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Burning Rates and Thermal Behavior of Bistetrazole Containing Gun Propellants

Jonathan Lavoie^[a], Catalin-Florin Petre^[b], Pierre-Yves Paradis^[c], Charles Dubois^{*[a]}

Abstract: The influence of two selected bistetrazoles, 5,5'-bis-(1H-tetrazolyl)-amine (BTA) and 5,5'-hydrazinebistetrazole (HBT), on the combustion behaviour of a typical triple-base propellant was investigated. Seven propellant formulations, one reference and six others incorporating respectively, 5%, 15% and 25% of either HBT or BTA compounds were mixed and extruded into a cylindrical, no perforations, geometry. The resulting propellants showed high burning rates, up to 93% higher than the reference formulation at 100 MPa. However, the increase in burning rates came at the cost of higher burning rate dependency on pressure, with a pressure exponent as high as 1.4 for certain formulations. HBT-containing propellants showed notably lower flame temperature when compared to the reference formulation, with a flame temperature reduction of up to 461 K for the propellant containing 25% HBT. The thermal behaviour of the propellants was also investigated through DSC experiments. The addition of bistetrazoles provided lower decomposition temperatures than the pure nitrogen-rich materials, indicating that the two compounds probably react readily with the –ONO₂ groups present in the nitrocellulose and the plasticizers used in the formulation. The onset temperature of all propellants remained within acceptable ranges despite the observed decrease caused by the addition of the bistetrazole compounds.

Keywords: Bistetrazole, Burning Rate, High Nitrogen, Nitrogen Rich, Propellant

1 Introduction

There are multiple challenges nowadays in the field of chemical propulsion. They range from increasing the performance, lowering the vulnerability, reducing the environmental impact, and minimizing the erosivity of the propellants, to name but a few. In recent years, a new family of energetic materials that has the potential to tackle these challenges has emerged in the form of nitrogen-rich molecules. These are often designated as nitrogen-rich materials due to their high nitrogen content, which can exceed 80% of the total weight of the molecule. This shifts the source of the energy produced in the molecule from the oxidation of the carbon backbone to the production of nitrogen gas from materials with high enthalpies of formation. On the other hand, most of the current research has focused on the synthesis of these new nitrogen-rich compounds, the characterisation of their physicochemical properties and their explosive performance, with little to no research on their effects when incorporated in actual propellants [1-3]. As an example, there has been some insight for the determination of the burn rates of some of the earlier nitrogen-rich materials, in their pure form, such as 3,6-dihydrazino-s-tetrazine (DHT), 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz), triaminoguanidinium-5,5'-azobis(1H-tetrazolate) (TAGzT), etc., under various pressure conditions [4-7]. Those works showcased high burn rates accompanied by very variable pressure exponents and linear burn rate coefficients.

The limited amount of work from the literature on nitrogen rich materials incorporated into gun propellants has focused on the effects of triaminoguanidinium nitrates (TAGN) and triaminoguanidinium azide (TAGAZ) [8], BTATz [9, 10] and TAGzT [6, 11, 12] on nitramine based

formulations. The formulations based on materials containing the triaminoguanidinium cation presented tremendously fast burning rates as well as increased pressure exponents. On the other hand, formulations incorporating BTATz showed lower pressure dependency, but high burning rates (at least 40% higher). Similarly, investigations of DAATO3.5 and BTATz as monopropellants for micro-thruster applications also showed low pressure exponents and high burning rates [13]. With one exception (Damse et al. [8]), the burn rate characterization of the nitrogen-rich propellants was conducted on low pressure ranges more suited to rocket propellants, that is on the order of 0.1 to 10 MPa which greatly differs from gun propellants where the pressure can reach upwards of 100 MPa while the combustion is still ongoing.

The past work on the burning behavior of nitrogen-rich materials demonstrated their potential usefulness as burn rate modifiers, which could also come with additional benefits, such as lower molecular weight combustion gases and lower flame temperature. It should however be noted that the amount of nitrogen-rich materials tested under such circumstances is fairly limited. The literature works previously performed also showed that the effects of such materials vary greatly from one nitrogen-rich material to another.

More recently, the number of nitrogen-rich materials based on the tetrazole ring that have been synthesized and characterized has significantly increased and they have shown desirable energetic content as well as fairly acceptable sensitivities. Tetrazoles are of particular interest as they strike the right balance between stability, nitrogen content and energy content through high enthalpies of formation. Among these materials, 5,5'-bis-(1H-tetrazolyl)-amine (BTA) and 5,5'-hydrazinebistetrazole (HBT), shown in Figure 1, have demonstrated a great potential, as their performance has been successfully compared to that

of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), two components often used in low vulnerability propellants [1, 2]. The synthesis of the precursor of HBT has successfully been scaled up to the multi-kilogram scale [14]. Care was taken to choose nitrogen rich molecules for which the synthesis could be scaled up with relative ease and with a small number of intermediaries.

