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DECOMPOSITION AND PERFORMANCE OF NEW HIGH NITROGEN PROPELLANTS AND EXPLOSIVES

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Abstract. As of late, molecules with high nitrogen content have received increased attention, due in large part to their novel energetic materials properties. At the Los Alamos National Laboratory, we continue to pursue the development and characterization of new high-nitrogen materials for applications in a wide variety of fields. In this work three molecules, triaminoguanidinium azotetrazolate (TAGzT), 3,6-bis-nitroguanyl-1,2,4,5-tetrazine and its corresponding bis-triaminoguanidinium salt, are studied all of which are high-nitrogen compounds with little or no oxygen, however, retain energetic material properties as a result of their high heats of formation. Because of this, the decomposition of this class of compounds have limited or no secondary oxidation reactions of carbon and hydrogen. Other materials discussed for comparison include 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides ($DAATO_{3.5}$) and 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz) and the nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The fact that many of these molecules approach 80% nitrogen content makes them potentially useful as gas generants or energetic materials with low flame temperatures, while simultaneously increasing the impulse of gun or rocket propellants. The burning rate, flash pyrolysis (T-jump/FTIR spectroscopy), explosive sensitivity and performance properties were determined. Some examples of interesting behaviors include that TAGzT exhibits one of the fastest low pressure burning rates yet measured for an organic compound, and 3,6-bis-nitroguanyl-1,2,4,5-tetrazine has one of the lowest pressure exponents yet measured for a pure organic compound.

Introduction

Energetic materials that derive their energy from a positive heat of formation rather than oxidation of a carbon backbone have recently attracted attention as gas generants or propellants because a relatively high theoretical specific impulse can be achieved despite the relatively low decomposition temperature. At the Los Alamos National Laboratory, the development and discovery of new high-nitrogen materials for applications in a wide variety of fields is an active pursuit.[1] The compound triaminoguanidium azotetrazolate (TAGzT) is a particularly interesting because of its high heat of formation and high molar and volumetric gas production, however, TAGzT contains no oxygen. Because of this, the chemistry that dominates the ignition and combustion, is more centered on reactions in the condensed phase rather than oxidation chemistry of the gas phase. As part of our further efforts in the area of heterocyclic chemistry of the tetrazine ring system, we have recently reported on the preparation of several novel nitroguanyl-substituted tetrazines,[2] which include 3,6-bis-nitroguanyl-1,2,4,5-tetrazine ($(NQ)_2Tz$) and its bis-triaminoguanidinium salt ($(TAG)_2(NQ)_2Tz$). The burning rate of these materials were studied at various pressures of inert gas, and laser ignition was performed to study fast heating response and ignition characteristics. T-jump/FTIR spectroscopy was utilized to provide a "snap shot" of the condensed phase reactions involved in the pathway of decomposition.

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 known as the pressure exponent.[3,4] A large pressure exponent (approaching 1), common with high explosive materials, typically indicates that 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. A low pressure sensitivity offers advantages in the design of gun and rocket propellants.

T-jump/FTIR spectroscopy is particularly well-suited for the study of decomposition processes that occur in the condensed phase.[5] Briefly, a thin layer of material, similar in size to the burning surface, is flash-heated to a predetermined temperature with the product gases rapidly quenched

in a cool inert gas environment, providing a snapshot of the decomposition chemistry with minimal effect from processes in the gas phase. This technique can provide information regarding the mechanism of decomposition of energetic materials, thus providing insight into the burn rate behavior.

Experimental

Material. The synthesis and physical properties of TAGzT were first reported by Hiskey *et al*.[6] The material is a bright yellow, needle-like crystalline solid having a theoretical maximum density of 1.60 g/cm^3, a decomposition temperature of 195°C and a heat of formation of +1076 kJ/mol.[6] The sensitivity of this material towards initiation by spark, friction and impact is reported in Table 1.

