R1-A.1: Characterization of Explosives & Precursors

Abstract— This project performs the essential "characterization" of explosive compounds and mixtures. Physical properties include infrared (IR), Raman, ^{1}H and ^{13}C NMR and mass spectroscopy. These properties are measured and made available, through an online database, to the homeland security enterprise, as well as to forensic labs. Plans are being made to include analysis methods and references. Other essential properties include thermal stability under a variety of conditions, heat of decomposition and detonation and destructive techniques.

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II. PROJECT OVERVIEW AND SIGNIFICANCE

Many laboratories that work directly or indirectly on homeland security issues are not able to purchase or store explosives, especially homemade explosives (HMEs). The database provides a valuable service to these laboratories. Standard chemical properties are measured and uploaded to a database for assessment by registered users. In addition, advice is available in terms of how to perform analyses in their own laboratory, and in a few cases, personnel have been sent to train in the URI lab. Getting rid of small quantities can also be a safety issue. URI has led the way in chemical digestion of unwanted HMEs. Fuel-oxidizer mixtures are a field where little definitive information is available, but much speculation exists in terms of what "works" and what "ought to work." Our research has two goals: First, to allow the homeland security enterprise to narrow or widen the list of threat oxidizers; Second, to collect and match sufficient small-scale data to large-scale performance so that small-scale data has greater predictive value.

III.   RESEARCH ACTIVITY

A.   *State-of-the-art and technical approach*

With the advent of the so-called "homemade" explosives, many people in the homeland security enterprise find themselves forced to handle them. For their safety, it is essential that they have been thoroughly characterized (see below).

A.1 Safe handling of Hexamethylene Triperoxide Diamine (HMTD)

A.1.1 Executive summary

HMTD has never found use as a military explosive due to its poor thermal stability and sensitivity to impact, friction and electrostatic charge. Nevertheless, counter-terrorist efforts require that law enforcement personnel and vendors of explosive detection instruments have access to it for training and for validation protocols. Therefore, we are endeavoring to completely characterize its stability and understand it formation and decomposition mechanisms. Specifically addressed are the hazards of making and storing amorphous non-crystalline HMTD, such as an incident that injured an operator's hand in a canine training exercise in May 2013. We have discovered, contrary to frequent safety advisories, that this material should not be stored under water and that even highly humid conditions accelerate its decomposition. Furthermore, a number of contaminants significantly destabilize it; most troublesome are citric acid, water, and hydrogen peroxide, three materials present in its synthesis which, if it is not re-recrystallized, could be retained in deceptively clean-looking white crystals of HMTD.

A.1.2 Background

HMTD is easily synthesized from reaction of hexamine with hydrogen peroxide. The oxidation is catalyzed by acid, usually citric acid. The structure of HMTD is unusual in that there is planar 3-fold coordination about the two bridgehead nitrogen atoms rather than pyramidal structure [1].   The ring strain in HMTD may account for its low thermal stability and high sensitivity to impact, shock and electrostatic discharge. Because there have been several accidents, such as an unexplained initiation in May 2013 which injured counterterrorism personnel, we have launched a study to better understand its chemistry and, for the purposes of detection, to identify its signature under a variety of conditions.

We have previously used manometers to determine the Arrhenius decomposition kinetics of HMTD (1st order Ea 107 kJ/mol, A =4.21 x 10^{10} s-1) from change in gas volume production with time [2]. A general protocol of this laboratory is that, following synthesis, a re-crystallization (i.e. purification step) is performed. Unfortunately, HMTD has only limited solubility even in highly polar solvents, requiring large volumes of ethyl acetate and acetonitrile for recrystallization. Trace amounts of these solvents are difficult to remove completely from purified HMTD. For that reason, a number of the following studies were performed both with crude and with the recrystallized HMTD to ensure presence of solvent traces did not bias results.

A.1.3 HMTD headspace

We suspected HMTD was undergoing significant decomposition at ambient temperature when we noticed that the material, when removed from storage at -15°C (freezer temperature), developed a noticeable odor after a couple of hours. Accordingly, headspace samples of both crude and recrystallized HMTD were analyzed by GC/MS immediately after recrystallization and after one-year storage at room temperature (Fig. 1 on the next page). Other than residual solvent associated with recrystallization (ethyl acetate), differences in the headspace content were not noticeable. However, Trimethylamine (TMA) and, particularly dimethylformamide (DMF), significantly increased upon aging. Dimethylformamide may be formed directly in the

decomposition of HMTD; however, it may also be formed by the oxidation of trimethylamine. The oxidation of TMA has been reported to form dimethylamine and formaldehyde. Although under the conditions of our experiments dimethylamine is not observed, it is reasonable to assume that dimethylformamide may be an intermediate in TMA oxidation [3].