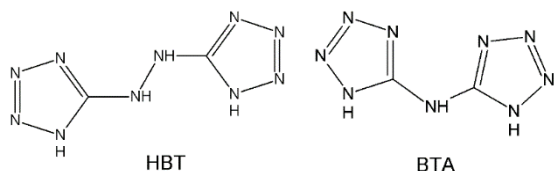


Figure 1. Chemical Structure of HBT and BTA

This work is concerned by the characterization of the effects of incorporating either BTA or HBT in a typical nitrocellulose-based triple base propellant. The burning performances of the resulted propellants were characterized via closed vessel tests. The thermal behavior of these propellants and their nitrogen-rich constituents has been investigated through differential scanning calorimetry (DSC) experiments. Furthermore, some of the properties of the bistetrazole molecules used, such as the sensitivity and density are also presented.

2 Results and Discussion

2.1 Bistetrazoles

Due to safety concerns associated with the handling of energetic materials, the sensitivities to impact and friction of the synthesised bistetrazole compounds were tested prior to mixing the propellant formulations. Similarly, in order to provide accurate calculations of the thermochemical properties of the propellant formulations, the density of the materials was measured through gas (helium) pycnometry. These values are reported in Table 1. Some differences were observed between the properties previously reported in the literature and the properties measured through experimentation.

Table 1. Selected Properties of the Nitrogen Rich Materials, RDX and HMX

	ρ (g/cm ³)	Impact (J) ^a	Friction (N) ^a
HBT	1.78	10	20
BTA	1.84	10	120
RDX	1.82	4	96
HMX	1.91	4	120

^a All sensitivity data was obtained using the same testing apparatus and methodology.

HBT proved to be much more sensitive than previously reported in the literature, as the reported sensitivities were greater than 30 J for impact and greater than 108 N for friction [2]. The impact

sensitivity is still better than that of many energetic materials used in low vulnerability ammunitions, such as RDX and HMX (see Table 1). However, HBT proved to be much more sensitive to friction than anticipated based on the values reported in the literature. The ¹H and ¹³C NMR performed on the HBT revealed no impurities to which the increase in sensitivity could be attributed. However, impurities below the detection threshold of NMR would not have been detected. Both HBT and BTA were not recrystallized either. The sensitivity results are in accordance with the testing previously done on HBT synthesized in much smaller quantities at our facilities.

BTA is less sensitive to friction than HBT and similarly sensitive to impact. Conversely, while BTA has proven to be more sensitive than previously reported (30 J, >360 N) [1], it still has lower sensitivity than materials with similar detonation parameters such as HMX (see Table 1). Both nitrogen-rich materials had slightly lower density than previously reported [1, 2], however, this could be attributed to the method used to calculate the density. Values previously reported in the literature were of 1.84 g/cm³ and 1.86 g/cm³ for HBT and respectively BTA and were measured through XRD. On the contrary, the density measurements in this work were obtained by performing gas pycnometry on the dry powders.

2.2 Thermochemical Data

A total of seven (7) propellant formulations were manufactured, starting with the reference formulation containing no nitrogen-rich components and followed by three formulations for each bistetrazole compound. The reference propellant was composed of 53% nitrocellulose, 39% trimethylolethane trinitrate (TMETN), 7% triethylene glycol dinitrate (TEGDN) and 1% stabilizer. Ethyl centralite was used as the stabilizer. The plasticizers were chosen after multiple CHEETAH calculations, which demonstrated that in order to maintain performance only a minimum amount of oxygen was required in the propellant. To obtain the bistetrazole propellants, parts of the reference propellant constituents were replaced by, respectively, 5%, 15% and 25% of bistetrazoles on a mass basis and in such a way that the nitrocellulose to plasticizer ratio remained the same for all formulations. The calculated thermochemical properties of the resulted propellant formulations are presented in Table 2.

