F1-A1: Synthetic routes to new and improvised high explosives

Abstract — The project deals with alternative routes for synthesis of triacetonetriperoxide (TATP) without the use of liquid peroxides. The research aims to explore commonly available chemicals which can be used as precursors along with 'over the counter' materials which have the ability to produce TATP. One of the most promising chemicals for the synthesis of TATP are percarbonates giving yields higher than with liquid peroxides Commonly available cleaners containing percarbonates were investigated. Full analytical characterization of these materials; x-ray diffraction (XRD), nuclear magnetic resonance (NMR), mass spectrometry, thermo-gravimetric analysis (TGA) is being conducted. This effort will be conducted in close collaboration with ALERT partners. We are also closely coordinating with industrial contacts from the United States, Canada (University of Alberta), and Europe (Cambridge University). Transition and accomplishments of previous efforts will also be described. The relevance to the DHS for this work is to readily identify new precursors for the synthesis of illicit explosives.

I. PARTICIPANTS

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II. PROJECT OVERVIEW AND SIGNIFICANCE

The objectives of this work are to:

1) Determine alternate sources of peroxide precursors which can be used to synthesize explosives beyond hydrogen peroxide.

2) Provide a technical capability of chemical synthesis of energetic compounds to all ALERT team members. Explosives synthesis, characterization, forensic analysis, and even detonation experiments can be conducted at TTU.

III. RESEARCH AND EDUCATION ACTIVITY

A. State-of-the-Art and Technical Approach

The easily prepared improvised explosive triacetonetriperoxide (TATP) has garnered substantial interest because of the threat it poses in the hands of terrorists and the inherent challenges in sensing it. Typically, TATP is precipitated from aqueous solution as a kinetic product. The sensitivity characteristics of TATP are also known to be unpredictable, which further complicates safe handling and disposal of this material. Several studies have investigated the product composition of this reaction with varying acid catalysts and reaction conditions [1]. Recently, Keinan et al. found that this kinetic synthesis produces concomitant polymorphism of TATP, which is sensitive to the acid used to catalyze the reaction [2].

We have been interested in studying the factors which influence the sensitivity characteristics of energetic materials with the aim of generating safer materials, or at least better defined storage and handling methods. [3-6] Because of this work, we became interested in standardizing our preparation of TATP in order to reproducibly generate specimens with the same physical and chemical characteristics. One source of variability in the preparation of TATP is the aqueous hydrogen peroxide, which diminishes in oxidizing strength as it ages. In order to develop a more reliable standard procedure, we adopted the use of sodium percarbonate as the source of oxidant, since this material can be stored until use without degradation. Upon examining the product of the TATP synthesis from percarbonate by powder X-ray diffraction (PXRD), it became clear that the product was not a mixture of concomitant polymorphs as in the case of the conventional syntheses using aqueous hydrogen peroxide [2]. Instead, a single polymorph was identified by PXRD. This observation led us to examine the influences of our reaction conditions on the solid state structure of the products and their resulting stability.

In the summer of 2012, Texas Tech participated in the DHS Minority Serving Institution Summer Research Team. Dr. Conrad Jones, an Assistant Professor at Southern University in Baton Rouge, Louisiana, spent 10 weeks at Texas Tech working on synthetic pathways of energetic materials. In addition, Dr. Jones brought one undergraduate student (Ms. Danielle Moses) who is working on low density materials. Ms. Moses has already indicated that she intends to apply to graduate school at Texas Tech. Upon completion of the Summer Research Team program, the Minority Serving Institution has an opportunity to apply for DHS funding to continue the collaboration. The ALERT team will work diligently with Dr. Jones to make this a reality. We anticipate having full details of this summer interaction in the next annual report.