Figure 1 shows the gas chromatograph (GC) trace of HMTD headspace as sampled by SPME (solid-phase mi-cro-extraction); sampling by syringe gave the same results. No molecular HMTD appeared in the headspace. This raised the question of whether it was there but decomposed under our analytical protocols, or was it never present in the headspace. To answer this, we used the same experimental conditions and injected a solution of HMTD; the molecular ion was observed, which led us to conclude that if the HMTD molecule had been present in the vapor headspace, we would have observed it. This point will be further explored since it is critical that those preparing safe stimulants, e.g. canine training aids, accurately model the vapor plume.
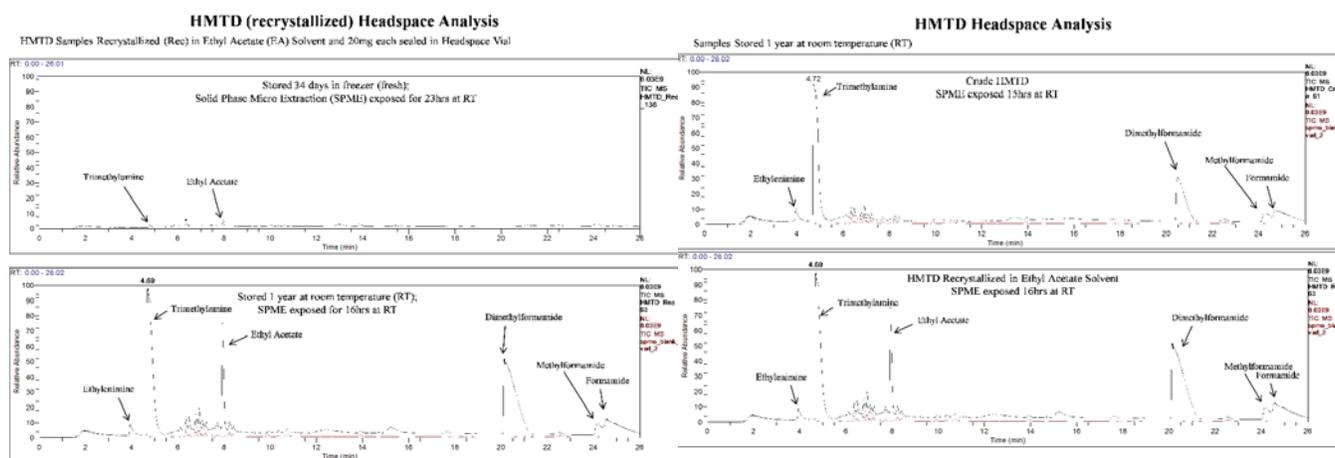

Figure 1: HMTD headspace for fresh recrystallized, 1-yr-old recrystallized & 1-yr-old crude HMTD.

A.1.4 Effect of humidity on HMTD decomposition

General safety advisories suggest primary explosives be stored moist. Indeed this approach has been rec-ommended for HMTD [4]. To address the validity of this approach, DSC (differential scanning calorimeter) measurements on dry and moistened HMTD were obtained. The results (as seen in Fig. 2) show that water actually accelerates decomposition of HMTD. Samples of HMTD were then exposed to less severe aqueous conditions. Samples of amorphous non-crystalline HMTD were held at $60°C$ and fixed humidity values (0, 29.26, 74.5, and 100%) and monitored each week for four weeks. After two weeks, the samples of HMTD, at highest humidity, were completely degraded; no HMTD was observed via GC with mass selective detector (MS). The bar graph (Fig. 3 on the next page) shows the degradation of HMTD over a month. The plots in Figure 4, on the next page, show how fast crude HMTD decomposes in the humidity in just one week as com-pared to the recrystallized HMTD.
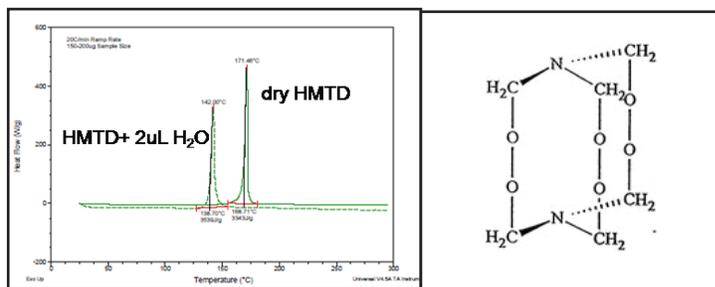

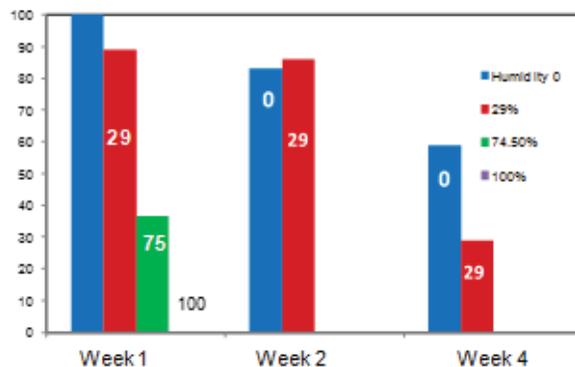**Figure 2: DSC of HMTD & Structure thereof.**

