																								
Mix 91: 50% Sucrose/ 50% KBrO ₃	6	179	257	186	206	4	240	1110	483																
Mix 91: 50% Sucrose/ 50% KBrO ₃ SDT	3	184	355	189	191	0.2		480	97	368	425	373	375	1		45	26								
Mix 14: 50% Sucrose/ 50% KClO ₃	3	167	279	170	175	9	201, 222, 248	2037	420																
Mix 14: 50% Sucrose/ 50% KClO ₃ SDT	3	177	248	183	188	1		777	330	308	366	310	334	10		59	31	389	467	392	422	17		52	44
Mix 95: 50% Sucrose/ 50% K ₂ CrO ₇	3	224	272	231	241	2		127	81																
Mix 95: 50% Sucrose/ 50% K ₂ CrO ₇ SDT	3	394	432		400	2		22	6.1	468	514	471	489	3		23	11								
Mix 62: 50% Sucrose/ 50% KIO ₃	4	159	224	165	187	6	213	1425	316																
Mix 62: 50% Sucrose/ 50% KIO ₃ SDT	4	184	233	184	191	0.8		123	9	426	469	435	438	1		143	42								
Mix 18: 50% Sucrose/ 50% KNO ₃	4	214	308	238	262	3		242	86	372	425	391	397	3		1016	451								
Mix 55: 50% Sucrose/ 50% KNO ₃	6	203	284	219	250			1040																	
Mix 55: 50% Sucrose/ 50% KNO ₃ SDT	3	204	299	225	248	8		1281	301																
Mix 26: 50% Sucrose/ 50% KClO ₃	3	241	303	249	281	0.9		138	9	407															
Mix 26: 50% Sucrose/ 50% KClO ₃ SDT	3	443	552	497	501	11		1125	309																
Mix 65: 50% Sucrose/ 50% KIO ₃	2	148	204	155	167	6	176	2054	506																
Mix 65: 50% Sucrose/ 50% KIO ₃ SDT	3	177	256	178	185	0.8		62	18	270	389	338	349	0.3	295	195	7	404	500	440	442	1		328	21
Mix 36: 50% Sucrose/ 50% KMnO ₄	4	194	331	225	236	3	273, 305	1064	120																
Mix 68: 20% Sucrose/ 80 % AN	4	151	216	163	182	8	189	1793	397	305	360	324	334	29	336	839	413								
Mix 68: 20% Sucrose/ 80 % AN SDT	3	151	489	170	174	3	212, 238, 349	1423	350																
Mix 71: 20% Sucrose/ 80% AP	3	468	488	476	477	14		1357	134																
Mix 71: 20% Sucrose/ 80% AP SDT	3	202	473	292	317	1	235, 269, 392, 430	1260	101																
Mix 79: 20% Sucrose/ 80% KBrO ₃	4	172	282	176	207	22	207, 281	1718	514	349	400	364	368	14	349	694	220								
Mix 79: 20% Sucrose/ 80% KBrO ₃ SDT	3	178	317	182	191	4	255	306	141	344	470	363	371	17	383, 447	395	258								
Mix 73/59: 20% Sucrose/ 80% KClO ₃	5	162	307	191	240	6	171, 285	2091	858	328	372	331	342	25		165	112								
Mix 73: 20% Sucrose/ 80% KClO ₃ SDT	3	172	272	179	184	0.7		610	83	321	432	330	360	41	352.0	210	106	500	636	557	608	4	571	243	50
Mix 94: 20% Sucrose/ 80% K ₂ CrO ₇	3	225	264	231	244	0.4		102	48	395	403	395	396	3		14	4.1								
Mix 77: 20% Sucrose/ 80% KIO ₃	5	166	217	169	185	2		838	220																
Mix 77: 20% Sucrose/ 80% KIO ₃ SDT	3	267	373	274	293	1	348	92	5	420	477	435	436	3		222	73								
Mix 72: 20% Sucrose/ 80% KNO ₃	3	371	429	377	386	11	409	681	514																
Mix 72: 20% Sucrose/ 80% KNO ₃ SDT	5	350	541	356	432	5	371, 540	1027	277	512	592	525	562	0.7		50	2								
Mix 78: 20% Sucrose/ 80% KNO ₃	2	177	243	180	210	2		1689																	
Mix 78: 20% Sucrose/ 80% KNO ₃ SDT	3	196	329	214	250	0.6		462	31	419	570	442	446	7	459, 519	981	300								
Mix 74: 20% Sucrose/ 80% KClO ₃ SDT	4	445	582	506	538	2	503	869	812	574	653	602	622	5		217	63								
Mix 76: 20% Sucrose/ 80% KIO ₃	4	160	230	170	183	8	178	1805	391																
Mix 76: 20% Sucrose/ 80% KIO ₃ SDT	3	175	252	176	184	0.3		64	12	280	388	339	349	0.07	297	168	13	398	528	435	437	6	462	374	88
Mix 75: 20% Sucrose/ 80% KMnO ₄	2	222	342	232	237	1	278	1798							590, 615, 722										
Mix 75: 20% Sucrose/ 80% KMnO ₄ SDT	3	218	450	288	300	0.2	240, 390	472	163	546	744	637	686	13		306	52	761	825	762	793	10		109	66