The syntheses of $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$ were recently reported by Chavez et al.[2] Briefly, 3,6-bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine[7] was reacted with the sodium salt of nitroguanidine in a methanolic solution. This reaction provided the bis-sodium salt of $(NQ)_2Tz$, which was isolated and converted to $(NQ)_2Tz$ by treatment with aqueous acid, or to $(TAG)_2(NQ)_2Tz$ by treatment with an aqueous solution of triaminoguanidinium hydrochloride (TAG•HCl).

$(NQ)_2Tz$ is a orange-pink solid with a gas pycnometry density of 1.76 g/cm^3. The material was determined to have a DSC onset of 228 °C, with fast decomposition at 269 °C. A heat of formation was measured using combustion calorimetry, and a value of +389 kJ/mol (+/- 8 kJ/mol) was obtained. When compared to the heat of formation of nitroguanidine itself (-98.7 kJ/mol)[8], it is evident that the tetrazine core contributes significantly to the overall heat of formation of the molecule. The sensitivity of this material towards initiation by spark, friction and impact is described in Table 1. The impact sensitivity of $(NQ)_2Tz$ was decreased significantly by formulation with 5 wt% Viton A. This formulated material remained insensitive to spark and friction and retained a similar thermal stability (Table 1).

Table 1: Sensitivity parameters for TAGzT, $(NQ)_2Tz$, $(TAG)_2(NQ)_2Tz$, BTATz, $DAATO_{3.5}$ and HMX

Material	Impact Sensitivity (H_{50}, cm)	DSC onset, °C	Friction sensitivity, kg	Spark sensitivity, @0.36J
TAGzT	25	195	10.0	0.312
$(NQ)_2Tz$	65	228	> 36	> 0.36
$(NQ)_2Tz$ + 5% Viton A	254	228	>36	> 0.36
$(TAG)_2(NQ)_2Tz$	114	166	> 36	> 0.36
BTATz	40[a]	264[a]	>36[a]	>0.36[a]
$DAATO_{3.5}$	25[a]	177[a]	2-14[a]	fails
HMX	25.2	249.9	13.6	>0.36

[a] Ali, Son, Hiskey and Naud[5b]
[b] Ward, Son and Brewster[9]

$(TAG)_2(NQ)_2Tz$ is a reddish-brown solid, with a density of 1.61 g/cm^3 as determined by gas pycnometry. The thermal stability of $(TAG)_2(NQ)_2Tz$ is lower than $(NQ)_2Tz$ as determined by DSC analysis. The onset of decomposition begins at 166 °C, with a fast exotherm beginning at

175 °C. $(TAG)_2(NQ)_2Tz$ was determined to have a very high heat of formation of +1255 kJ/mol (+/- 3 kJ/mol) by combustion calorimetry. When normalized on a per atom basis, a value of 23.2 kJ/mol atom is realized. In this respect, $(TAG)_2(NQ)_2Tz$ has a similar heat of formation to that of TAGzT.[6] The sensitivity of $(TAG)_2(NQ)_2Tz$ to initiation by impact, spark and friction is also described in Table 1. Although $(TAG)_2(NQ)_2Tz$ is less thermally stable than TAGzT, it has a higher overall heat of formation (similar on a per atom basis), but is much less sensitive, particularly with respect to impact.

For comparison, three other compounds are discussed, 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz), 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides ($DAATO_{3.5}$), and the nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), where the burning rate data are cited previously.[5b,9]

Burning Rate. Cylindrical pellets 6.3 mm in diameter and 6.4 mm long of the neat TAGzT were burned in a 2L stainless steel vessel under pressurized nitrogen of 2 - 70 atm. 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 Krylon® clear acrylic. The pellets were ignited by means of a resistively heated nickel chromium wire. The combustion event was filmed at 30 fps and 250 fps using a Canon XL1 3CCD Digital Video Camcorder and Red Lake MotionScope PCI 8000S high-speed-video system, respectively. 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 for burning rate analysis are shown in Fig. 1, which is a frame sequence of burning TAGzT at 200 psig, filmed at 30 fps. The flame front is moving from left to right, and the orange luminosity on the left of the pellet is the o-ring of the pellet fixture being heated by the hot exhaust gasses.

