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Synthesis and Combustion Characteristics of Novel High-Nitrogen Materials

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Abstract
The synthesis of high-nitrogen energetic materials has been of ongoing interest at the Los Alamos National Laboratory (LANL). We have discovered that high-nitrogen materials can offer interesting performance and sensitivity properties not accessible through conventional energetic materials. For example, some of the high-nitrogen materials developed at LANL have extremely fast burn rates and very low dependence of the burn rate on pressure. Examples of this include 3,6-bis (tetrazol-5yl-amino) tetrazine(BTATz) and diaminoazotetrazine N-oxides (DAATOx) materials. In this paper, we will discuss our recent developments in our continuing efforts towards the synthesis of new high-nitrogen materials that feature interesting combustion and explosives properties. In particular, we will describe the synthesis of the high nitrogen materials dinitroazotriazole (DNAT), dinitroazoxytriazole (DNATO) and the corresponding triaminoguanidinium salts (TAGDNAT, TAGDNATO), and present chemical properties such as density, and heat of formation, as well as their sensitivity properties. Thermo-equilibrium calculations (Cheetah Code) were used to predict decomposition products as well as propellant and explosives behaviors. Finally, we will present burning rate data for these new materials.

1 Introduction

The search for new environmentally friendly, high performing energetic materials is of ongoing focus. High-nitrogen materials continue to be pursued as target materials with high potential to meet the current and future needs [1-6]. Interest in high-nitrogen materials is due in large part to the unique energetic materials properties that these materials possess [7-9]. An example of one of these unique properties is seen burn-rate modifying properties of the bis-triaminoguanidinium azotetrazolate (TAGzT) when incorporated into nitramine-based propellant systems. It has been shown that replacement of a portion of RDX with TAGzT in a some types of gun propellant systems leads to a dramatic increase in the overall burn rate of the propellant [10]. Several studies aimed at studying the combustion characteristics of TAGzT and its mixtures with RDX have been reported and insight into the burn-rate modification mechanisms are being elucidated [11].

The burn-rate modifying ability of TAGzT is a very useful property. However, the ability to design an optimized burn-rate modifier from first principles would have a

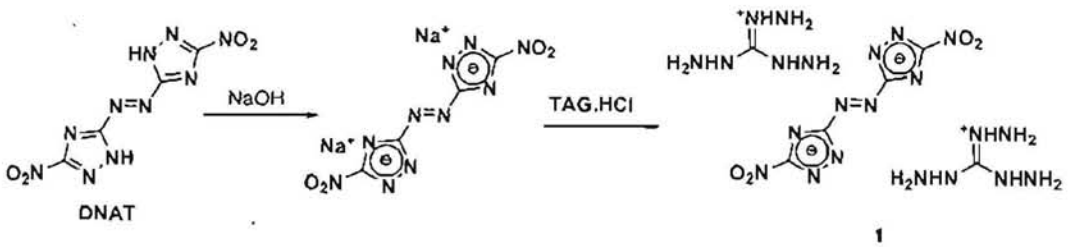
dramatic effect on new material development. In order for first-principle design of materials to become reality several important questions must be answered. As part of our effort to support the development of burn-rate modification in general, we have been studying numerous triamino-guanidinium salts of a variety of heterocyclic anions, investigating structure-function relationships with respect to burn rate modification. This paper describes the synthesis and characterization of several new high-nitrogen materials, including burn rate studies, small-scale sensitivity and thermal analysis.

2 Results and Discussion

2.1 Synthesis and Characterization

3,3'-dinitro-5,5'-azo-1,2,4-triazole (DNAT) has previously been described in the literature, but no information regarding it's burn rate characteristics has been published [12-13]. The synthesis of the triaminoguanidinium (TAG) salt of DNAT has not been published. Similarly, 3,3'-dinitro-5,5'-azoxy-1,2,4-triazole (DNATO) has been synthesized on a very small scale [13], but it's triaminoguanidinium salt has not been synthesized or studied. TAGDNAT (**1**) can be easily synthesized through neutralization by treatment with sodium hydroxide, followed by cation methathesis with triaminoguanidinium hydrochloride (Scheme 1). The reaction was performed in water and the product was isolated in excellent yield as a yellow crystalline solid. The material was found to have a thermal decomposition onset temperature of 205 °C, using a 10 °C/ min. heating ramp rate. The energy released upon decomposition was 1681 J/g. The heat of formation of TAGDNAT was measured using combustion calorimetry. A Parr 6300 calorimeter was employed and the heat of combustion was measured for the pure material in triplicate. Based on the values for the heat of combustion for TAGDNAT, a heat of formation of 711 kJ/mol was determined. In comparison, the heat of formation of DNAT was reported to be 406 kJ/mol [13].