Table 2. Thermochemical Properties of the Gun Propellants

	Ref.	5% HBT	15% HBT	25% HBT	5% BTA	15% BTA	25% BTA
F (J/g)	1138	1121	1084	1040	1138	1137	1134
T (K)	3224	3137	2954	2763	3187	3111	3032
P _{max} (MPa)	211	209	204	197	212	214	215
M _g (g/mol)	23.6	23.3	22.7	22.1	23.3	22.8	22.2
RF (%)	100	99.0	96.4	93.2	100	101	107

The thermochemical data provides some interesting insight as to the changes incurred from the

addition of nitrogen-rich materials to the propellant formulations. One of the first changes concerns the flame temperature. The reference formulation was mildly hot with a flame temperature of 3224 K, while the formulation incorporating 25% HBT proved to be what is considered a relatively cold propellant with a flame temperature of 2763 K, a reduction of 461 K. BTA yields hotter propellant formulations than HBT due to its higher enthalpy of formation (633 kJ/mol) compared to that of HBT (414 kJ/mol). However, all nitrogen-rich propellants yielded lower flame temperatures than the reference formulation. This probably resulted from the loss of oxygen content and the nature of nitrogen-rich materials, which shifted some parts of the gas generation from the oxidation of carbon backbones to the production of nitrogen. Despite this, the changes in oxygen balance were relatively moderate. The reference propellant has an initial oxygen balance of -36.7% while the propellants containing 25% of HBT or BTA, respectively have an oxygen balance of -42.3% and -42.4%. From the thermochemical calculations, both propellants generated final combustion products with lower molecular weight. These lower molecular weight combustion gases are believed to help offset the lower adiabatic flame temperatures, which in turn explains the relatively small loss of impetus. This is especially true for HBT, for which a reduction of impetus by 8.6% was accompanied by a reduction of flame temperature of 14.3% (almost double the decrease in impetus). Lower flame temperatures are of interest partly due to gun barrel erosion concerns. Not only does a lower flame temperature limit the reaction occurring between gun barrel steel and the hot combustion gases, it also limits thermal expansion and contraction during repeated firings, that were shown to lead to the cracking of the protective coatings generally used in gun barrels (i.e., hard chromium) [16]. In addition, when compared to the reference value (0.29), the N_2/CO ratio (a key parameter of the chemical erosivity of gun propellants) was found to be more than double (0.64 and 0.62) for, respectively, the 25% HBT and the 25% BTA propellants.

2.3 Burning Rates

The burning rate data was obtained from the pressure vs. time data recorded in the closed vessel, the thermochemical data calculated using CHEETAH, the propellant density and the geometrical dimensions of the propellant grains. In order to obtain good accuracy for the burning rate calculations, the density of the propellant grains was also measured using gas pycnometry rather than calculated using the density of the propellant constituents. The density of the reference was 1.559 g/cm³. The density of the propellants containing HBT varied from 1.570 g/cm³ to 1.623 g/cm³ and those of the propellant containing BTA from 1.559 g/cm³ to 1.606 g/cm³. As both HBT and BTA are notably denser than the reference formulation main ingredient (NC), replacing the latter by one of the former resulted in an increase in density with the increased concentration of these molecules.

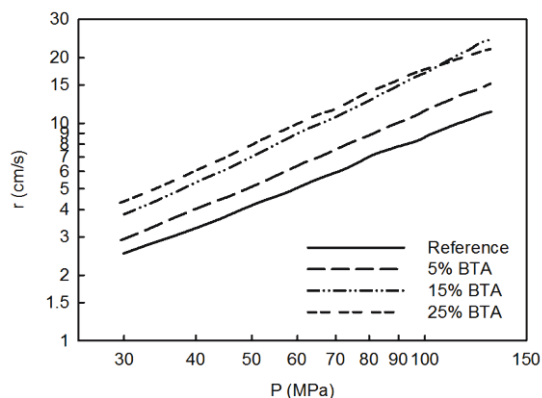


Figure 2. Burning Rates for the BTA Containing Propellants

The initial pressure raise caused by the igniter was subtracted from the pressure time data prior to the burn rate calculations. The burn rate laws were calculated in the 40-130 MPa range according to Vieille's law as shown in equation 1. Where r is the burning rate in cm/s, β is the linear burn rate coefficient and α is the pressure exponent. The burn rate-pressure curves for the reference and nitrogen rich propellants are shown in Figures 2 & 3.