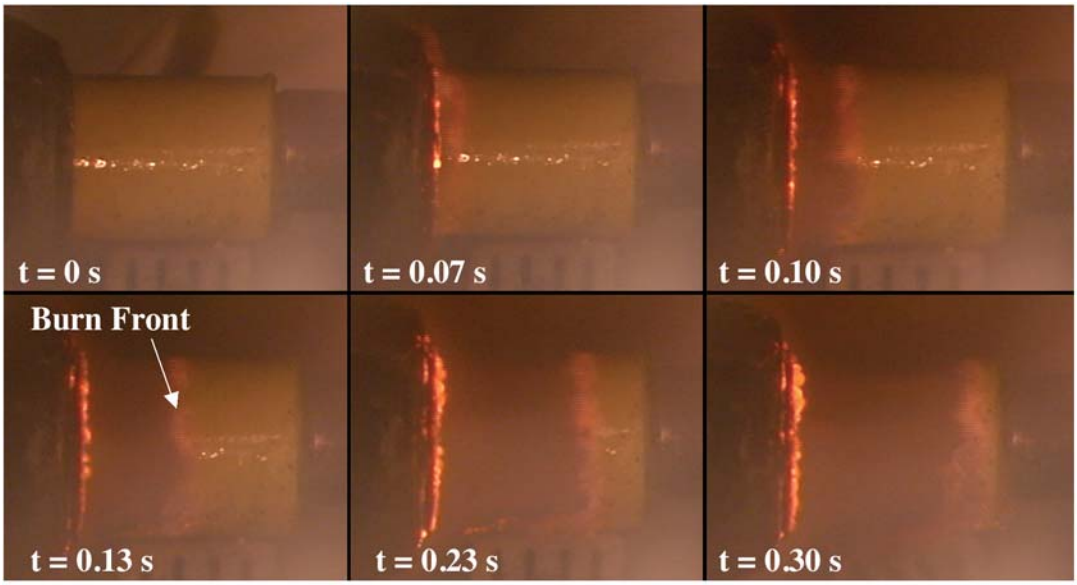


Figure 1. Frame sequence of burning TAGzT at 200 psig, filmed at 30 fps. The burn front is moving from left to right, with orange luminosity on the left from the heated o-ring by hot exhaust gasses.

Flash Pyrolysis/FTIR Spectroscopy. T-Jump/FTIR spectroscopy was performed and this technique has previously been described in detail.[5] Briefly, approximately 200 μg of sample was thinly spread onto the center of a Pt ribbon filament. This filament was inserted into a 25 cm^3 cell with ZnSe windows to allow the diagnostic IR beam to pass a few millimeters above the surface of the filament to obtain gaseous product spectra in near real time as they evolve. The Pt ribbon filament was connected to a high-gain, fast-response power supply in order to very rapidly heat the filament (2000°C/sec) to a constant, predetermined set temperature. The set temperature of the filament is determined by calibration using melting point standards in the same gaseous environment as the experiments.

Results and Discussion

Explosive Performance. The explosive performance of $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$ were investigated through the use of rate stick and plate dent experiments.[10] $(NQ)_2Tz$ was formulated with 5 wt% Viton A and pressed into 0.5 in. x 0.5 in. cylinders. The pellets could be pressed to greater than 95% of the theoretical maximum density. The detonation velocity and detonation pressure are shown in Table 2. The explosive performance of nitroguanidine (NQ) formulated with 5 wt% Estane is provided for comparison.[11] $(TAG)_2(NQ)_2Tz$ was pressed without a binder into cylinders similar in size to those described above. The pellets could be pressed to greater than 93% of the theoretical maximum density. The detonation velocity and the detonation pressure are presented in Table 3. The corresponding properties for TAGzT are given in Table 3 as well. Unfortunately, these data are not experimental values, but rather the calculated values for this material.