Table 23. Endotherms from Sulfur mixtures

[illegible]

Table 24. Exotherms from Sulfur 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	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	537
Mix 39: 50% Sulfur/ 50% AN	3	172	243	204	213	10	198, 232	2328	438
Mix 85: 50% Sulfur/ 50% AP	3	391	434	416	422	5	389, 408	1747	896
Mix 85: 50% Sulfur/ 50% AP SDT	3	298	509	413	444	3	347	817	69
Mix 90: 50% Sulfur/ 50% KBrO ₃	2	193	382	213	320	15		815	150
Mix 38: 50% Sulfur/ 50% KClO ₃	4	149	242	171	183	3	220	723	96
Mix 88: 50% Sulfur/ 50% KIO ₃	3	169	418	324	350	22	259, 354, 409	2299	280
Mix 88: 50% Sulfur/ 50% KIO ₃ SDT	3	241	411	308	330	0.6	301, 358	526	125
Mix 40: 50% Sulfur/ 50% KNO ₃	6	294	438	324	336	12	305, 337, 354, 370	1054	258
Mix 87: 50% Sulfur/ 50% KNO ₂	3	189	430	255	300	13	248, 368	2094	199
Mix 87: 50% Sulfur/ 50% KNO ₂ SDT	1	251	362	269	272			1278	
Mix 84: 50% Sulfur/ 50% KClO ₄	3	428	482	458	468	8	456	1612	279
Mix 84: 50% Sulfur/ 50% KClO ₄ SDT	3	556	652	577	596	3		157	5.9
Mix 89: 50% Sulfur/ 50% KIO ₄	4	182	376	242	300	6	264, 281, 301, 366	2353	571
Mix 89: 50% Sulfur/ 50% KIO ₄ SDT	3	212	386	294	304	9	269, 300	1246	82
Mix 86: 50% Sulfur/ 50% KMnO ₄	3	189	397	298	309	0.3	332	2360	251
Mix 86: 50% Sulfur/ 50% KMnO ₄ SDT	3	252	401	293	315	0.6	304	696	79

Table 25. Endotherms for Aluminum 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.
20% Aluminum/ 80% KBrO ₃	4	no endotherms															
20% Aluminum/ 80% KClO ₃	3	341	363	351	357	1	340	96	26								
20% Aluminum/ 80% KIO ₄	2	no endotherms															
20% Aluminum/ 80% KNO ₃	3	126	137	128	130	2		35	10	323	339	325	331	4		46	22
20% Aluminum/ 80% AP	4	246	256	247	247	2		5	2								
20% Aluminum/ 80% AN	2	no endotherms															