Scheme 1. Preparation of TAGDNAT



The particle morphology of an energetic material is of considerable importance with respect to formulation. The particle morphology of TAGDNAT was investigated by scanning electron microscopy (SEM). The TAGDNAT particles are rhomboid in shape and with particle dimensions of roughly 100 X 100 micron and 20-30 microns in thickness. This is in contrast to TAGzT, which precipitates out as needles with a large aspect ratio. TAGDNAT was also studied by X-ray crystallographic analysis. An X-ray

quality crystal was grown from water and the crystal structure is displayed in Figure 1. The molecule crystallized in the monoclinic crystal system with a density of 1.68 g/cm^3[14]. The density of TAGzT, for comparison is only 1.61 /cm^3[15-17].

Figure 1. 50% thermal ellipsoids plot of Triaminoguanidinium 3,3-dinitroazotriazolate (TAGDNAT). Only one of the triaminoguanidinium molecules and ½ of the 3,3-dinitroazotriazolate is crystallographically unique.

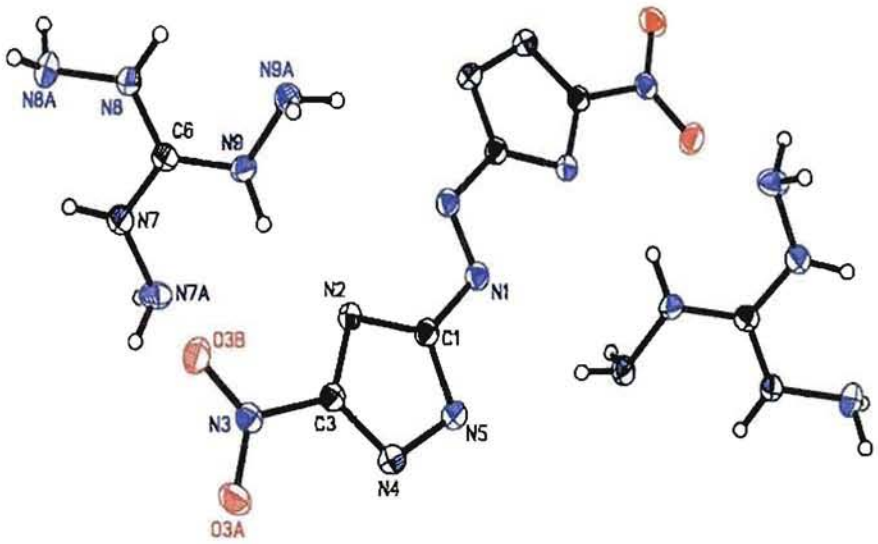
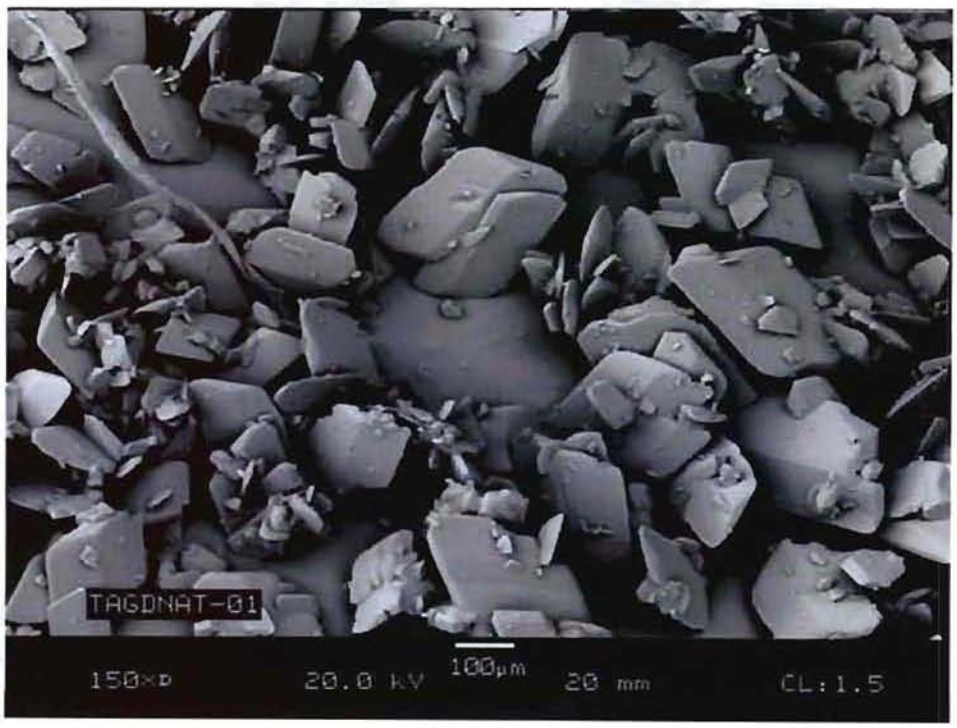
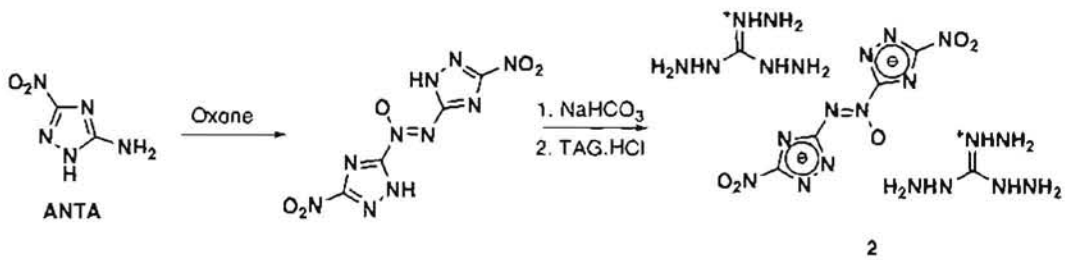


