BURNING RATE STUDIES OF BIS-TRIAMINOGUANIDINIUM AZOTETRAZOLATE (TAGzT) AND HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE (RDX) MIXTURES

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ABSTRACT

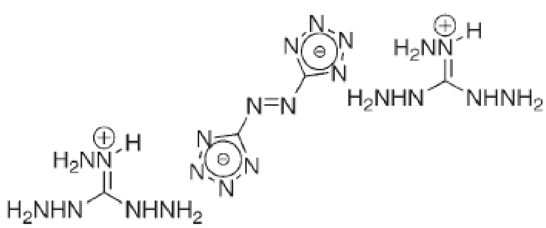
In this study of the combustion behavior bis-triaminoguanidium azotetrazolate (TAGzT), interesting increases in burning rates were observed when the TAGzT has been formulated with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). In order to study the interaction between TAGzT and RDX, formulations were produced of the two materials at various percent compositions and burning rates of the pressed materials were determined. It was found that the burning rate of the mixtures of TAGzT with RDX is greater than the weighted average burning rate of the pure materials at each ratio, and in the case of the 90/10 mixture of TAGzT/RDX, the burning rate in the regime of 10–100 atm was greater than that of even pure TAGzT, while having a lower pressure sensitivity then that of both parent compounds. Burning rate measurements in these formulations showed a greater data scatter than normal, presumably because of heterogeneity of the mixture from pellet to pellet. Detonation studies were also performed and indicate that the mixtures are insensitive to shock at low RDX loadings, with a self-sustained detonation only occurring at mixtures as high as 50% RDX at a diameter of 12.5 mm. Pure TAGzT, in fact, exhibited no detonation propagation even at 25.4 mm. Gas-phase CHEMKIN calculations were performed on this system and indicated a synergistic affect between the reaction products of TAGzT and RDX, yielding some explanation in the observed phenomenology. Thermochemical calculations indicate that reductions in temperature can be achieved with reasonable sacrifices in performance in various propellant applications.

INTRODUCTION

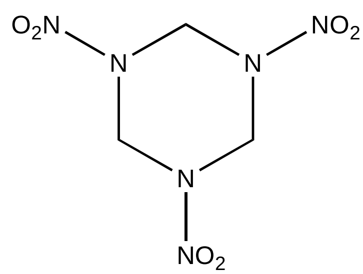
The compound bis-triaminoguanidium azotetrazolate (TAGzT) [see Fig. 1(a)] is in the class of energetic materials that derive their energy from high heats of formation, rather than oxidation of a carbon backbone as with typical explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [see Fig. 1(b)]. TAGzT is unique in its high molar volumetric gas production and its high hydrogen content (more so than liquid hydrogen itself by volume), thus having large potential impulse due to the formation of low molecular weight hydrogen gas, (as well as a large amount of fuel available for after-burning), both properties that can improve the performance of propellants and explosives alike. In addition, higher concentrations of nitrogen in the products can be better for barrel erosion.

The burning rate of a material is an important consideration when designing a rocket or gun propellant. The linear burning rate of a material can be described in relation to pressure by the empirical equation $r_b = cp^n$, where c is an empirical constant and n is the pressure exponent.[3,4] A large pressure exponent (approaching 1), common with high explosive materials, typically indicates that overall 2nd order gas-phase reactions dominate the combustion process. A lower pressure exponent, however, is usually indicative of condensed phase reactions dominating combustion, and thus results in a burning rate that is very insensitive to changes in pressure. Lower pressure sensitivity offers advantages in propellant applications.

Figure 1 shows the chemical structure of TAGzT and RDX used in these experiments.



(a)



(b)

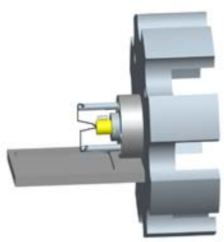
Figure 1: (a) TAGzT chemical structure, and (b) RDX chemical structure

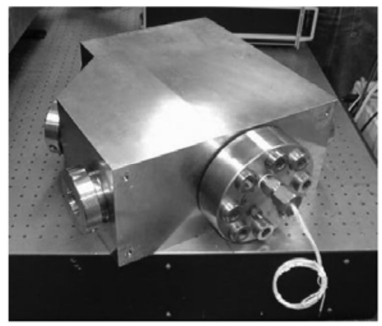
EXPERIMENTAL METHOD

Mixtures of 75%, 50%, 25%, and 10%, of RDX with TAGzT powders were mixed in the non-solvent methanol with stirring and evaporation then pressed into 6.35 mm x 6.35 mm pellets. The burning rates of the mixtures were determined in order to investigate the interaction of RDX and TAGzT independent of other ingredients commonly found in propellants. The TAGzT used for these experiments was synthesized by the Naval Surface Warfare Center (NSWC) at Indian Head and was re-crystallized from water before use.