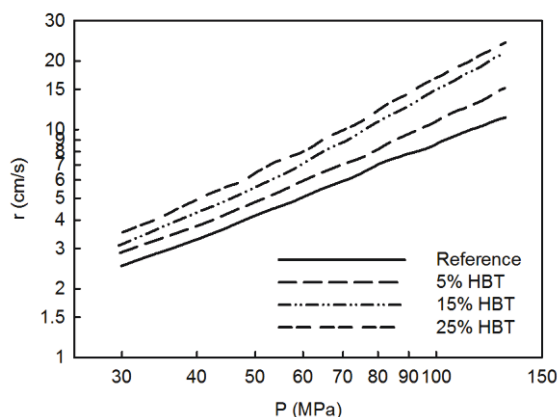


Figure 3. Burning Rates for the HBT Containing Propellants

As a first observation, all formulations containing nitrogen-rich molecules showed increased burn rates when compared to the reference propellant formulation. The reference was chosen from the literature for its reported relatively low pressure exponent, $\alpha=0.74$ [17] and also for its good oxygen content, most likely a result of the two nitrated esters used as plasticizers. However, the burn rate calculations performed showed a much higher pressure exponent than initially anticipated, $\alpha = 1.037$ for the reference propellant. Despite the higher than initially anticipated burning rates, the positive effects of the bistetrazoles on the increase of the burning rate are clearly visible from Figures 2 and 3.

The general effect of either of the two bistetrazoles on the burn rate of the propellants followed the same trend, which is an increase of the pressure exponent along with a decrease of the β coefficient at low concentrations. As the bistetrazole

concentration increases, the pressure exponent stabilizes at concentrations around 15% and then decreases slightly at concentrations of 25% (see Table 3). In the case of HBT, the β coefficient remained lower than that of the reference propellant and the pressure exponent α remained similar at concentrations of 15% and 25%. In the case of BTA, after an initial decrease of the β coefficient for the first two concentrations, the coefficient ended up being higher than that of the reference propellant with a pressure exponent equivalent to the reference propellant at 25% concentration. Such high pressure exponents are generally indicative that the combustion of the propellant is driven by gas phase reaction of an order greater than one. In the case of the propellant containing BTA, the decrease in burn rate would indicate a greater contribution from reactions occurring in the condensed phase. These results are similar to those obtained by Damse et al. [18] where both TAGAZ and TAGN showed a high increase of the pressure exponent of the same order at concentrations of 15%. On the other hand, the results from this study differ greatly from the burn rates measured for other pure nitrogen rich materials such as BTATz [4], where low pressure exponents and high burn rate coefficients were observed. The results here also differ from the ones for propellants containing BTATz, where the addition of the nitrogen-rich compound yielded lower pressure dependency in the form of low α and high β coefficients [10]. In the case of the propellants containing BTATz, RDX was used as the main component, different decomposition pathways are likely occurring, resulting in the difference in pressure exponent. Pure BTATz also shows very low pressure exponent likely further contributing to the decrease in pressure exponent of the formulation. Obviously, such high pressure exponents may not be desirable as it could induce instabilities during the combustion process.

Table 3. Closed Vessel Data for the Propellant Formulations

	Ref.	5% HBT	15% HBT	25% HBT	5% BTA	15% BTA	25% BTA
$\uparrow\%$ ¹	2.62	107	119	136	111	148	167
30 ²	± 0.1	± 6.6	± 5.8	± 5.3	± 5.8	± 6.2	± 5.5
$\uparrow\%$ ¹	5.29	112	136	153	122	171	188
60 ²	± 0.4	± 6.8	± 6.6	± 6.5	± 6.7	± 6.6	± 6.8
$\uparrow\%$ ¹	9.14	119	165	189	126	190	193
100 ²	± 0.6	± 7.0	± 7.3	± 7.2	± 7.0	± 7.0	± 7.8
β	0.074	0.043	0.024	0.028	0.057	0.044	0.110
	± 0.01	± 0.00	± 0.00	± 0.00	± 0.01	± 0.00	± 0.00
α	1.037	1.205	1.396	1.391	1.152	1.295	1.095
	± 0.03	± 0.04	± 0.01	± 0.03	± 0.02	± 0.00	± 0.01
RQ (%)	100	110	142	150	118	159	166
	± 0.0	± 4.1	± 1.1	± 0.9	± 1.3	± 1.0	± 1.7
RF (%)	100	101	103	99.0	99.9	98.2	96.1
	± 0.0	± 4.3	± 1.8	± 0.8	± 2.2	± 1.5	± 0.4

¹ Reference burning rate data in cm/s, all other data in percentage increase. ² Pressure in MPa.

Of note is the behavior of the propellant incorporating 25% BTA. The pressure exponent is in the range of common values for gun propulsion applications and the linear burn rate coefficient also

increases with the increase in nitrogen-rich concentration. As such, BTA could be used in high concentrations to generate quicker propellant formulations when needed while also reducing the flame temperature and probably increasing the performance. HBT on the other hand should likely be of use at lower concentrations, in slower propellant formulations, as a way of both reducing the flame temperature and increasing the burning rate. The decrease in the burn rate at higher pressure observed at 25% BTA concentrations was also noted in the case of RDX-TAGzT mixtures [11] and the authors attributed this to an increase in the amount of hydrazine-like free radicals produced during combustion. It remains to be seen whether the effect observed at 25% concentration of BTA could also be observed at higher (than 25%) concentrations of HBT.

