Economical and Innovative Energetics for Stand-off Initiation and Microcharges

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Abstract

We here report two research endeavors toward practical green energetics for standoff initiation:

- **Metal Hydrazine Perchlorates:** we have established the syntheses, structures, and sensitivities of these complexes. Furthermore, collaborators have computationally determined the very high power of these primary explosives. They are formed from simple transition metal perchlorate salts and a common feedstock chemical, hydrazine. They exhibit a low critical diameter and are initiated by very low laser power.
- **Nitrocellulose Aerogels:** we have prepared the first alcogels and aerogels of this common propellant and investigated its microstructure. Suspending carbon nanotubes in the nitrocellulose matrix causes the material to ignite upon exposure to laser light.

Relevance

Understanding the microscopic structure/property relationships and not just macroscopic properties of explosive materials is a matter of foremost importance since energetic performance relies directly on solid state structure. For crystalline compounds, knowing the exact atomic coordinates of a structure allows for implementation of state-of-the-art computational techniques for prediction of energy liberated in the process of explosion. In the case of amorphous materials, microstructural analyses also allow correlation between structure and function. We use these fundamental approaches to understand and design better energetic materials from green and economical precursors.

Technical Approach

Metal Hydrazine Perchlorates

- Syntheses affording diffraction-quality crystals of nickel hydrazine perchlorate (NHP) and cobalt hydrazine perchlorate (CHP), and nickel hydrazine nitrate (NHN) were established. NHN and NHP were known in the literature but their structures were unknown.
- The structures of NHP, CHP, and NHN were determined by single crystal X-ray diffraction to reveal continuous metal hydrazinate polymers.
- In house sensitivity tests indicated that these metal complexes are highly sensitive to heat, flame, spark, impact and laser light and possess very low critical diameters for detonation.
- Based upon the atomic coordinates determined by X-ray diffraction, our collaborators established that these species generate power comparable to modern secondary explosives.

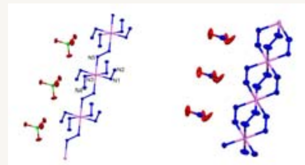

Figure 1: Fragments of the polymeric threads of nickel hydrazine perchlorate (NHP) (left) and nickel hydrazine nitrate (NHN) (right). CHP is structurally analogous to NHP.

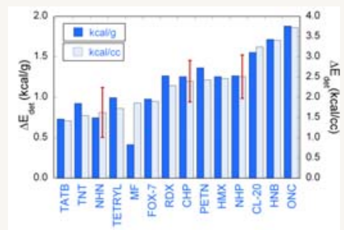

Figure 2: Bar diagram representation of the literature ΔH_{det} values for the eleven HEs along with the predicted ΔH_{det} for NHN, CHP, and NHP. Also indicated are the error margins for the predicted values at the 95% confidence level. Both mass-density (kcal/g) and volume-density (kcal/cc) of the heat of detonation are indicated, and the heats arranged in the increasing order of volume-density (kcal/cc).

Nitrocellulose Alcogels and Aerogels

- Robust alcoholic gels (alcogels) of nitrocellulose were prepared by either partial evaporation of a nitrocellulose solution or gradual precipitation of nitrocellulose by hexanes.
- Stable aerogels were prepared by removal of the liquid from the gel pores by critical point drying with carbon dioxide.
- Thermal analysis demonstrates that the nitrocellulose aerogels display the same thermal properties as bulk nitrocellulose.
- Gas sorption analyses and scanning electron microscopy demonstrate the highly porous nature of the aerogels.
- Suspending carbon nanotubes in the nitrocellulose solution prior to gelation affords laser-sensitive materials.

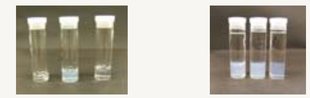

Figure 3: NC alcogels by partial evaporation (left) and by hexane precipitation (right). In both sets, the gels are derived from nitrocellulose solutions containing ethanol, 2-propanol, and 1-butanol solutions, from left to right.

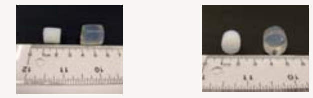

Figure 4: NC aerogel versus NC alcogel

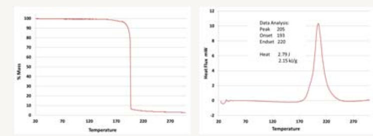

Figure 5: Thermogravimetic analysis (left) demonstrates that the nitrocellulose aerogels autoignite at ~200°C with a clean burn off. Differential scanning calorimetry indicates a heat of combustrion of 2.15 kJ/g. [Scan rate = 5°C /min]

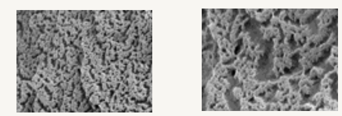

Figure 6: NC gel prepared by evaporation from EtOH/Collodion is characterized by a sponge-like morphology with channels by SEM. Gas sorption analyses indicate surface areas of 280-350 m^2/g depending on preparative technique.

Accomplishments Through Current Year

Crystal structures and theoretical heats of detonation for metal hydrazine perchlorates were determined for the first time. Monolithic nitrocellulose alcogels and aerogels were prepared for the first time. It has been found that both the metal hydrazine perchlorates and nitrocellulose materials can be initiated by laser pulse. Manuscripts disclosing these results are submitted and in preparation, respectively.

Future Work

Future work will be focused on studying and broadening the scope of high nitrogen-containing ligands which can be applied for less sensitive explosive complexes or composition. Loading the nitrocellulose-nanotube composites with high explosives to afford laser-initiatable nuggets with adjustable power will also be studied.

Opportunities for Transition to Customer

The new nickel and cobalt hydrazine perchlorates provide an alternative to lead-based primary explosives. Furthermore, these molecules also provide equivalent amounts of power in a smaller unit of mass, and therefore would provide higher "atom economy" in applications. Their small critical diameters make them suitable for use in microcharges.

Nitrocellulose provides a convenient and economical support matrix for new compositions of explosives. The ability laser-initiate the nitrocellulose aerogels enhances their potential as a functional support medium for standoff initiatable explosives.

Publications Acknowledging DHS Support

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