Table 2. Explosive Performance Properties for $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$.

	$(NQ)_2Tz$ (5% Viton A)	NQ (5% Estane)	$(TAG)_2(NQ)_2T$	TAGzT
D_v (km/s)[ρ, g/cm^3]	7.84 [1.70]	8.28 [1.70]	7.62[1.51]	9.05 calc.
P_{CJ} (kbar)[ρ, g/cm^3]	260	268	219	292 calc.

Burning rate. TAGzT has an exceptionally high burning rate with a pressure exponent of 0.672 (Table 3, Fig. 2). This exponent falls between conventional materials such as HMX and several other high nitrogen materials (see Fig. 2 and Table 3). In fact at the higher pressure range, the burning rate for TAGzT is in the neighborhood of the fastest measured CHN and O material, $DAATO_{3.5}$ and the high nitrogen material, BTATz [2]. HMX has a more typical burning rate and pressure exponent and burns slower in the pressure range studied [3].

Table 3: Burning rate parameters for TAGzT, $(NQ)_2Tz$, $(TAG)_2(NQ)_2Tz$, BTATz, $DAATO_{3.5}$ and HMX.

Material	Burning Rate @68 atm, cm·s^{-1}	Burning Rate exponent	Calculated[c] I_{sp} (sec)
TAGzT	4.89	0.67	217[c]
$(NQ)_2Tz$	2.0	0.163	219[c]
$(TAG)_2(NQ)_2Tz$	2.3	0.366	237[c]
BTATz	4.59[a]	0.49[a]	219[c]
$DAATO_{3.5}$	5.39[a]	0.275[a]	258[c]
HMX	2.11[b]	0.84[b]	266[c]

[a] Ali, Son, Hiskey and Naud,[5b] [b]Ward, Son and Brewster[9]

[c] Calculated BKW EOS using the Cheetah 2.0 code at 68.03 atm (1 atm exit pressure).

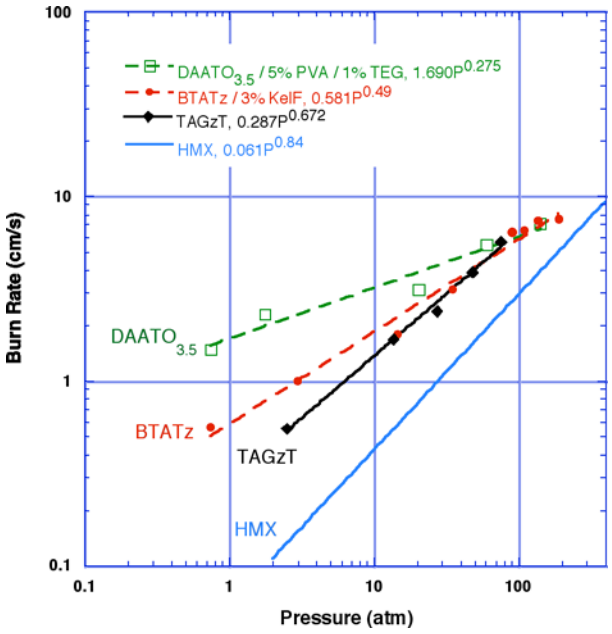


Figure 2. Burning rate vs. pressure curve of TAGzT with comparison materials.[5b,9]

Certain features of high-nitrogen materials are immediately apparent. The fact that much of the decomposition occurs in the condensed phase suggests that burning rates can be faster at lower pressure, while having a lower pressure dependence because solid phase reactions are relatively independent of pressure. The reactions governing the decomposition of TAGzT will be discussed in the following section.