B. Major Contributions

Percarbonate synthesis of TATP. A Journal of Chemical Education article previously investigated the use of laundry percarbonate as an oxidant source in organic oxidations for undergraduate teaching labs. this article and its supplemental information provide a useful summary of the potentially applicability of different commercial products for illicit TATP synthesis. Sodium percarbonate, a well-known source of hydrogen peroxide, was selected as a shelf-stable oxidant in the synthesis of TATP. Sodium percarbonate is a perhydrate, meaning that instead of waters of hydration, there are hydrogen peroxides of hydration co-crystallized within the sodium carbonate lattice. These molecules of hydrogen peroxide are liberated upon dissolution of the sodium percarbonate. Sodium persulfate failed to yield any precipitate under analogous TATP synthesis conditions. Sodium perborate tetrahydrate failed due to its relatively low solubility in water. Since sodium percarbonate is basic and the formation of TATP is acid catalyzed, its use as a peroxide source in the preparation of TATP requires that it first be neutralized and then acidified. Here hydrochloric acid was used. After dissolution, neutralization, and acidification of the sodium percarbonate in aqueous solution, addition of acetone resulted in the precipitation of a fine white powder with energetic properties. NMR spectroscopy confirmed the identity of the species as TATP. Examination of the powder X-ray diffraction (PXRD) pattern revealed this material to be a phase pure specimen, by comparison to the PXRD patterns calculated from single-crystal X-ray structures. Figure 1 shows the PXRD patterns from the TATP synthesized. The material synthesized is shown in the top pattern. 1a-b are database structures with 1a being the most stable. It is important to note that there are 6 polymorphs of TATP. Our material matches a less stable form (1b), which is surprising, but is hypothesized to be due to the ionic strength. This might be a useful tool for source attribution of TATP since synthesis protocols appear to determine the polymorph generated.

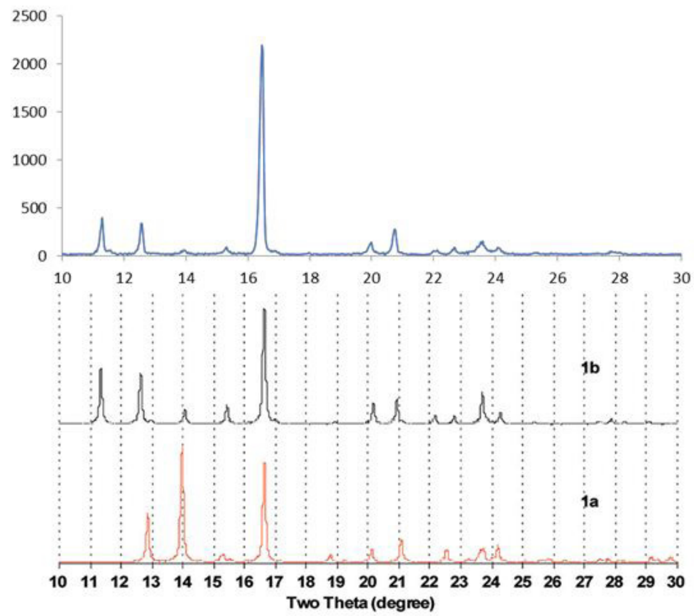

Figure 1: Comparison of experimental TATP PXRD pattern from high ionic strength solutions (top) and calculated PXRD patterns from the SCXRD structures Polymorph 1a is the most stable polymorph formed upon sublimation of TATP.

Figure 2: The three cleaning agents used in the initial work to determine which can be readily used to produce TATP. Only Oxy-Boost produced TATP.

We have also confirmed that the TATP synthesis works when using Oxy-boost as a commercial oxidant. Oxy-boost is available for discrete purchase online (20 lbs/$60.00). LA's Totally Awesome Oxygen Based Cleaner and Oxiclean Baby Stain Soaker did not generate TATP, even though these cleaners worked for the organic reaction described in the J. Chem. Ed. Paper, which indicates that the TATP synthesis may require a substantially potent oxidant to work effectively. Figure 2 shows the pictures of the cleaners used.

Increasing the ratio of Na2CO3 : Na2CO3 ½ H2O2 renders the synthesis of TATP unsuccessful. Since all the cleaners are not pure sodium percarbonate, rather they are a mixture of with sodium carbonate, we hypothesized that a critical amount of sodium percarbonate was necessary to produce TATP. This was tested by both testing the TATP formation by both synthesis from the commercial cleaners for which the carbonate/percarbonate ratio is reported and also by mixing different ratios of carbonate/percarbonate in the laboratory. The yields of the lab mixed percarbonate:carbonate ratios match those of the neat compounds well. This indicates that TATP synthesis may be mitigated by the use of an adulterant material such as sodium carbonate. See Table 1 for carbonate/percarbonate ratios and corresponding TATP yields.