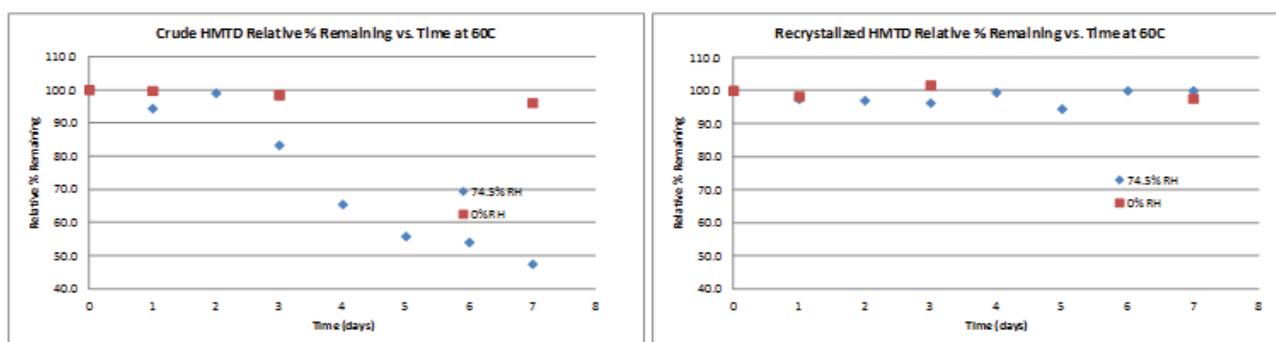**Figure 3: Decomposition of HMTD (crude) held at 60°C with fixed humidity.**

Figure 4: Decomposition of HMTD (crude, left & recrystallized, right) held at 60°C for 8 days.

A.1.5 *Effect of additives on HMTD decomposition*

While humidity might be partially responsible for the May 2013 incident, unconsumed reactants or other contamination may also have contributed to the instability of the HMTD. Since that batch of HMTD was not recrystallized, it was prudent to determine the effects of remaining reactants, as well as accidental contaminants. Table 1, on the next page, shows DSC results and Table 2, on the next page, shows remaining HMTD after storage for one week at 60°C, as measured by GC/MS.

Most additives shifted DSC exotherms of HMTD to lower temperatures (as seen in Table 1 on the next page), indicating a destabilization of HMTD. Exceptions observed were with the additives benzoic acid, phosphate and bicarbonate; the former two may have had a slightly stabilizing effect. We have previously demonstrated that concentrated mineral acid could be used to destroy HMTD [2], and it was reported by Taylor and Rinkenbach [5] that KOH also decomposed it rapidly (within a day at room temperature). Perhaps species which buffer its pH enhance the stability of HMTD. Of concern was the fact that water and citric acid, both of which are used in the synthesis of HMTD, lowered its thermal stability markedly. This emphasizes the need to recrystallize HMTD even though the synthesis results in the precipitation of deceptively clean-looking, white crystals.

In previous studies we had observed a significant HMTD decomposition at 100°C . Isothermal studies performed at 60°C using HMTD (i.e. not recrystallized) in a chamber held at 30% relative humidity (as seen in Table 2 on the next page). The trends observed by DSC were confirmed. The deleterious effect of water was marked, although it was slightly ameliorated by addition of sodium bicarbonate to the water. Water, citric acid, and hydrogen peroxide (HP) enhanced the HMTD decomposition rate; all three potentially could have

remained in HMTD when the product was not re-crystallized. Headspace monitoring revealed that water and citric acid sped up the production of TMA and DMF in the gas phase.

Material	pH	pKa of Additive	pKb of Additive	Onset Exotherm (°C)	Exotherm Maximum (°C)	ΔExotherm Maximum (°C)	Heat Released (J/g)
18.2MΩ H₂O	5.87	14.00	0.00				
HMTD Crude	6.52	N/A	N/A	159	161		2146
HMTD Rec 70/30 EA/ACN	6.79	N/A	N/A	168	171		3183
HMTD Rec EA	6.32	N/A	N/A	148	150		2513
HMTD Crude + 2ul H2O	N/A	N/A	N/A	136	140	-21	3076
HMTD Rec 70/30 EA/ACN + 2ul H2O	N/A	N/A	N/A	140	143	-28	3161
HMTD Rec EA + 2ul H2O	N/A	N/A	N/A	132	136	-14	5238
HMTD Crude + Benzoic Acid 15%	3.63	4.20	9.80	155	160	-1	2634
HMTD Rec EA + Citric Acid 5%	3.49	3.13	10.87	137	142	-8	2174
HMTD Rec EA + Citric Acid 15%	2.92	3.13	10.87	128	135	-15	1430
HMTD Crude +2ul pH4 Buffer	4.00			126	129	-32	3734
HMTD Rec EA + Asorbic Acid 15%	3.50	4.04	9.96	126	135	-15	4011
HMTD Rec EA + deoxy-D-ribose 15%	6.49	12.61	1.39	126	135	-15	1514
HMTD Crude + KH2PO4 15%	5.72	2.16	11.84	163	165	4	2064
HMTD Rec EA + NaHCO3 15%	8.37	6.35	7.65	151	154	4	2843
HMTD Rec EA + Saccharin 15%	3.10	11.68	2.32	139	146	-4	2377
HMTD Crude + 2ul pH7 Buffer	7.00			134	137	-13	3309
HMTD Crude + 2ul pH10 Buffer	10.00			137	139	-11	3088
HMTD Crude + NaOH 15%	12.11	14.00	0.00	160	161	0	2286
HMTD Crude + NaOH 30%		14.00	0.00	162	164	3	2102
HMTD Rec EA + Acetamide 15%	7.08	15.10	-1.10	135	136	-14	2177
HMTD Crude + Potassium Tertbutoxide 15%	11.72	17.00	-3.00	159	160	-1	2244

Table 1: Summary of DSC of HMTD with Various Additive (Scan Rate 20°/min).