As a way to measure the dynamic vivacity and the amount of usable energy generated by the propellant formulations, the relative quickness (RQ) and relative force (RF) were also calculated. Both the RQ and RF were calculated according to a procedure similar to that prescribed by the MIL-STD-286C standard [19]. The four data points used were those prescribed by the standard as a function of the maximum pressure of the reference formulation, 27%, 40%, 53% and 66% of the maximum pressure of the reference propellant. The relative force on the other hand was calculated as the average of the ratio of the maximum pressure for the firings of each propellant incorporating HBT and BTA to that of the reference propellant. The values of the relative quickness and relative force are shown in Table 3 and Figure 4.

The RQ is a good way of comparing the rate of pressure increase of new propellants to a reference. In this case, both nitrogen-rich materials showed great potential as quickness enhancers. The addition of either of the two bistetrazole compounds showed a similar trend. The increase in RQ happens at a much higher rate in the 0 to 15% concentration range and starts to plateau afterwards. Of the two materials, BTA gives the higher RQ of the two. This clearly shows the potential of both bistetrazoles as quickness enhancers for slow-burning propellant formulations. However, as mentioned above, the increase in quickness came at the cost of an increased BR dependency to pressure.

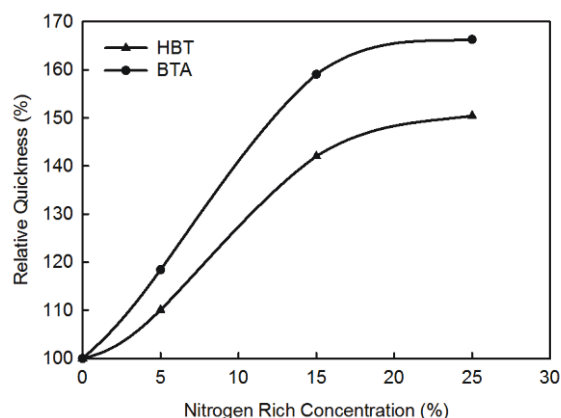


Figure 4. Relative Quickness of the Bistetrazole Containing Propellants

The RF calculated from the closed vessel tests is close to the one calculated from the thermochemical data. However, HBT propellants were found to yield a slightly higher RF when the closed vessel data is used for calculations, while the BTA propellants yielded slightly lower values (Table 2 vs Table 3). This could be attributable to the difference in propellants flame temperature. While the heat losses in the closed vessel were all in the same range, the propellants containing HBT showed slightly lower heat losses (evaluated using BRLCB v3.0). The maximum pressure calculated from the thermochemical data assumes adiabatic conditions while the closed vessel test did not ensure adiabatic conditions. Lower flame temperatures are expected to have lower heat losses to the jacket of the closed vessel and, as a result, the actual maximum pressure in the closed vessel would be closer to the theoretical adiabatic value. The same effect should be observed in an actual gun.

2.4 Thermal Behavior

DSC was performed on low mass samples (~0.5 mg) in order to avoid the effect of propellants self-heating from interfering with the heating rate of the apparatus. Initial tests were conducted at heating rates of 2, 5, 7 and 10 degrees Celsius per minute in order to determine the activation energy for the decomposition process observed. The Arrhenius plots used for the calculation of the activation energy are available in the supporting information section. The DSC curves for each propellant are presented in Figures 5 and 6 for the heating rate of 50C/min. All other presented values have also been evaluated at this heating rate. Also, the results derived from the DSC experiments are presented in Table 4. To avoid gas losses if any gas-phase reaction occurred, hermetic aluminium pans were used for the DSC experiments.

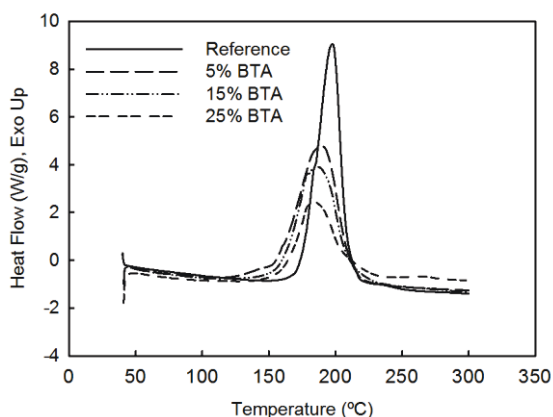


Figure 5. DSC Curves of the BTA Containing Propellants.