Fig. 3 is a single frame showing the burning of $(NQ)_2Tz$. It is interesting to note that the highly luminous nature of the burn was not observed during the combustion of $(TAG)_2(NQ)_2Tz$, and is likely attributed to the difference in oxygen balance. Figures 4a and 4b display plots of the burn rates vs. pressure for both $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$. Data points for lower pressures were not obtained for $(NQ)_2Tz$ due the smoke obscuring the burn front during the experiments. Both $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$ displayed a very small pressure dependence on burning rate in the pressure ranges measured. However, $(NQ)_2Tz$ had an exceptionally low pressure exponent of 0.163, the lowest pressure dependence known in the literature for a mono-propellant. Table 3 displays the results of the burning rate experiments for $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$, with HMX (a material with a large pressure exponent) and BTATz (a high-nitrogen material with a low pressure exponent). Also reported in this table are the calculated I_{sp} values for those materials, indicating the potential usefulness of the nitroguanyl-substituted tetrazine compounds.

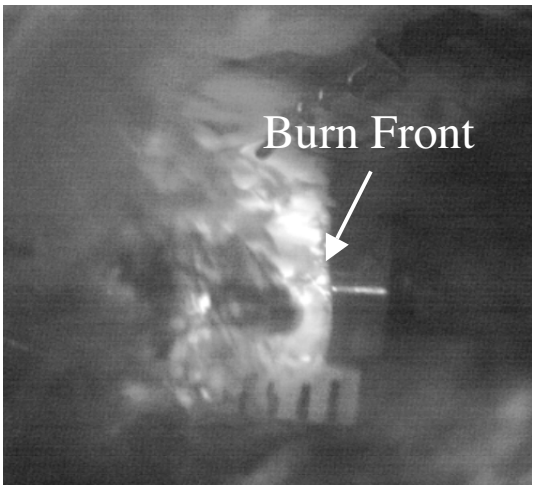


Figure 3. Single frame of NQ_2Tz linear burn rate as viewed through window in combustion bomb at 55 atm N_2. The burn front is traveling from left to right, and a small portion of the un-burnt pellet can be seen to the right of the flame.

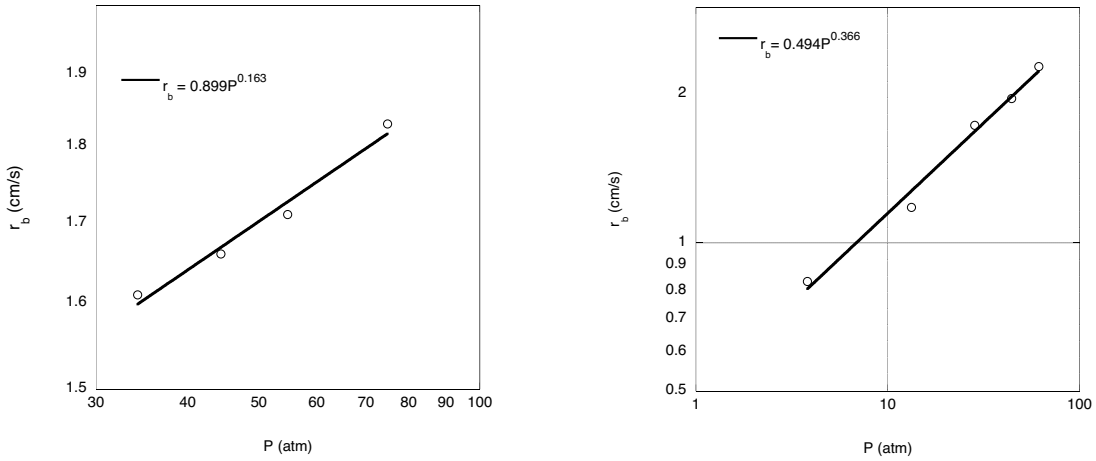


Figure 4 a and 4b: Burn rate vs. pressure for NQ_2Tz (left) and TAG_2NQ_2Tz (right).

T-jump/FTIR Spectroscopy. T-jump/FTIR spectroscopy was performed and the temperature, time-to-exotherm (TTX) and cell pressure of the experiment are provided in Table 4. Pyrolysis was performed up to 8 atm, however, no effect was observed on pyrolysis product gases or ratios, therefore all results reported are for 1 atm argon gas.

Table 4. T-jump Conditions for TAGzT, $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$.