HMTD Crude	93.3
+ 15% NaHCO3	86.7
+ 15% citric acid	20.0
+ 200 uL 50% hydrogen peroxide	22.9
+ 200 uL H2O	53.6
+ 10% NaHCO3	62.6
N2 purge	49.8

Table 2: Remaining HMTD (crude) after 1 Week 60°C 30% Relative Humidity.

A.2 Fuel-oxidizer mixtures: their stabilities and burn characteristics

A.2.1 Objective

In fuel-oxidizer explosives, it is important to understand the range of useful oxidizers, the effects of various fuels and to be able to catalog results of laboratory-scale tests with the long-term goal of correlating these tests to real-world performance.

A.2.2 Executive summary

Differential scanning calorimetry (DSC) and simultaneous differential thermolysis (SDT) were used to compare the thermal stabilities of eleven solid oxidizers (i.e. $KClO_4$, $KClO_3$, NH_4ClO_4, KNO_3, KNO_2, NH_4NO_3, KIO_4, KIO_3, $KBrO_3$, $KMnO_4$ and $K_2Cr_2O_7$), both neat and with various sugars. General observations include: 1) There was wide variability in DSC results, even within a given batch; 2) There was surprisingly little difference in the DSC traces of oxidizer mixes with 50wt% sucrose and those with 20wt% sucrose; 3) SDT traces often differed markedly from those of DSC; and 4) In many cases, decomposition of the mix was linked to phase change of one or both components. Interestingly, the neat oxidizers appeared to undergo decomposition roughly in line with their standard reduction potentials. Hot-wire ignition tests were performed, but to date no strong correlation with thermal stability tests have been observed.

A.2.3 Background

Inorganic oxidizers find applications ranging from oxygen sources to sources of energy and propulsion. Examples include ammonium perchlorate with hydroxy-terminated polybutadiene for rocket fuel and ammonium nitrate with fuel oil for commercial mining. Many of these formulations have also found illicit use [6]. We have selected a number of solid oxidizers of varying oxidizing power to test on the lab-scale in mixtures with various sugars. The objective was to test for hazardous behavior and threat potential and to evaluate the usefulness of small-scale tests. Many of the oxidizers were oxy halide salts. These anions, with the highly oxidized central atoms, tend to be useful oxidizing agents which work most effectively in acidic solutions. The potassium, rather than the sodium, salts were used, since formulations with potassium cation tend to be less hygroscopic than those of sodium. The ammonium salts have different chemical behavior than potassium salts of the same anion because they carry and use, if required, their own fuel. Our initial choice of fuels was limited to sugars. These melt at relatively low temperatures. The oxidizer-fuel mixtures were prepared in 50/50 wt% and 80/20 wt% ratios. These fuel-rich mixtures are typical for pyrotechnic formulations and the oxidizer-rich mixtures in explosive mixtures.

In an effort to compare oxidizing power, we used standard reduction potentials (Volts, 1M aq solution against standard hydrogen electrode) of oxidizer [7]. These are shown in Table 3 starting on the left with species having most positive potential, noting that actual potentials depend on the pH of solutions and final products. In addition, the weight percent oxygen of each species was calculated and shown in Table 3.

Oxidizer	KIO_4	$KMnO_4$	$KBrO_3$	$KClO_3$	$K_2Cr_2O_7$	NH_4ClO_4	$KClO_4$	KIO_3	KNO_3	NH_4NO_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
wt % oxygen in oxidizer	28%	25%	29%	39%	16%	34%	46%	22%	40%	20%	28%

NO_3^- -> NO, HNO_2, NH_4^+, NO_2 0.96, 0.94, 0.87, 0.80 respectively

Table 3: Standard Reduction Potentials in Volts & Oxidizer Content for Oxidizers.

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 [8]. In our burn tests, 250 mg, instead of 30g, and sucrose or aluminum powder were used instead of cellulose (Fig. 5 on the next page). Response to hot-wire ignition was assessed by the length of the burn and the light output. Table 4 on the next page orders the oxidizers left to right, as highest oxidizing power to lowest in terms of electromotive potential. This trend is roughly followed by burn time; either measured by eye or light sensitive detector. Fastest burn time oxidizers are on the left (highest oxidizing power) and those with longest burn times are on the right. Light output, when the fuel was sucrose, did not show a clear trend.

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	--	0.2	--	0.4	1.7	0.8	0.4	0.4	0.7	2.7	0.3
Ave Burn Time Thor Labs (s)	0.2	2.1	0.4	1.0	--	3.5	2.7	--	--	--	1.0
Std. Dev	0.1	0.3	0.1	0.3	--	0.6	0.8	--	--	--	0.2
Ave Peak Light Signal Thor Lab (mV)	56	25	346	104	--	3	11	--	--	--	32
Std. Dev	29	6	98	43	--	1	4	--	--	--	12
Notes	purple flickering	orange flame	purple flame	purple flame	charring, no flame	yellow flame	purple flame	charring, no flame	charring, no flame	dim yellow flame	yellow flame

Table 4: Hot Wire Burn Times.