We attempted to leach the peroxide out of the percarbonate by allowing it to soak in acetone overnight, centrifuging, and decanting the acetone. The question to be addressed is whether it is possible to concentrate the percarbonate which can then be used for synthesis of TATP. This was a preliminary study and initial results did not produce TATP which may indicate the carbonates are suitable adulterants to prohibit TATP synthesis.

IV. FUTURE PLANS

In search for alternate sources of peroxide to make TATP, a search was performed including all of the peroxide containing compounds used in industry. Note: the naming system is different in the encyclopedia from common chemical names.

The list includes:

1. peroxides, hyperoxides, and ozonides of the alkali and alkaline earth metals
2. Peroxoacids and their salts:
   a. Sodium peroxoborate:

b. Peroxosulfuric acids:

c. Peroxophosphoric acids and their salts

3. Hydrogen Peroxide Additions

a. Percarbonates

b. Urea peroxohydrate

The primary focus in the first year was on hydrogen peroxide additions, specifically percarbonates. Since these produced significant results, our next focus will be on Urea Peroxohydrate (UP). UP is also commercially available and is a very strong oxidizer. It is most commonly found in tooth whitening agents and as a solid bleaching agent. In the next year we will continue the synthesis aspect of this worked expanded to these peroxide formers found. Another strong contender is the Peroxophosphoric acids and their salts. Oxone is another commercially available chemical used in cleaners and for water purification. Precedence exists in the literature for the formation of TATP from Oxone but conditions for this reaction are not well documented. The final deliverable of this work will be to create a database of known peroxide formers which yield TATP and other peroxide based explosives.

V. RELEVANCE AND TRANSITION

Prior to transitioning this work to alternative pathways for TATP synthesis, the project focus was on thin films and vapor pressure equilibria. The results from previous studies on the thin films have been shown to be relevant to the outside community including thin film semiconductor processing. In fact, the first Ph. D. student working on the thin film (Gengxin Zhang) is now a group leader at Intel (AZ) in the Packaging Division. The results have also been shown to be relevant to the Army which has a program in high explosives. The Army's goal is to make miniature detonators and our work on the microstructure of the explosives is extremely important for this application. We have been invited to a DoD workshop in both 2010 and 2011 and are one of only two Universities involved. This project is also directly relevant to the DHS in developing better collection techniques. We are not only focused on the wipe, rather we also look at the most effective surfaces to swipe on a passengers bag for example.

The vapor pressure studies yielded a new optical technique for determining vapor pressure of energetic and other materials. Previous methods relied exclusively on gravimetric techniques while our current method is stand-off. Initially, we believed this technique would be useful for stand-off determination of vapor pressures of materials but the signal to noise drops exponentially with increasing distance. This project has been transitioned to a newly funded project to expand the technique to materials beyond explosive and we are working with a company to commercialize the product. Current funding for this project is $1M.

From *J. Chem. Ed.* Supplemental Information % Percarbonate

Oxy-Boost:68.3%	OxyClean:56.9%	LA's: 55.1%
TATP from Oxy-Boost • 30mg • 25mg	TATP from OxyClean Baby Stain Soaker •2.7mg •0mg	TATP from LA's Totally Awesome Oxygen Based Cleaner •0.0mg •0.0mg
TATP from 68.3% Percarbonate:Carbonate •25mg •19mg	TATP from 56.9% Percarbonate:Carbonate 1.3mg 0.0mg	TATP from 55.1% Percarbonate:Carbonate 0.0mg 0.0mg

Table 1: Gives the concentration of percarbonate in each of the cleaners; yield of TATP from the 'neat' cleaner; and yield from a lab produced mixture of percarbonate:carbonate.

Two patents have been applied for. One on a thermal drop hammer apparatus to investigate thermal initiation and a second on a new class of materials identified in F1B. Lawrence Livermore and Texas Tech will jointly apply for the patent.