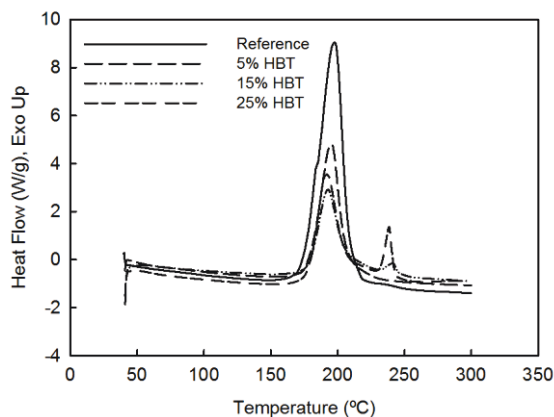


Figure 6. DSC Curves of the HBT Containing Propellants.

The activation energy needed for the decomposition of the propellants was calculated according to the Ozawa-Flynn-Wall method [20] as prescribed by ASTM standard E698 [21]. In order to verify the applicability of the method, the term E_a/RT used for the approximation of the integral was evaluated and it was verified that it remained between the 20-60 range, which verifies the applicability of the method. The activation energy for the propellant containing 25% BTA (312 kJ/mol) was found to fall outside of the applicability range of the method ($E_a/RT \approx 80$). Therefore, the value may not be accurate; however, it is presented as a qualitative comparison to the other activation energy values.

Table 4. DSC Data on the Propellants

	Ref.	5% HBT	15% HBT	25% HBT	5% BTA	15% BTA	25% BTA
Onset (°C)	177	179	179	179	157	162	160
Peak (°C)	198	196	192	192	190	186	186
E_a (kJ/mol)	170	174	197	213	148	141	N/D

The onset temperature of the decomposition process is a good indicator of the thermal stability of a propellant. The onset temperatures were measured for all seven propellants. The propellants containing BTA presented the lowest values for the onset temperature among the tested propellants. This is probably indicative that BTA readily reacts with the other constituents of the propellant formulations, most likely the $-ONO_2$ groups present both in the nitrocellulose and the plasticizers. Pure BTA showed an onset temperature much higher than that of any propellants studied here, with an onset at 246°C and decomposition peak temperature of 257°C. Propellants containing HBT on the other hand, showed no noticeable increase of the onset temperature meaning that the decomposition of the propellant is initiated by the decomposition of its other constituents. This would be indicative that HBT does not react as readily as BTA with the other constituents of the propellant formulations. The lower peak temperature for the propellants containing HBT probably indicates

that while HBT doesn't play a part in initiating the decomposition of the propellant, it still reacts with the other constituents and causes the propellant to undergo faster decomposition. From the safety concerns and thermal stability standpoints, HBT proved to be the most interesting of the two tested molecules.

Given the similarity between the two bistetrazole compounds, one can conclude that the chemical group present between the tetrazole cycles, in this case amine for BTA and hydrazine for HBT, has a direct effect on the thermal stability of the propellants. A similar trend can be observed with the activation energies of the main decomposition of the propellants. The activation energy for the HBT-containing propellants increases with the increase of the HBT content, which corroborates with the high thermal stability provided by HBT. On the contrary, for the BTA-containing propellants due to their lower thermal stability, the calculated energy of activation was found to decrease with the increase of the BTA content (see Table 4), which is also in agreement with the measured lower onset temperature of these propellants.

For the cases of the propellants containing 15% and 25% HBT, a second decomposition peak can be observed at higher temperatures (Figure 5). This peak is very small for the propellant containing 15% HBT, but becomes significant for the propellant containing 25% HBT. This second peak cannot be attributed to the decomposition of unreacted pure HBT. HBT's decomposition peak generally occurs at lower temperatures (226oC) than the decomposition peaks observed in Figure 5 (237oC). On the contrary, the propellants containing BTA do not show any additional decomposition peaks, except maybe for a very small peak at 25% concentration. It is likely that multiple decomposition reactions also occur for the propellants containing BTA, but they occur simultaneously rather than sequentially. Once again, the difference in the decomposition mechanisms can be attributed to the different chemical groups lodged between the two tetrazole rings.