Thermal stability is often assessed by the temperature at which heat release is observed in a differential scanning calorimeter (DSC) or by simultaneous differential thermal analysis (SDT), which runs thermogravimetric analyzer (TGA) and DSC at the same time. For DSC analyses, the exothermic peak onset, peak maximum and heat release are usually recorded. The higher the exotherm temperature, the more thermally stable the species is considered, and the larger the heat release the more energetic. TGA indicates at what temperature during the thermal scan the sample loses weight. One advantage of SDT thermal analysis was that it allowed scanning to higher temperatures. Since the crucibles were not sealed thermal traces differed markedly from DSC thermal analysis of samples sealed in glass micro-ampoules. For example, the exotherm in the AN thermal trace at 316°C in SDT became an endotherm at 292°C due to the volatilization of the AN. This same observation was made with a number of compounds and formulations.

Figure 5: The hot wire setup.

A.2.4 Oxidizer salts

The thermal traces of the oxidizers alone were not simple. They included phase change(s), decompositions and heats of fusion (i.e. melts) of the decomposition products. For example, KNO$_3$ undergoes an orthorhombic to rhombohedral transformaion at ~130°C and melts (333-334°C) to a liquid stable to 550°C. Some salts, such as EO$_4$, undergo intra-conversion with the related oxide EO$_3$, where E = Cl or I (eq 1, 2). For example, periodate decomposed to iodate about 330°C and thereafter their thermograms were identical [9-13]. Use of the open pans in the SDT complicated thermal scans with vaporization of some components competing with decomposition. Neat oxidizers appeared to undergo decomposition roughly in line with standard reduction potentials (Table 5) although a few decompose endothermically. Most of the oxidizers produced some heat when decomposed without fuel, but it is a few hundreds of Joules per gram compared to 1500 to 3000 J/g when decomposed with sugar. The exceptions, of course, are the ammonium salts which produce 1000 to 1500 J/g without fuel and double that with fuel.

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
Decompostion °C alone	350	305	446	590	398	404	653	553	702	316	424, 930
J/g heat flow	85	145	230	450	186	1081	266	609	433	1407	80, 178

Red DSC values indicated exothermic; and blue endothermic.

Table 5: Summary of Principle DSC Exothermic (red) or Endothermic (blue) Peaks & Heat (J/g).

The oxides of chlorine released the most heat which is in line with the general trend that the larger the electronegative difference between oxygen and the central element, the more stable the oxy-halide. This order of stability was attributed to the degree of pi-bonding in each species: ClO$_4$- > ClO$_3$- and NO$_3$- > NO$_2$- [14-

15]. Among the oxo-chlorine or oxo-nitrogen species, perchlorate and nitrate are more stable than the less highly oxidized chlorate and nitrite. Chlorates are generally more sensitive than perchlorates. If oxygen is not allowed to escape, the pairs nitrate/nitrite, perchlorate/chlorate, and periodate/iodate can establish a psuedo-equilibrium (eq 1-2) [14].

$$KClO_4 \leftrightarrows KClO_3 + 0.5\ O_2 \qquad\qquad (1)$$

$$KClO_3 \leftrightarrows KCl + 1.5\ O_2 \qquad\qquad (2)$$

Figure 6 shows ammonium perchlorate (AP, NH4ClO4) as an example. It exhibited an endotherm around 245°C (~70 J/g) as a result of an orthorhombic to cubic phase change. Continued heating of AP in a sealed DSC ampule resulted in a single exotherm which began around 350°C and reached a maximum about 400°C (~1300 J/g). The SDT results appeared quite different. Immediately after the 245°C phase change, a small exotherm (~360 J/g) at ~318°C was observed with a second endotherm centered on 435°C. This apparent difference in AP behavior has been explained by the sublimation of AP above 350°C competing with its decomposition. In the sealed DSC ampule, AP did not sublime [16]. As heating of the open pan in the SDT was continued, a small endotherm at 757°C was observed, the melt of KCl.
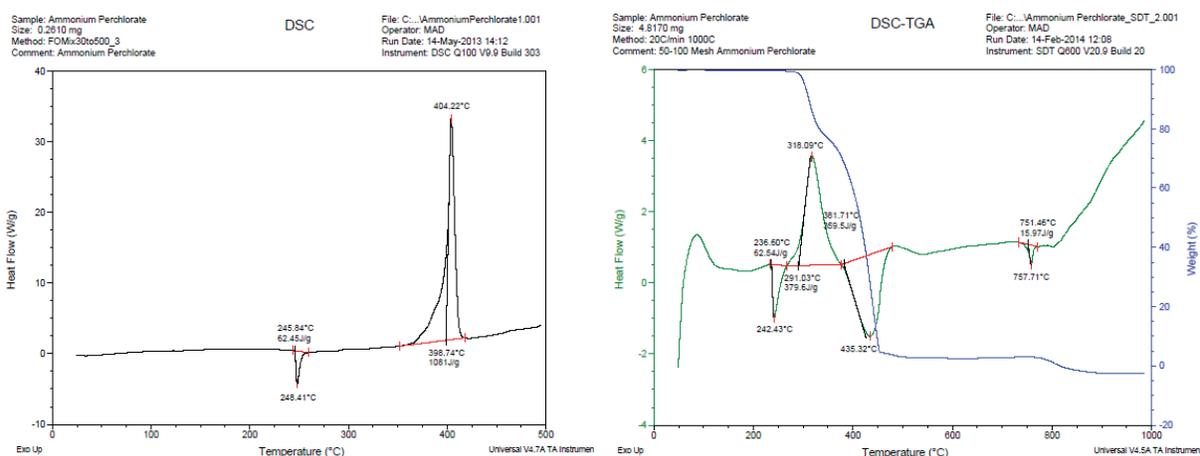