	Temperature (ºC)	Average TTX (sec.)	Pressure Ar (atm)
TAGzT	264	4.66±0.6	1
$(NQ)_2Tz$	332	4.2±1.4	1
$(TAG)_2(NQ)_2Tz$	264	3.5±0.9	1

In Fig. 4 the IR spectra of the gaseous products from the flash pyrolysis of TAGzT are shown. Equation 1 gives the atom balance of these products normalized to carbon. Cyanamide (NH_2CN) and its dimer, dicyanamide ($(NH_2)_2CNCN$) (2255, 1585 cm^{-1} and 2205, 2160, 1641, 1566 cm^{-1},

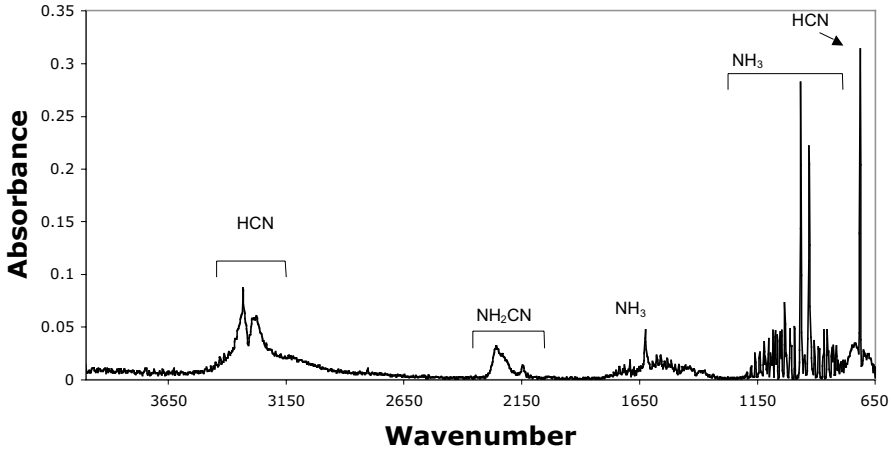
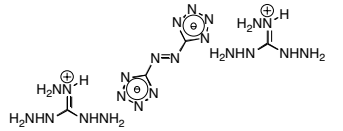


Figure 5. T-jump/FTIR Product Spectrum of TAGzT at 264°C.

respectively) are observed, but not quantified due to the difficulty in the determination in their absolute absorptivity.[12] N_2, shown in italics, is not IR active, but is assumed to form and is included at the amount to balance the equation.



TAGzT

→ 5.08 NH_3 + 4.00 HCN + *?*NH_2CN + *6.46* N_2 (1)

The resulting elemental atom balance is $C_4H_{19.2}N_{22}$; the expected elemental atom balance is $C_4H_{18}N_{22}$. Because the equation is normalized to carbon, and dinitrogen is added to balance the equation, there is no deviation from the expected result in the carbon and nitrogen. Thus the amount of hydrogen is the only indication of the accuracy of the measurement. A 7% excess of hydrogen in observed, and with the presence of a small amount of cyanamide, one should expect a slight skewing toward excess hydrogen.

Cheetah calculations considering a rocket chamber at 68 atm and 1 atm exhaust pressure indicate the formation of 11.00 N_2, 6.06 H_2, 1.47 CH_4 and 2.53 C, on a mole product per mole explosive basis. Assuming the reactive condensed phase products seen in the T-jump, 5.08 NH_3 + 4.00 HCN, react to produce the products 4.50 N_2 + 5.65 H_2 + 2.53 C + 1.47 CH_4 seen in the Cheetah calculation leads an exothermic reaction yielding - 416 kJ/mol, which when added to the heat of reaction in equation 1, which is exothermic by –770 kJ/mol, yields a net heat of reaction of –1186 kJ/mol. In accordance the heat of formation of TAGzT is 1076 kJ/mol or about 10% less than the net heat of reaction. Together, this suggests that roughly 65% of the reaction energy is released in the condensed phase, which is concurrent with the assumption based on the slope of the burning rate.