Figure 2. Scanning electron microscopy images of TAGDNAT. The crystals have an aspect ratio of 1:2



In order to synthesize TAGDNATO, we discovered that we needed an improved method to access DNATO. We discovered that the treatment of 5-amino-3-nitro-1,2,4-triazole (ANTA) with Oxone lead the isolation of DNATO in reproducible yields (Scheme 2). DNATO was then treated with sodium bicarbonate and converted to TAGDNATO (**2**) through cation metathesis, to provide a yellow crystalline product. Interestingly, TAGDNAT was found to have a significantly lower onset of thermal decomposition, 152 °C, using a 10 °C/min heating ramp rate. The energy released upon decomposition was 2526 J/g. The heat of formation of TAGDNATO was determine to be 712 kj/mol. The particle morphology of TAGDNATO was needle-like, with the aspect ratio being somewhat shorter than that of TAGzT. X-ray quality crystals of TAGDNATO were grown from water and analysis showed that the crystal belonged to the triclinic space group, and had a density of 1.698 g/cm^3 (@113 K). The crystal structure is displayed in Figure 3.

Scheme 2. Preparation of TAGDNATO

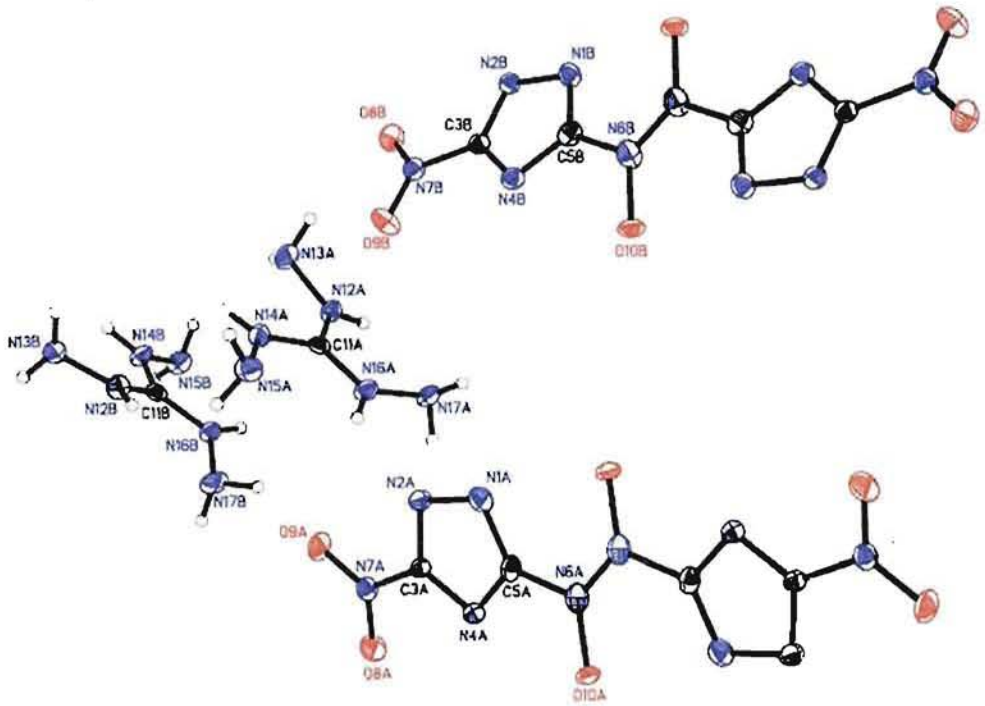


The sensitivity properties of TAGDNAT and TAGDNATO were measured and are displayed in Table 1. The data are compared to TAGzT and PETN as references. TAGDNAT is slightly more thermally stable than TAGzT, and has improved sensitivity properties with respect to impact spark and friction.

Table 1. Explosive Sensitivity Data for 1

Material	H_{50} (J)	DSC (°C)	Friction (N)	Spark (J)
1	9.3	202	157	0.125
2	5.3	151	127	0.125
TAGzT	6.1	195	98	0.0625
PETN	12	161	64	0.0625

Figure 3. 50% thermal ellipsoids plot of Triaminoguanidinium 3,3-dinitroazoxytriazolate (TAGDNAT).



2.2 Explosive Performance