Table 26. Exotherms for Aluminum 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	Additional Max & Shoulders (°C) seen in some traces	Heat Released (J/g)	Std Dev Heat Rel.
20% Aluminum/ 80% KBrO ₃	4	419	452	421	430	7		149	90
20% Aluminum/ 80% KClO ₃	3	no exotherms							
20% Aluminum/ 80% KIO ₄	2	339	362	347	356	1		76	7
20% Aluminum/ 80% KNO ₃	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

Insensitive Munitions Mixtures DSC runs at 20°C/min.															
Sample	#	Start Endo (°C)	End Endo (°C)	Onset Temp (°C)	Endo Temp Min. (°C)	Stdev min	Heat Absorbed (J/g)	Stdev heat abs	Start Endo (°C)	End Endo (°C)	Onset Temp (°C)	Endo 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	70	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

[illegible]

Appendix IV: Data from the Insensitive Munitions Project Isothermal Studies

Table 1. Averaged isothermal data for neat DNAN

180°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	0.97	0.02	-0.026	0.02
5 days	432000	0.92	0.1	-0.084	0.1
6 days	518400	0.99	0.07	-0.0059	0.07
7 days	604800	0.89	0.2	-0.11	0.2
8 days	691200	0.87	0.2	-0.14	0.2
9 days	777600	0.865	0.09	-0.15	0.1
10 days	864000	0.95	0.05	-0.055	0.05
11 days	950400	0.94	0.02	-0.058	0.02
12 days	1036800	0.94	0.007	-0.058	0.007
200°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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	186000	0.91	0.005	-0.091	0.006
3 days	259200	0.87	0.03	-0.14	0.04
4 days	345600	0.82	0.02	-0.20	0.02
5 days	432000	0.51	0.1	-0.68	0.3
5d 4h	446400	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					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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	14400	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	0.06	0.04	-2.8	0.6
250°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	1.03	0.07	0.029	0.07
15 min	900	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					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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
80 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	6300	0.38	0.05	-0.97	0.1
110 min	6600	0.053	0.07	-2.9	1
300°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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

180°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	0.99	0.02	-0.0080	0.02
5 days	432000	0.98	0.03	-0.016	0.03
7 days	604800	0.94	0.02	-0.062	0.02
8 days	691200	0.93	0.01	-0.075	0.01
9 days	777600	0.87	0.1	-0.14	0.1
10 days	864000	0.62	0.2	-0.48	0.30
11 days	950400	0.47	0.03	-0.76	0.07
12 days	1036800	0.38	0.007	-0.98	0.020
200°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	1.00	0.05	-0.0025	0.05
1 day	86400	0.94	0.03	-0.067	0.03
2d 3h 40min	186000	0.90	0.02	-0.11	0.02
3 days	259200	0.73	0.1	-0.32	0.2
4 days	345600	0.41	0.3	-0.89	0.7
4d 12h	388800	0.11	0.05	-2.3	0.5
4d 16h	403200	0.078	0.02	-2.6	0.3
4d 20h	417600	0.062	0.009	-2.8	0.1
5d	432000	0.21	0.1	-1.6	0.6
5d 4h	446400	0.059	0.06	-2.8	1
5d 8h	460800	0.027	0.02	-3.6	0.7
5d 12h	475200	0.033	0.03	-3.4	1
240°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	0.99	0.06	-0.010	0.06
15 min	900	1.07	0.05	0.066	0.05
30 min	1800	1.19	0.2	0.180	0.2
45 min	2700	0.93	0.3	-0.073	0.3
60 min	3600	0.98	0.08	-0.019	0.09
120 min	7200	0.89	0.03	-0.11	0.04
180 min	10800	0.84	0.05	-0.17	0.06
240 min	14400	0.79	0.05	-0.24	0.07
300 min	18000	0.48	0.2	-0.73	0.5
360 min	21600	0.43	0.3	-0.85	0.6
420 min	25200	0.065	0.07	-2.7	1
480 min	28800	0.033	0.01	-3.4	0.4
540 min	32400	0.021	0.004	-3.9	0.2
600 min	36000	0.014	0.001	-4.3	0.09
660 min	39600	0.014	0.003	-4.3	0.2
720 min	43200	0.013	0.001	-4.3	0.1
250°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	0.97	0.01	-0.028	0.02
15 min	900	0.94	0.02	-0.060	0.03
30 min	1800	0.88	0.07	-0.130	0.07
45 min	2700	0.88	0.06	-0.13	0.07
60 min	3600	0.81	0.08	-0.20	0.1
270 °C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	1.02	0.08	0.023	0.08
15 min	900	0.95	0.03	-0.052	0.03
30 min	1800	0.72	0.2	-0.33	0.2
45 min	2700	0.52	0.2	-0.65	0.3
60 min	3600	0.20	0.1	-1.6	0.5
280°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	0.96	0.07	-0.037	0.08
15 min	900	0.93	0.07	-0.070	0.07
30 min	1800	0.68	0.1	-0.38	0.2
35 min	2100	0.39	0.1	-0.95	0.3
40 min	2400	0.21	0.1	-1.5	0.5
45 min	2700	0.24	0.1	-1.4	0.6
50 min	3000	0.063	0.03	-2.8	0.4
60 min	3600	0.034	0.02	-3.4	0.6
75 min	4500	0.014	0.003	-4.3	0.2
300°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
Room Temp	0	0.92	0.08	-0.083	0.09
15 min	900	0.29	0.2	-1.2	0.7
30 min	1800	0.019	0.01	-4.0	0.3
45 min	2700	0.0063	0.01	-5.1	1