Figure 6: Ammonium Perchlorate DSC (left) vs SDT (right).

A.2.5 Fuel/oxidizer mixtures

The monosaccharrides, glucose and frutose, and the disaccharides, sucrose (glucose and fructose) and lactose (glucose and galactose), were examined as mixtures with oxidizers. The disaccharides and glucose alone exhibited endotherms around 150-176°C, while for frutose the endotherm was at lower temperature 128°C. When these sugars were added to the oxidizers the thermograms were more complex. Of interest, DSC thermograms of most of the sugar/oxidizer mixtures appeared similar regardless of whether 20wt% or 50wt% sucrose was added or which sugar was used. Not surprisingly, comparing the DSC traces of samples with 50wt% sucrose additive to those with the more stoichiometric 20wt% sucrose, we found a larger exotherm immediately after the melt of the sucrose-around 160-170°C. We assume this to be related primarily to the degradation of excess sucrose.

For a single oxidizer compared among the sugars—sucrose (m.p. 173°C), fructose (m.p. 128°C), lactose (m.p. 151°C), and glucose (m.p. 165°C)--the most noticeable difference is related to the melting point (m.p.) of the sugar. For many of the oxidizers, melting of the sugar triggers reaction with the oxidizer; thus, when oxidizer was mixed with low melting fructose, it decomposed at lower temperature than when mixed with higher melting sugars. (see Fig. 7 (top) to Fig. 8, on the next page).
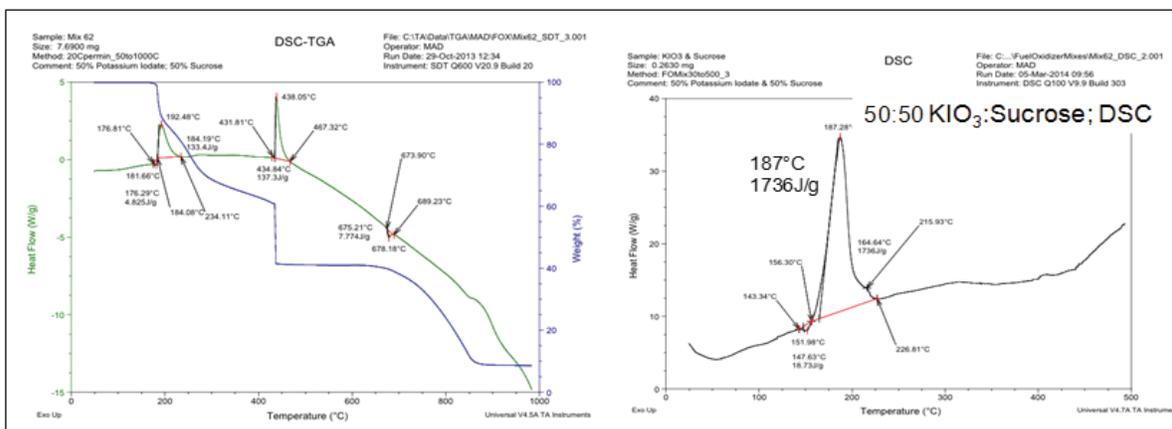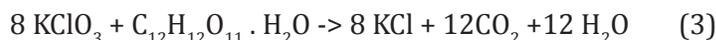
Figure 7: Examples of Effect Sucrose Content for KClO₃/sucrose (top) & AN/sucrose (bottom).

Figure 8: DSC traces for KClO₃ with various sugars.

Difference were observed when comparing DSC (i.e. sealed micro-ampules) versus SDT (i.e. open pans), for example, Figure 9 on the next page. The differences between DSC and SDT traces appeared to be related to the ability of reactants/products to vaporize in the SDT open containers. Evidence for this interpretation was three-fold: 1) sometimes exotherms in DSC samples appeared as endotherms in SDT samples; 2) some promenent DSC exotherms were split into two exotherms due an overlapping endotherm observed in the SDT run; and 3) total heat released was usually lower in the open crucible SDT samples than in the closed DSC capillary tubes.

Figure 9: Comparing SDT (left) vs DSC (right) of KIO$_3$/sucrose.