The RDX used was from the DE-1 LANL explosives inventory and certified to contain less than 0.1% HMX. Held in place by the fixture shown in Fig. 2a, the pellets' burning rates are determined within a sealed 2L pressure chamber (Fig. 2b) under pressurized nitrogen or argon from 0.1 to 11 MPa (2 to 110 atm). The volume of the pressure chamber is sufficiently large that the decomposition gases have little effect on the pressure.The pellets are ignited by means of a resistively heated ni-chrome wire. The combustion event is filmed at 250 frames per second using a Red Lake MotionScope PCI 8000S high-speed-video system.The pressure is monitored with an Omega Model PX605-10KGI static pressure transducer. The recorded burns are analyzed using motion analysis software in order to obtain the burning rate data. Figure 3 shows typical images.

a)





b)

Figure 2: In part a), a schematic of a pellet stand is shown. Part b) is a photo of the windowed pressure vessel used. The maximum pressure obtainable is 200 atm with windows in place.

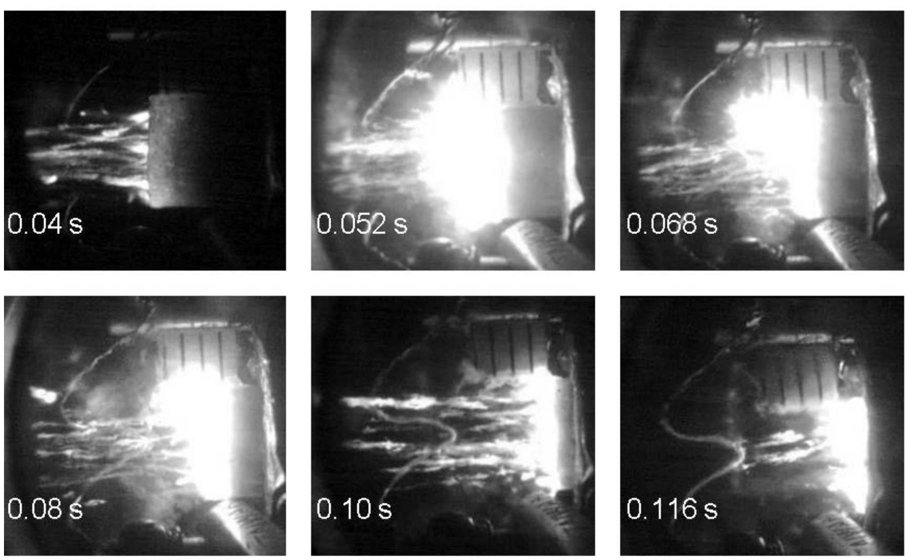


Figure 3: Frame sequence of burning 90% TAGzT/RDX at 7.5 MPa (76 atm) in nitrogen

The sensitivity of TAGzT and the 50% TAGzT and 50% RDX mixture towards initiation by spark, friction, and impact is reported in Table 1 with a HMX standard for comparison. The impact sensitivity of the 50% TAGzT and 50% RDX increased slightly over pure TAGzT; however it is expected to decrease significantly by formulation with even a small amount of binder.

Table 1: Sensitivity measurements for TAGzT, 50% TAGzT/50% RDX and HMX impact standard.

Material	**Impact Sensitivity (H_{50}, cm)**	**DSC onset, (°C)**	**Friction sensitivity, (kg)**	**Spark sensitivity, @ 0.36 J**
TAGzT	25	195	10.0	0.312
50% TAGzT/50% RDX	18.9	167	8.2	> 0.36
HMX	22.4	249.9	13.6	>0.36

RESULTS AND DISSCUSSION

The burning rate data collected from the experiments are shown in Fig. 4, along with the burning rates of pure RDX and TAGzT collected by Tappan et al.[2]