The explosive performance of TAGDNAT was investigated using the rate-stick/plate-dent experiment[18-19]. TAGDNAT was formulated with 5% KEL-F binder and pressed into cylindrical pellets (1.27 cm x 1.27 cm) of 94% theoretical maximum density. The measured detonation velocity and estimated detonation pressure are shown in Table 2 along with the predicted values calculated using the Cheetah 5.0 code [20]. We have also tried to obtain the same experimental data for TAGzT, however we have found that this material does not detonate using the same cylinder size, nor does it detonate at cylinders of 1 in. x 1 in. We have provided the predicted values for TAGzT using the Cheetah 5.0 code, which differ from the previously reported calculated values were using TIGER code. [15]

Table 2. Explosive Performance Properties for 1 and **2**.

	1 (exp)	1 (calc)	TAGzT (exp)	TAGzT (calc)
D_v (km/s)[ρ, g/cm^3]	7.6 [1.58]	8.2 [1.58]	N/A	8.9 [1.60]calc.
P_{CJ} (GPa)[ρ, g/cm^3]	23.0	22.9	N/A	266 calc.

2.3 Burning Rate

Cylindrical pellets 6.3 mm in diameter and 6.4 mm long of the neat TAGDNAT and DNAT were burned in a 2L stainless steel vessel under pressurized argon of 0.2 – 7.1 MPa. The volume is sufficiently large that the decomposition gases have little effect on the pressure. To prevent the flame front from spreading down the pellet sides, burning of the pellet sides was inhibited with a thin film of silicone vacuum grease. The pellets were ignited by means of a resistively heated nickel chromium wire. The combustion event was filmed between 50 fps and 1000 fps using a Red Lake MotionScope PCI 8000S high-speed-video system and a Phantom MIRO3 from Vision Research. The pressure was monitored with an Omega Model PX605-10KGI static pressure transducer. Optical records were analyzed using commercially available computer graphics software to obtain the burning rate data. Typical images are shown in Fig. 4.

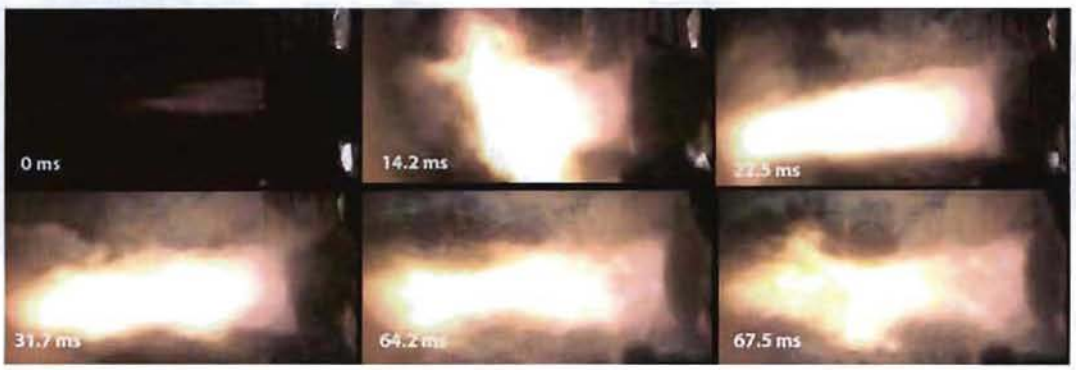


Figure 4. Typical images from the burning of TAGDNAT at 6.9 MPa.