Table 3. Averaged isothermal data for neat TNT

200°C					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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					
Incubation time	Time (s)	Fraction Remaining	St. Dev.	Ln Fraction Remaining	St. Dev.
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

200°C							
50:50 DNAN:NQ							
Incubation time	Time (s)	DNAN Fraction Remaining	St. Dev.	DNAN Ln Fraction Remaining	St. Dev.	NQ Fraction Remaining (approx)	NQ Ln Fraction Remaining
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							
Incubation time	Time (s)	DNAN Fraction Remaining	St. Dev.	DNAN Ln Fraction Remaining	St. Dev.	NTO Fraction Remaining (approx)	NTO Ln Fraction Remaining
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							
Incubation time	Time (s)	DNAN Fraction Remaining	St. Dev.	DNAN Ln Fraction Remaining	St. Dev.	NTO Fraction Remaining (approx)	NTO Ln Fraction Remaining
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
2 hr	7200	0.64	0.1	-0.45	0.2		
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

200°C							
50:50 DNT:NQ							
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
200°C							
50:50 DNT:NTQ							
Incubation time	Time (s)	DNT Fraction Remaining	St. Dev.	DNT Ln Fraction Remaining	St. Dev.	NTQ Fraction Remaining (approx)	NTQ 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		
200°C							
80:20 DNAN:NTQ							
Incubation time	Time (s)	DNT Fraction Remaining	St. Dev.	DNT Ln Fraction Remaining	St. Dev.	NTQ Fraction Remaining (approx)	NTQ 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 8h	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