Figures 6 and 7 show the IR spectra of the gaseous products from the flash pyrolysis of $(NQ)_2Tz$ and $(TAG)_2(NQ)_2Tz$, and equations 2 and 3 provide the atom balance of these products normalized to carbon. N_2, shown in italics, is not observed in IR spectroscopy, but is assumed to form and is included to balance the equation. Product gases indicate that the TAG cation dramatically affects the decomposition pathways. The formation of large amounts of NH_3 suggests that CN^+-H bond cleavage of the TAG cation is the dominating facile reaction of the thermal decomposition. Large amounts of NH_3 are also observed in the pyrolysis of the TAGN.[13] In $(NQ)_2Tz$, bond energies and the evolution of NO_2 indicate that N-NO_2 homolysis is the facile reaction of the decomposition for this molecule. The observation that NO_2 is not present during the decomposition of $(TAG)_2(NQ)_2Tz$, but is most certainly released subsequent to the rate-determining step, can be attributed to the reaction depicted in equation 4, where the NO_2 is reacted to form N_2O and H_2O. Based on the lower energy products, the higher decomposition temperature and the longer time-to-exotherm in $(NQ)_2Tz$, it can be inferred that the trigger mechanism for decomposition proceeds through higher energy pathways. This may also explain the lower burning rate exponent of $(NQ)_2Tz$ as lower energy products formed during condensed phase first order reactions limits the second order reactions available in the gas phase.

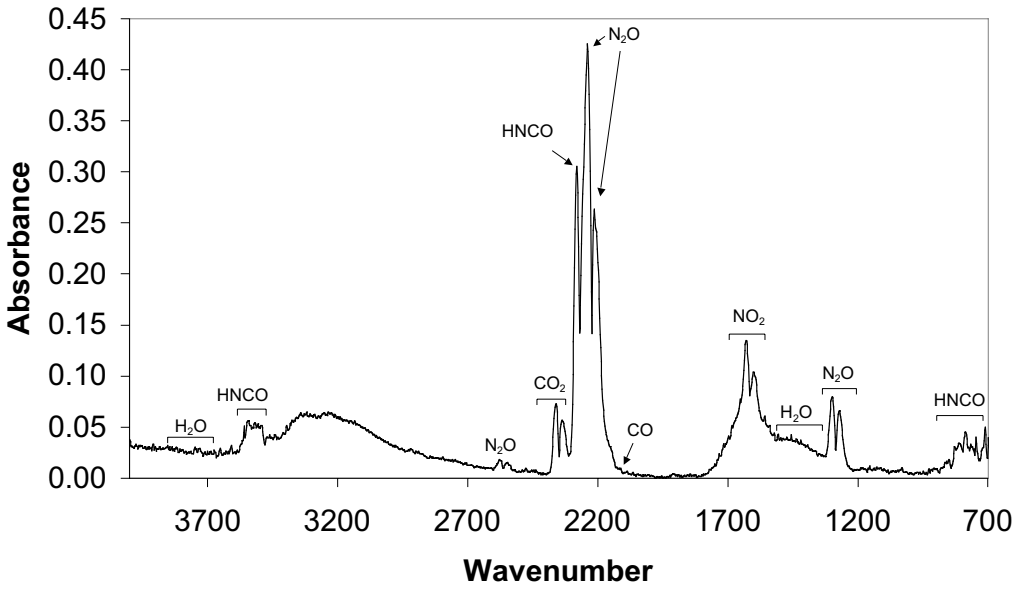


Figure 6. The IR spectra of the gaseous products from flash pyrolysis of NQ_2Tz.