In figure 5 we see the measured burning rates of TAGDNAT and DNAT as compared to the previously measured rates of TAGzT and HMX. [21-23] Most notably, the TAGDNAT shows a burning rate that exceeds that of TAGzT, with a lower pressure sensitivity. In fact, except at the lowest of pressures, TAGDNAT displays a rate that is even faster than DAATO3.5, when analyzed on a mass burning rate basis[22]. This is because despite the higher density of DAATO3.5 (1.90 g/cm^3), the morphology of the crystals only allow for a pressing density of 65% of theoretical density. Figure 6 shows the mass burning rate of TAGNDAT compared with that of DAATO3.5. Figure 7 displays the burn rate comparison of TAGDNAT and TAGDNATO.

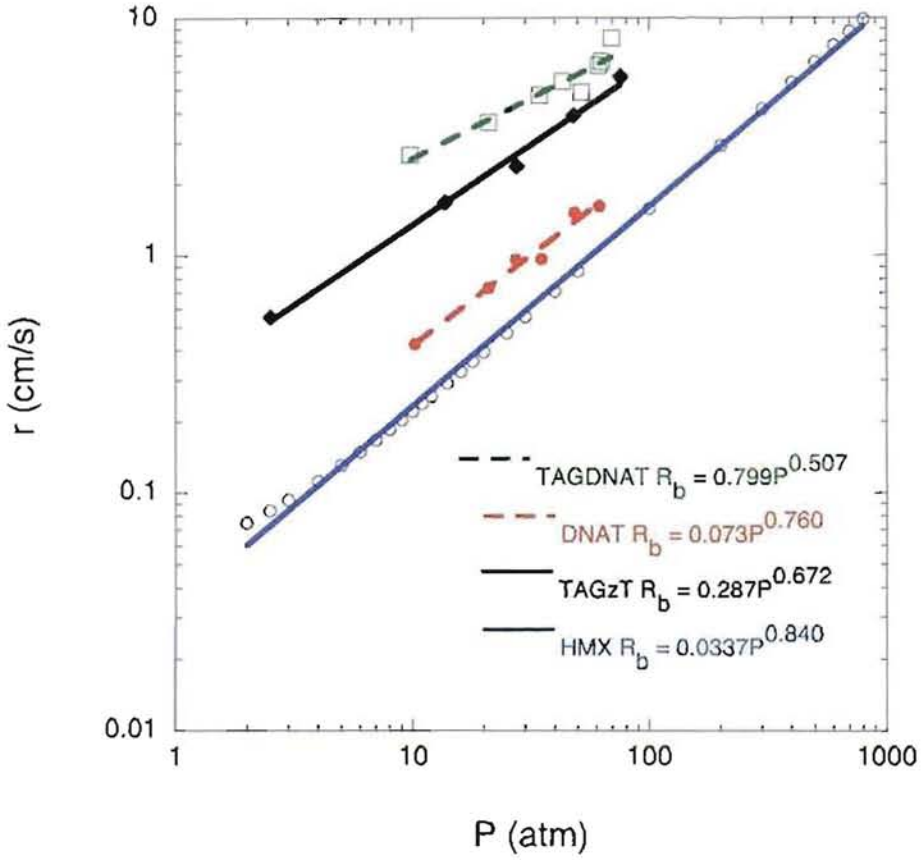


Figure 5. Burning rates of TAGDNAT and DNAT compared with TAGzT and HMX.