180°C									
43:37:20 DNAN:NQ:NTO									
Incubation time	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	1	0
15 min	900	0.96	0.1	-0.037	0.1	1	0	1	0
30 min	1800	0.73	0.2	-0.32	0.3	0.7	-0.36	1	0
45 min	2700	0.71	0.2	-0.35	0.2	0.3	-1.2	0.9	-0.11
60 min	3600	0.57	0.2	-0.55	0.3	0.1	-2.3	0.8	-0.22
75 min	4500	0.64	0.09	-0.45	0.1	0.06	-2.8	0.7	-0.36
90 min	5400	0.45	0.2	-0.80	0.4	0.07	-2.7	0.6	-0.51
200°C									
43:37:20 DNAN:NQ:NTO									
Incubation time	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	1.08	0.2	0.078	0.2	1	0	1	0
10 min	600	0.94	0.3	-0.061	0.4	0.4	-0.92	0.8	-0.22
15 min	900	0.49	0.09	-0.71	0.2	0.07	-2.7	0.6	-0.51
25 min	1500	0.43	0.1	-0.85	0.2	0.05	-3.0	0.6	-0.51
30 min	1800	0.45	0.1	-0.81	0.3	0.05	-3.0	0.4	-0.92
45 min	2700	0.42	0.2	-0.86	0.5	0.04	-3.2	0.3	-1.2
60 min	3600	0.23	0.2	-1.5	1	0.04	-3.2	0.2	-1.6
180°C									
43:37:20 DNT:NQ:NTO									
Incubation time	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
15 min	900	0.95	0.1	-0.052	0.1	1	0	1	0
30 min	1800	0.87	0.2	-0.14	0.2	0.9	-0.11	0.9	-0.11
45 min	2700	0.82	0.1	-0.20	0.2	0.8	-0.22	0.8	-0.22
60 min	3600	0.82	0.1	-0.20	0.2	0.5	-0.69	0.8	-0.22
75 min	4500	0.84	0.1	-0.18	0.2	0.3	-1.2	0.7	-0.36
90 min	5400	0.77	0.3	-0.26	0.4	0.3	-1.2	0.6	-0.51
105 min	6300	0.74	0.2	-0.30	0.2	0.2	-1.6	0.5	-0.69
120 min	7200	0.71	0.3	-0.35	0.4	0.2	-1.6	0.4	-0.92
135 min	8100	0.58	0.3	-0.55	0.5	0.1	-2.3	0.3	-1.2
150 min	9000	0.63	0.2	-0.46	0.4	0.1	-2.3	0.2	-1.6
200°C									
43:37:20 DNAN:NQ:NTO									
Incubation time	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	1.07	0.2	0.065	0.2	1	0	1	0
15 min	900	1.18	0.2	0.170	0.2	0.3	-1.2	0.6	-0.51
25 min	1500	0.81	0.3	-0.20	0.3	0.2	-1.6	0.5	-0.69
30 min	1800	0.83	0.08	-0.18	0.1	0.1	-2.3	0.08	-2.5
45 min	2700	0.68	0.2	-0.38	0.3	0.1	-2.3	0.06	-2.8
60 min	3600	0.54	0.4	-0.61	0.7	0.07	-2.7	0.2	-1.6
65 min	3900	0.32	0.05	-1.10	0.2	0.06	-2.8	0.03	-3.5
4 hr	14400	0.12	0.1	-2.1	1			0.008	-4.8
6 hr	21600	0.012	0.003	-4.5	0.3				
12 hr	43200	0.015	0.01	-4.2	0.8				

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. ln fraction remaining for TNT at 200°C

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

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

Figure 12. Time vs. ln fraction remaining for NQ in the DNAN or DNT 3-part mix at 200°C

Figure 13. Time vs. ln fraction remaining for DNT, NTO, & NQ in the 3-part mix at 180°C

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

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

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

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

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

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

Figure 20. Time vs. ln 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	neat			T (K)	1/T(K)	ln (k)	
	DNAN	DNT	TNT			DNAN	DNT
180	4.0E-08	8.7E-07	--	453	0.00221	-17.04	-13.96
200	2.4E-06	7.6E-06	1.6E-05	473	0.00211	-12.94	-11.78
240	1.3E-05	1.2E-04	--	513	0.00195	-11.25	-9.03
250	1.3E-05	4.7E-05	--	523	0.00191	-11.27	-9.96
270	2.4E-05	4.3E-04	--	543	0.00184	-10.63	-7.75
280	3.0E-04	1.1E-03	3.5E-03	553	0.00181	-8.13	-6.86
300	5.4E-04	2.0E-03	--	573	0.00175	-7.53	-6.23

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