DSC heat release values showed large variations sample to sample. Some of the variation in heat release may result from poor mixing despite the use of an acoustic mixer. However, in the past we have found that even scanning neat ammonium nitrate resulted in 15% variation. We suspect that with energetic materials, it may be difficult for the thermocouples to accurately track the very fast release of heat. Nevertheless, the poorest oxidizer in terms of heat release was potassium dichromate with roughly 100 to 200 J/g heat release with the sugars. The rest of the oxidizers released heat ranging from 1100 to 2200 J/g with an average of 1500 J/g regardless of the sugar. Of those oxidizers, nitrite released the least heat ~1000 J/g, while the two ammonium salts released the most heat (~2000 J/g).

For the systems examined, the reaction of the fuel and oxidizer was often triggered by phase changes of one of the components: either solid-liquid or solid-solid. Furthermore, there was often an exotherm around 300-350°C, where KIO_4 and $KMnO_4$ decompose and KNO_3, KNO_2, $KClO_3$, and $K_2Cr_2O_7$ experience phase changes or melts. For KIO_4 the 350°C exotherm signaled its decomposition. For the neat oxidizer this decomposition was conversion into KIO_3, the rest of the thermal scan (up to 1000°C) was identical to that observed for KIO_3. Decomposition of the 50/50 chlorate/lactose mixture has been examined in detail [16]. As in this study, perchlorate formation was not observed. Interconversion of oxidizers becomes unimportant compared to the reaction with the fuel (eq. 3). It is speculated that the decomposition of the chlorate was initiated when molten lactose partially solubilizes $KClO_3$. Solvents with OH groups, like the sugars, readily dissolved chlorate. This observation may extend to a number of oxidizers.

$$8 \text{ KClO}_3 + \text{C}_{12}\text{H}_{12}\text{O}_{11} \cdot \text{H}_2\text{O} \rightarrow 8 \text{ KCl} + 12\text{CO}_2 + 12 \text{ H}_2\text{O} \qquad (3)$$

B.   Major Contributions

Physical properties are used by forensic labs, including U.S. military labs overseas, and by vendors of explosive trace detection instruments. Elucidation of destruction techniques aids those in the laboratory who have small amounts to dispose of and the EOD (explosive ordnance disposal) community which occasionally finds improvised materials they can't "blow in place." Safe handling benefits all.

C.   Future Plans

Both projects—characterizing HMTD and FOX mixtures—have just begun. We hope to determine the mechanism by which HMTD decomposes. The thermal properties of the FOX mixtures are being characterized, we hope to relate this data to burn characteristics and friction sensitiveness. We also hope to benchmark explosive performance to small-scale test (see Project Report R1-B.1).

C.1 Safe handling of Hexamethylene Triperoxide Diamine (HMTD)

There are many mysteries that need be resolved in this story. In some cases, acids and, in other cases, bases accelerate decomposition of HMTD (Table 1 in section A.1.5). The chromatograms of decomposed HMTD contain unidentified species as well as hexamine. If hexamine is formed, it questions recently published formation mechanisms [17]. As with TATP, it is necessary that we completely understand conditions of formation and decomposition before we are able to devise gentle destruct methods and make reasonable approaches to blocking its synthesis.

C.2 Fuel-oxidizer mixtures: their stabilities and burn characteristics

That a phase change may trigger the fuel-oxidizer reaction requires further investigation, especially since the goal of this study is not only to understand the specific fuel-oxidizer system examined but to recognize trends found in laboratory-scale tests that may predict behavior at full-scale. Thus, this study will be extended to fuels beyond sugars and possibly to other oxidizers and definitely to other analysis methods.

IV.   EDUCATION & WORKFORCE DEVELOPMENT ACTIVITY

Each URI project supports one or more graduate students. (See listing with projects.) This is their best learning experience. Undergraduates are also supported on the projects as their class schedules permit.

This will be our 4th summer to host a Minority Serving Institute (MSI) professor. Polymer work was shared with our MSI (minority serving institute) professor (Dr. Gan) and his student. It resulted in one paper and follow-on funding for Dr. Gan at California State University Pomona. Working with the interaction of explosives with polymers has been a particularly useful area to share with our MSI professors. This allows them to return to an institute where they cannot work with explosives and perform meaningful follow-on research.

Every summer our Center funds are used to support high school teachers. They conduct research in URI labs under the mentorship of a graduate student. The teachers worked fulltime for 8-10 weeks. In addition, this summer (2014) we have 2 forensic scientists from Qatar and 2 professors and their students from West Point.

Eight professional classes were offered so far in 2014, providing training for well over 160 professionals. For over a decade we have offered classes to DHS and its components. Since 2014 we have offered three week-long courses with lecture and labs to TSA.

K-12 outreach continues to be hosting high school teachers in the summer and providing chemical magic shows at schools K-12.

V.   RELEVANCE AND TRANSITION

A.   Anticipated end-user technology transfer

In 2007, URI established a database of explosive properties. This is a convenient repository for this data. We have 600 registered users with over 100 joining this year. It is used throughout the explosive community—forensic labs, federal facilities, manufacturers of ETD instruments, trainers of explosive detection canines. Data is also released by publication and lectures.

VI.   LEVERAGING OF RESOURCES

We have had one offer to purchase our database and one offer to license it, but for security reasons, neither of these options was considered.