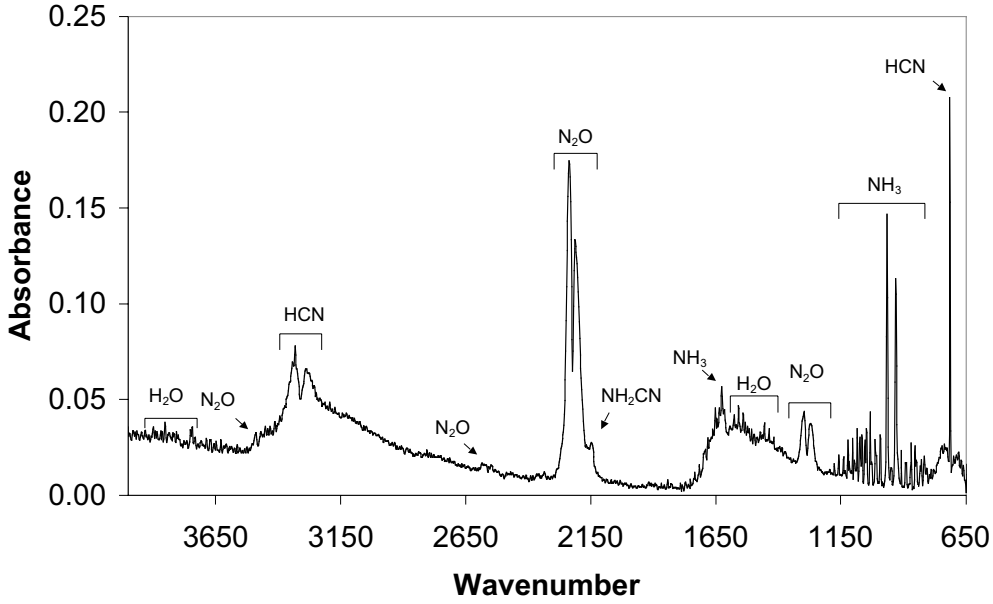
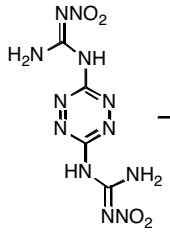
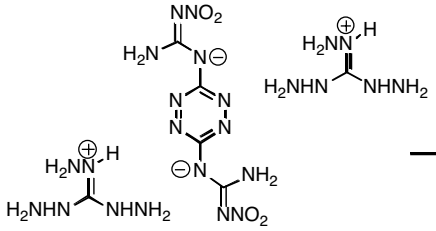


Figure 7. The IR spectra of the gaseous products from flash pyrolysis of TAG_2NQ_2Tz.



$$\longrightarrow \quad 2.1\ HCNO + 1.8\ H_2O + 0.98\ CO + 0.31\ CO_2 + 3.1\ N_2O + 1.0\ NO_2 + 2\ N_2 \qquad (2)$$



$$\longrightarrow \quad 4.6\ NH_3 + 1.8\ H_2O + 5.3\ HCN + 2.5\ N_2O + 7.1\ N_2 \qquad (3)$$

$$2\ NH_3 + 2\ NO_2 \longrightarrow N_2O + 3\ H_2O + N_2 \qquad (4)$$

Conclusions

Collectively, the measurements made in the burning rate experiments and T-jump/FTIR spectroscopy indicates that both the burning the decomposition behavior of TAGzT are dominated by condensed phase reactions. T-Jump/FTIR spectroscopy indicates that around 65% of the energy released in decomposition is by the condensed phase reactions, which helps to explain the remarkably high burning rates at low pressures.
3,6-Bis-nitroguanyl-1,2,4,5-tetrazine and its bis-triaminoguanidinium salt are two new energetic materials with high nitrogen content and can be easily accessed through a simple two-step procedure. These materials were studied to determine their explosive performance properties as well as their combustion and thermal decomposition behavior. We have discovered that these materials exhibit very low pressure dependence during combustion, and in particular, $(NQ)_2Tz$ has been shown to have to lowest pressure exponent known in the literature for a neat material. T-jump/FTIR spectroscopy studies have provided some insight into the nature of the low burn rate pressure dependence. The interesting combustion behavior displayed by these materials make them suitable candidates for gas- generating and propellant applications and further study in these areas is currently being pursued.

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