While the exact decomposition mechanisms resulting from the addition of HBT and BTA remain unknown for now, a difference between the decomposition of the two bistetrazole compounds in the condensed phase can be observed through the DSC experiments. One interesting fact is that the decomposition mechanisms of bistetrazole containing propellants can be easily influenced by the presence or absence of certain chemical groups present between two tetrazole rings. This also suggests that the decomposition pathways of both compounds are probably different. As a result, the burning properties of bistetrazole containing propellants could be altered to a certain extent through the use of different chemical groups linking the two tetrazole rings, while the nitrogen and energetic content still remains high. This could also explain the difference observed in the burning behavior of HBT and BTA containing propellants compared to that of BTATz containing

propellants [10] where BTATz presents a s-tetrazine between two tetrazole rings rather than an amine or hydrazine group. This approach could be an alternative to the use of ionic nitrogen-rich compounds where the various cations and anions are generally used to change the burning properties and the composition of the resulting molecule. Of course, both approaches can be used in conjunction, with a good example being the use of salts of bistetrazole and azotetrazole.

3 Experimental

HBT and BTA were synthesized according the procedures previously described by Klapötke et al. [1, 2]. The purity of all materials was verified through hydrogen, carbon and nitrogen nuclear magnetic resonance spectroscopy (¹H-NMR and ¹³C-NMR). BTA: ¹H NMR (400 MHz, DMSO-*d*₆, 25°C) = 11.92 ppm (s, 3 H, NH) ¹³C NMR (400 MHz, DMSO-*d*₆, 25°C) = 154.16 (s, 2 C, CN₃). HBT: ¹H NMR (400 MHz, DMSO-*d*₆, 25°C) = 9.67 ppm (s, 4 H, NH) ¹³C NMR (400 MHz, DMSO-*d*₆, 25°C) 159.48 ppm (s, 2 C, CN₃). All materials were synthesized with high yields as well as good purity. Precursors for the synthesis of these materials were procured from Sigma-Aldrich and used as is with the exception of sodium 5-5'-azobis(1H-tetrazolate) (Na₂ZT) which was synthesized on site according to the procedure described by Radack et al. [14]. In the case of HBT and its azotetrazolate precursor, the syntheses were performed at higher concentrations than reported in the literature in order to reduce the reactor volume required, the other experimental conditions remained the same as those reported in the literature. Grade C nitrocellulose, nitrogen content of 13.25%, wetted with ethanol was used as the polymeric binder and as an energetic component.

The propellant manufacturing facility was previously described in detail by Petre et al. [15]. The propellants were mixed in a sigma blade mixer using the solvent incorporation method until a dough judged to be adequate for extrusion was obtained. The dough was subsequently extruded, cut in cylindrical geometries with no perforations and dried until the weight loss due to solvent evaporation was negligible.

Closed vessel tests were conducted on the propellant grains to evaluate their burning characteristics. For this study, a RARDE (model CV21, V=700 cm³) closed pressure vessel was used with an internal metallic sleeve in order to bring the volume down to ~188 cm³. The closed vessel can be operated at pressures up to 248 MPa. A piezoelectric pressure transducer was used to measure the pressure-time relationship for each sample. Ignition of the propellants was achieved using an electric match and a small quantity of black powder. All formulations were fired at a loading density of 0.155 g/cm³. The use of the sleeve increased the heat loss in the vessel to an estimated 30%-35% for all firings. The burning rate coefficient (β) and pressure exponent (α) as well as the dynamic vivacity were calculated from the

pressure-time data recorded in the closed vessel and the use of the impetus and flame temperature data simulated through the use of the CHEETAH thermochemical code using the virial equation of state (BLAKE compatibility). The BRLCB v3.0 computer code was used to perform the burning rate regressions. The closed vessel temperature was maintained at 210°C through the use of a jacket where cold water was circulated.

The sensitivity of the nitrogen rich materials was assessed using a Julius-Peters BAM friction apparatus and impact sensitivity was evaluated using a Julius-Peters drop hammer. The sensitivity threshold for both materials was defined as the force or energy where no reaction, be it smoke, crackling, spark or other occurred for six consecutive tests.

Differential Scanning Calorimetry was carried out using a TA Instruments Q2000 DSC with auto sampler and aluminium hermetic pans at various heating rates under a nitrogen flow of 50 mL/min.

4 Conclusions

Both bistetrazole compounds tested in this work (BTA and HBT) have shown high potential as burn rate modifiers, even when only small quantities were added to the propellant. In addition, both bistetrazoles studied here can easily be synthesized from commercially available materials with good yields and purity which will be helpful in scaling up the synthesis if desired. Furthermore, the synthesis of the precursor of HBT was successfully scaled up to the multi-kilogram scale [14].

By adding 5% of HBT or BTA to the triple base propellant formulation used in this work, the relative quickness was found to increase with 10% and 18%, respectively. Furthermore, by adding 15% of either HBT or BTA the relative quickness increased with 42% and 59%, respectively. On the contrary, at higher concentrations (>15%), the burn rate modification effects slowed down and it is probable that, for this particular propellant formulation, higher concentrations of bistetrazoles will only yield small increases of the burning rate. While the increase in burning rates may not be as significant at high concentrations, other advantages such as lower flame temperature and less erosive combustion gases for similar relative force can be obtained with the use of these nitrogen-rich molecules. This could be especially expected for HBT, where a sensibly lower flame temperature and a higher amount of nitrogen gas produced could lead to interesting reduction in gun barrel wear, with no significant performance losses.

