Energetic Materials: Synthesis to Detonation

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Abstract
Energetics like 2,4,6-trinitrophenol (picric acid) have been around for over a century, and although use as a military explosive has dwindled since World War II, picric acid is a popular choice for armature chemists in part to the ease of production and availability of starting materials. To better understand the threat picric acid presents, five published synthetic routes were studied along with five starting materials. Reactions provided a wide range of conditions in which picric acid could be prepared. Recovered materials were methodically characterized using Raman and Infrared spectroscopies, differential scanning calorimetry, and X-ray analysis.

Characterization of recovered material shed light on the role synthetic conditions and starting materials play in the formation of picric acid as well as unexpected side-products. Generally, synthetic methods which used laboratory style starting materials or reagents produced pure picric acid. An exception to this was a multi-step reaction which, in addition to picric acid, produced lesser nitrated phenols. Methods that used commercially available or "over-the-counter" (OTC) starting materials or reagents like aspirin (acetylsalicylic acid) or a skin treatment powder (salicylic acid) exhibited the most deviation in recovered products. A simple substitution of concentrated sulfuric acid for drain cleaner led to the formation and isolation of 3,5-dinitrosalicylic acid instead of picric acid. Reactions which used potassium picrate as a nitration source saw the formation of the metal salt potassium picrate allowing for the easy identification of method used. Although the reaction types and materials tested were far from exhaustive, this work provides a better understanding of the preparation of picric acid.

There is a dual role that explosive materials must play for military ordnance, which seem to, at times, incompatible. They must be safe to handle, transport, and insensitive to accidental initiation. These same materials must also fully detonate when intended, leaving no unreacted material, and have the highest explosive performance possible. To obtain this goal additives were used to modify explosive behavior of a pressed explosive formulation of 1,3,5-trinitro-1,3,5-triazine (RDX) with polyethylene wax and pressed 2,4-dinitroanisole (DNAN).

Chemically inert additives like glass and polymer microspheres or balloons were tested against microencapsulated pentaerythritol tetranitrate (PETN) and thermally expandable microspheres (TEMs). Additives were incorporated into the RDX formulation, then pressed into 13 mm pellets for detonation testing as rate sticks. Incorporation of additives was assessed via micro–X-ray CT. Explosive tests were recorded by high-speed cameras. The detonation velocity of formulations containing inert additives were compared to those with reactive materials added. Although all additives tested reduced the detonation velocity of formulations compared to the base material, reactive additives allowed for the performance to be tailored. Formulations containing TEMs had a consistent detonation velocity (7.90-7.94 km/s) over a wide range of concentrations (0.5-2.5 % vol). However, after heating to 120°C for 30 minutes, the TEMs would irreversibly expand inside the formulation decreasing the density of the pellet, in turn, lowering the detonation velocity up to 20% for pellets with 20% vol additive. This drastic reduction in detonation velocity allows for the performance of an explosive formulation to be modified after manufacture, a long-sought goal for tunable munitions.

Addition of microencapsulated PETN in formulations had comparable performance to formulations with neat crystalline PETN added. Microencapsulation of PETN reduced the sensitivity of the nitrate ester to impact and friction, lowing the sensitivity of the material from 5.5 J (impact) and 60 N (friction) for the neat PETN, to over 109 J (impact) and 355 N (friction) once microencapsulated. Sensitivity to shock was measured, microcapsules of PETN were packed into a rate sick and shocked by booster pellets of RDX:wax. The reaction light coupled in from booster pellets quicky extinguished roughly halfway through the rate stick (24 mm) indicating that the microcapsules could not sustain a detonation. Pressed RDX:wax formulations that contained microencapsulated PETN performed similarly to those with crystalline PETN added (8.15 km/s vs 8.11 km/s at 5% and 7.83 km/s vs 7.78 km/s at 20%). In the case for pressed pellets of DNAN, microencapsulated PETN stabilized the detonation in the inert material. DNAN with added microencapsulated PETN had a detonation velocity of 5.10 km/s at 5% wt and 5.00 km/s at 20% wt, where neat DNAN would fail to detonate at the same 13 mm diameter scale. Although these mixtures had lower detonation velocities than DNAN mixed with crystalline PETN (5.24 km/s at 5% wt, and 5.30 km/s at 20% wt), microencapsulated PETN did not sensitize the mixture to impact or friction unlike the addition of crystalline PETN. Although in these formulations PETN was only present in very small amounts, in comparison to the bulk explosive, it did contribute to the detonation of tested formulations without sensitization of the formulation to impact or friction.

Initiation criteria of an explosive is of paramount importance. Small changes in pressure or detonation velocity can have a compounding effect. Characterizing and recording explosive events required high precision timing as events occur at rate at, or above kilometers per second. Mixtures of RDX with the tree resin "red gum" at 90:10, 95:5, and 98:8 (by weight) explosive to binder were prepared by dry- or wet-mixing. Coating RDX with red gum did not change the sensitivity of the material to impact or friction and had no effect in thermal decomposition by differential scanning calorimetry. Resulting powders were pressed into 13 mm diameter pellets with densities ranging from 1.628-1.683 g/cc.

Pellets were tested as rate sticks and recorded using high-speed cameras. Particle velocity at end pellets into an acrylic window was observed by photon doppler velocimetry (PDV). Formulations had detonation velocities between 8.04-8.50 km/s, and an output pressure between 24-29 GPa. Use of red gum as a molding powder afforded structurally ridged explosive pellets, with consistent detonation velocities and output pressures, all while not requiring specialized processing facilities to prepare said formulations. Due to the consistency and ease of preparation, RDX:RG is a good candidate for small-scall explosive testing.

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