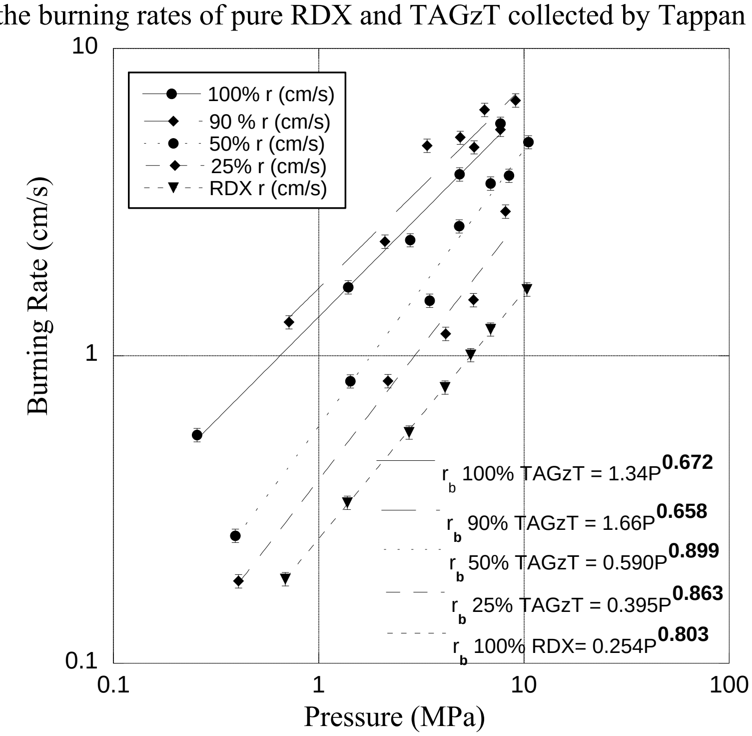


Figure 4: Burning rates of the TAGzT/RDX formulations versus pressure, RDX rate data[3]

The figure clearly shows that adding any amount of TAGzT to RDX will greatly increase the burning rate, with the 90% TAGzT/RDX mixture being the fastest. At 6.7 MPa (68 atm) an increase of 25% TAGzT by weight will increase the burning rate by more than 50%. Additionally at 6.7 MPa, the 90% TAGzT/RDX burn rate is almost 5 times as fast as pure RDX and 19% faster than pure TAGzT.

Table 2 shows the pressure exponent and the burning rate at this pressure for all of the mixtures tested. The pressure exponent is also lowest for the 90% TAGzT mixture; a property desirable for propellants. However, the data collected for this mixture has significant variability, which creates a large margin of error for the exponent, +/- 0.11. Despite this, even at the highest limit, the pressure exponent is still very low.

Table 2: Burning rate parameters for TAGzT, TAGzT/RDX mixtures and RDX

Material	**Burning Rate @ 6.7 MPa (68 atm), cm/s**	**Burning Rate Exponent (n)**	**Calculated[a] I_{sp} (sec)**	**Calculated[a] Exhaust Temp (K)**
100 % TAGzT	4.89	0.67	217	841
90% TAGzT/RDX	5.80	0.56	220	881
50% TAGzT/RDX	3.37	0.91	232	969
25% TAGzT/RDX	2.23	0.88	251	1137
100% RDX	1.198[b]	0.800	267	1570

[a] Calculated BKW EOS using the Cheetah 4.0 code at 68.03 atm (1 atm exit pressure).
[b] See Ward, Son, and Brewster.[3]

The TAGzT/RDX burning rate data scatter, as compared to pure RDX or pure TAGzT, is most likely caused by non-homogeneous mixtures and/or by variability in the TAGzT crystal sizes. If a mixture of finer TAGzT/RDX crystals were used the burning rates are expected to increase with less data scatter. Figure 5 shows the 90% TAGzT/RDX mixture mass burning rate fit and Table 3 shows the density of the pellet for each point. With a quick observation of the densities in Table 3 and the burning rates in Fig. 5, it is clear that the differing densities are not causing the variability in burning rates.