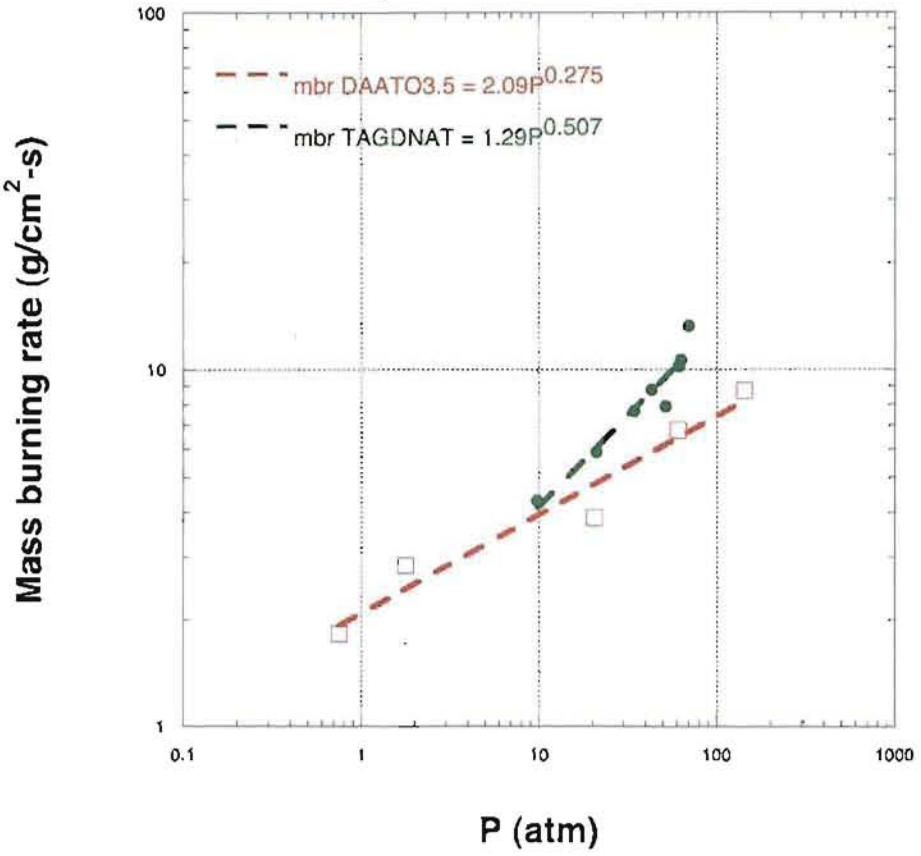
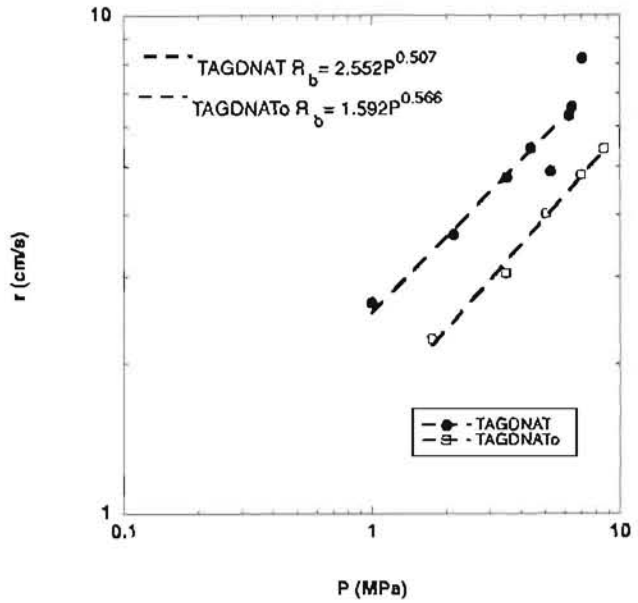


Figure 6. Mass burning rates of TAGDNAT and DAATO3.5.

Figure 7. Burning rates of TAGDNAT and TAGDNATO.



3 Conclusions

TAGDNAT and TAGDNATO are new high-nitrogen materials that shows promise as a potential propellant burn-rate modifier with useful properties. We have shown that TAGDNAT compares favorably with TAGzT in many aspects. For example, TAGDNAT has a higher density, is less sensitive to impact, spark and friction, and has a particle morphology that use much more useful in applications that require extrusion. We have also shown that TAGDNAT has a lower burn rate exponent compared to TAGzT and burns much faster in the pressure regime studied. In fact, TAGDNAT has one of the fastest burn rates measured for a neat material. These properties make TAGDNAT an interesting candidate for applications in areas such as propellants and gas generants. TAGDNATO, containing only one additional oxygen atom compared to TAGDNAT, is much less thermally stable, more sensitive to impact and friction and has poorer morphological properties. Further work is ongoing to characterize the burn-rate modification behavior of TAGDNAT and TAGDNATO.

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