VII.   PROJECT DOCUMENTATION AND DELIVERABLES

A.   Peer reviewed jounral articles

1. Oxley, J.C.; Smith, J.L.; Brady, J.; Steinkamp, F.L. "Factors Influencing Destruction of Triacetone Triperoxide (TATP)," Propellants, Explosives, Pyrotechnics, 2014, 39(2), 289-298.

2. Oxley, J.C.; Smith, J.L.; Steinkamp, L.; Zhang, G. "Factors Influencing Triacetone Triperoxide (TATP) and Diacetone Diperoxide (DADP) Formation: Part 2," Propellants, Explosives, Pyrotechnics, 2013, 6, 841-851.

3. Oxley, J.C.; Smith, J.L.;Vadlamannati, S; Brown, AC; Zhang,G.; Swanson, D.S.; Canino, J "Synthesis and Characterization of Urea Nitrate and Nitrourea;" Propellants, Explosives, Pyrotechnics, 2013, 38(3), 335–344.

4. Oxley, J.C.; Smith, J.L.; Bowden, P.; Ryan Rettinger "Factors Influencing TATP and DADP Formation: Part I" Propellants, Explosives, Pyrotechnics 2013, 38(2), 244-254.

B.   Other Presentations

1. Seminars

    a. Sensitivity and Stability of Fuel Oxidizer Mixtures J.C. Oxley; J.L. Smith; M. Donnelly ISICP; Poitiers; June 2014

    b. Peroxide Explosive-J.C. Oxley; J.L Smith; P. Bowen; J Brady; L. Steinkamp; J Canino ISICP; Poitiers; June 2014

    c. URI Explosive Research" Ludwig-Maximilian University of Munich: June 2014

    d. TED Conference "Explosive-Polymer Interactions"-J Oxley, J Smith, J Canino, D. Swanson, G. Zhang, Charlottesville, NC; April 8-11, 2014

    e. TED Conference New Approaches to Swabbing-J. Canino, J. Smith, J. Oxley Charlottesville, NC; April 8-11, 2014

    f. ISADA: "Taming the Peroxides and Other HME" J. Oxley Oct, 2013 Den Haag

    g. NATAS "Thermal Impact vs Sensitivity?" Aug. 4, 2013; Bowling Green, KY

2. Short Courses

    a. Fundamentals of Explosives Jan, May 2014

    b. Explosive Safety for Technicians Feb 2014

    c. Fundamentals of Explosives for TSA-Explosive Specialists Feb, April, May 2014

    d. Combustion March 2014

    e. Fundamentals of Explosives for EOD Mar 2014

    f. IABTI Regional Meeting; "Explosive Short Course" Colorado Spring; CO Sept 17, 2013

3. Briefings

    a. Safe Training Aids for Bomb-Sniffing Dogs--Eighth Annual National Security Innovation Competition-J. Canino, J. Oxley, J Smith April 2014

    b. Alpha Chi Sigma "Explosive Studies for Safety & Security" Oct. 26, 2013; URI

    c. Studying Energetic Materials for Safety and Security-J. Oxley Springfield College; April 2014

4. Invited Lectures

   a. Energetic Materials Needs and R&D Goals GRC June 2014

   b. Plenary Lecture: "Explosive Detection: How We Got Here and Where are We Going?" International Symposium on Chemical Propulsion & Energetic Materials June 2-6 2014; Poitiers, FR

   c. "The Explosive Threat" McCabe Lecture Springfield College, MA April 2, 2014

   d. Alpha Chi Sigma "Explosive Studies for Safety & Security" Oct. 26, 2013; URI

   e. ADSA (Algorithm Development for Security Applications Workshop), "Addressing Issues with Sample Collection" Oct, 22, 2013; Boston

   f. CT Valley ACS "Explosive Research for Safety and Security" Oct 17, 2013

   g. ISADE "The Explosive Threat: Is there Something New Under the Sun?" Oct 8, 2013 Den Haag, Netherlands

   h. FACSS/SciX "Taming the Peroxide Explosives and Other HME;" Milwaukee; Oct 2 2013

C.   Student theses or dissertations produced from this project

1. "Energetic Salts: Degradation & Transformation," Sravanthi Vadlamannati, PhD dissertation in Chemistry, June 2013

2. "Transfer of Residue in Fingerprints," Morgan Turano, MS Thesis in Chemistry, Sept 2013

D.   Transferred Technology/Patents

1. Patent Applications Filed

   a. Non-Detonable Explosive or Explosive-Simulant Source J Oxley, J Smith, J Canino

   b. Non-Contact Collection of Explosive Residue Source J Oxley, J Smith, J Canino; G. Kagan, Compositions for Security-Safe Hydrogen Peroxide   J Oxley, J Smith, J Brady

   c. Melt Castable Explosive Formulations Containing Erythritoltetranitrate J Oxley, J Smith; A Broun, R Rettinger

E.   Software Developed

1. Databases

   a. Explosive Database founded 2007 ~ 600 registration, 119 between Ap 24, 2013 – Feb 7, 2014

F.   Requests for assistance/advice

1. From DHS

   a. Several requests about threat compounds—confidential

VIII.   REFERENCES

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