The work specific to TATP synthesis is expected to be transitioned directly to the DHS and first responders. The goal is to produce a database of known peroxide formers which can be used for TATP or other peroxide based explosives synthesis. We have shared some of these new synthetic pathways with local first responders and are even performing training with the local bomb squads on both large scale explosives and small scale synthesis (described more in the next section).

VI. LEVERAGING OF RESOURCES

The DHS project has been instrumental in building new relationships with companies, local and federal agencies. We have built a good relationship with MRI Global (Kansas City, MO) and have received approximately $500K for CBRNE research and training workshops. This is to support an OCONUS project. This specific project has ended with the drawdown of assets in the Middle East. However, in 2011 we started a new collaboration with Rocky Mountain Scientific who have come to use facilities at Texas Tech made possible by ALERT funding. The current project is a DOJ funded opportunity investigating ammonium nitrate. Outreach with local first responders has been a very strong point of this project. We have worked with the Lubbock County Bomb Squad since the inception of ALERT on training. In May 2011, we had a West Texas wide range day. We were able to attract ATF, DHS, Bomb Squads from as far away as Dallas (350 miles). Representative pictures are in Figure 3.

In 2012 we have commitments to work with a group of West Texas Bomb Squads (Midland-Odessa, Lubbock and Amarillo) to observe the synthesis of TATP and produce materials for canine training. The final date has not been set but is expected to be in August 2012. In July 2012, we participated with the Lubbock Swat team training on the use of bullet sensitive ammonium nitrate (Tannerite). Texas Tech provided all the targets used in this exercise and the Lubbock bomb squad/SWAT team is now trying to incorporate bullet sensitive targets into training scenarios since the explosives are legally sold at local sporting goods stores. One aspect of the July 2012 training was that tannerite explosives were incorporated with various other explosives (det. cord, boosters, detonators, etc.) to see if it is possible to use tannerite as a remote detonator through sympathetic detonation (initiated by a bullet). The interesting prospectus is that the detonator would have no electrical or metal components whatsoever, decreasing some signatures for detection. The results from these tests are in but the potentially sensitive nature cannot be disclosed at this time.

VII. DOCUMENTATION

A. Publications

1. O.S. Bushuyev, P. Brown, Maiti A, Gee R.H., Peterson G.R., B.L. Weeks and L.J. Hope-Weeks 'Ionic polymers as a new structural motif for high-energy-density materials' Journal of the American Chemical Society, 134 1422-1425 (2012)
2. O .S. Bushuyev, F.A. Arguelles, P. Brown, B.L. Weeks and L.J. Hope-Weeks 'New energetic complexes of copper(II) and the acetone carbohydrazide schiff base as potential flame colorants for pyrotechnic mixtures' European Journal of Inorganic Chemistry, 29 4622-4625 (2011)
3. G.X. Zhang, B.L. Weeks and M Holtz, Application of dynamic scaling to the surface properties of organic thin films: Energetic materials' Surface Science, 605 463-467 (2011)

B. Technology Transfer

1. A patent disclosure has been submitted related to the thermal drop hammer test in 2010.

Figure 3: May 10th at the Texas Tech range. Approximately 30 local first responders attended.

2. A patent disclosure on NHP, prepared by Lawrence Livermore, was submitted in 2011.

C. Seminars, Workshops and Short Courses

1. North American Thermal Analysis Society Annual Meeting (August 2012) – Weeks and Hope-Weeks are organizers for explosives section – ALERT team members are presenting from URI, UPM, and TTU.
2. SPIE Defense Security Symposium, April 2011 and April 2012

VIII. REFERENCES

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[3] Pitchimani, R.; Zheng, W.; Simon, S. L.; Hope-Weeks, L. J.; Burnham, A. K.; Weeks, B. L., Thermodynamic analysis of pure and impurity doped pentaerythritol tetranitrate crystals grown at room temperature. Journal of Thermal Analysis and Calorimetry 2007, 89 (2), 475-478.

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[6] Yüksel, G. Y.; Titiz, S.; Bulutcu, A. N., Solubility of Sodium Perborate Tetrahydrate in Water and Sodium Metaborate Solutions. Journal of Chemical & Engineering Data 1996, 41 (3), 586-588.