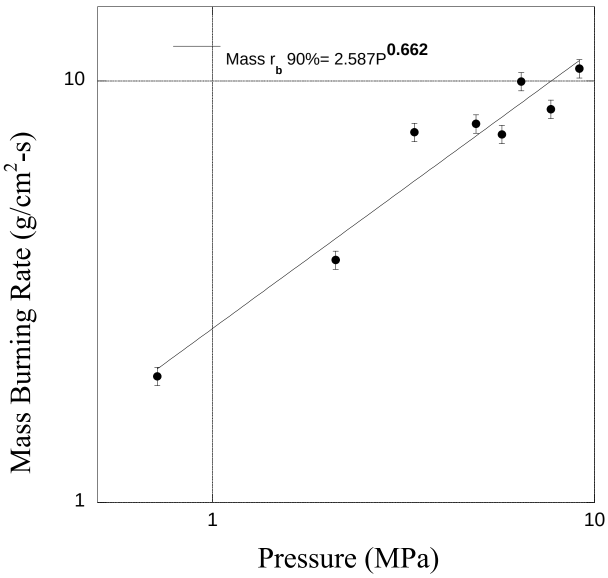


Figure 5: Mass burning rate data for 90% TAGzT/RDX

Preliminary calculations were performed using the chemical kinetics code CHEMKIN (Fig. 6). Homogenous thermal explosion calculations were performed on gaseous mixtures of RDX vapor and decomposition products of TAGzT as determined by t-jump FTIR spectroscopy.[2] These calculations show an acceleration of the RDX reaction with the addition of TAGzT products. More work is needed to examine this effect.

Table 3: Pellet Densities for 90% TAGzT/RDX

Point #	Density	% TMD
1	1.548	0.955
2	1.597	0.985
3	1.566	0.966
4	1.543	0.952
5	1.565	0.966
6	1.579	0.974
7	1.575	0.972
8	1.579	0.974

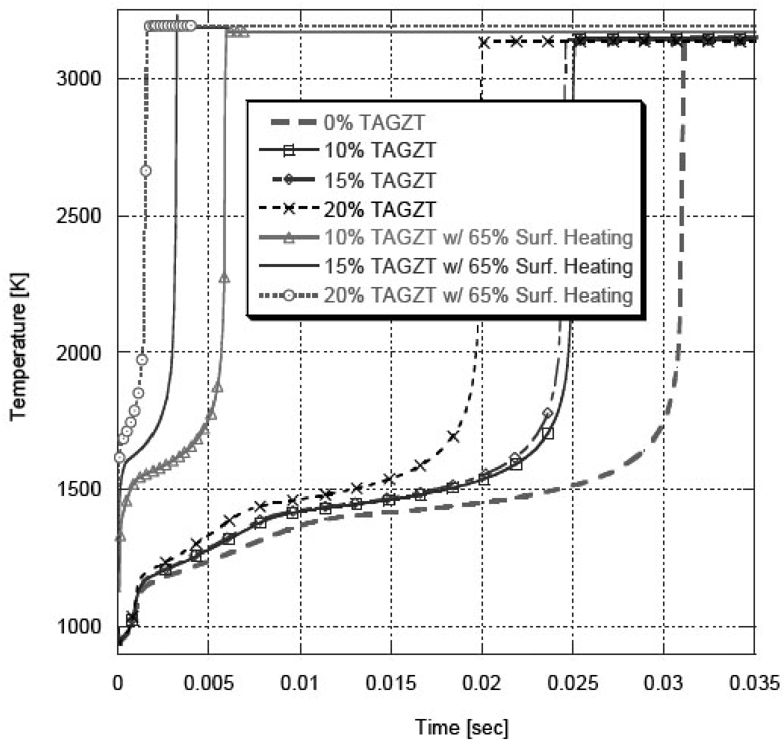


Figure 6: Chemkin calculations of the gas phase composite TAGzT/RDX combustion at constant pressure thermal explosion 0.1 MPa (1 atm).

Experiments were also performed to determine the detonability of the pure TAGzT and the mixtures with RDX. Tests on pure TAGzT showed that detonation failed at diameters up to 25.4 mm unconfined with an input shock of approximately 29 GPa. Rate sticks at diameters of 12.7 mm were produced of the 25% and 50% RDX loadings in which the 25% RDX fail to sustain detonation, and the 50% RDX detonated at a velocity of 7.69 mm/µs with a P_{cj} of 27.3 GPa.

CONCLUSIONS

The high nitrogen/high hydrogen compound bis-triaminoguanidium azotetrazolate (TAGzT) can significantly increase the burning rate of RDX when used as a burning rate modifier. RDX and TAGzT have a synergic interaction during combustion that can increase the burning rate of the compound to rates higher than pure RDX and even pure TAGzT. This effect is both empirically observed and also predicted by Chemkin calculations. At a mixture of 10% RDX and 90% TAGzT, the burning rate is 5 times faster than pure RDX and about 1.12 times as fast as pure TAGzT. The burning rate exponent is also lower than RDX and TAGzT at this ratio. Detonation studies demonstrated that at loadings of 25% RDX in TAGzT or less are shock insensitive and thus good candidates for propellant applications.

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