The main disadvantage of the two chosen bistetrazoles is probably their effect on the pressure dependency of the burning rates. The presence of these materials was found to increase the pressure exponent (α) by a non-negligible amount and this is not desirable as it could yield combustion instabilities.

Of the two bistetrazole, HBT provided the better thermal stability to the resulting propellant. This in turn could result in safer propellants, despite the fact

that HBT itself was found to be more sensitive than its counterpart, which in turn provided a greater increase of burning rate properties. It is also important to note that the compatibility of the materials used in the propellant formulations was summarily evaluated. No short term compatibility issues were observed; however long term stability was not investigated.

Finally, the DSC experiments brought to light that, despite their similarities, both bistetrazole lead to different decomposition mechanisms when incorporated into the same propellant formulation. However, more work is needed in order to determine the exact decomposition pathways favored by these two molecules.

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References

- [1] T. M. Klapotke, P. Mayer, J. Stierstorfer, and J. J. Weigand, Bistetrazolylamines-synthesis and characterization, *J. Mater. Chem.* **2008**, 18, 5248-5258, 2008.
- [2] T. M. Klapotke and C. M. Sabate, Bistetrazoles: nitrogen-rich, high-performing, insensitive energetic compounds, *Chem. Mater.* **2008**, 20, 67-75.
- [3] R. E. Kaczmarek, M. S. Firebaugh, B. M. Rice, T. M. Klapötke, J. M. Short, R. D. Lynch, et al., *Topics in Energetics Research and Development*, ESPC Press, **2013**.
- [4] S. F. Son, H. L. Berghout, C. A. Bolme, D. E. Chavez, D. Naud, and M. A. Hiskey, Burn rate

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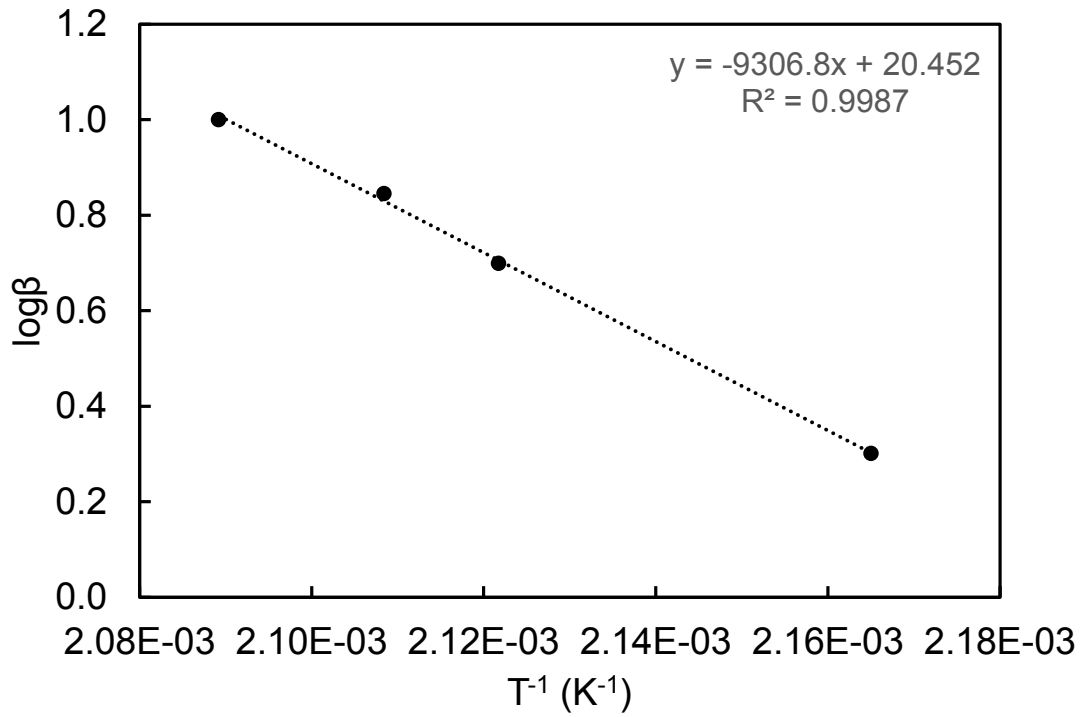
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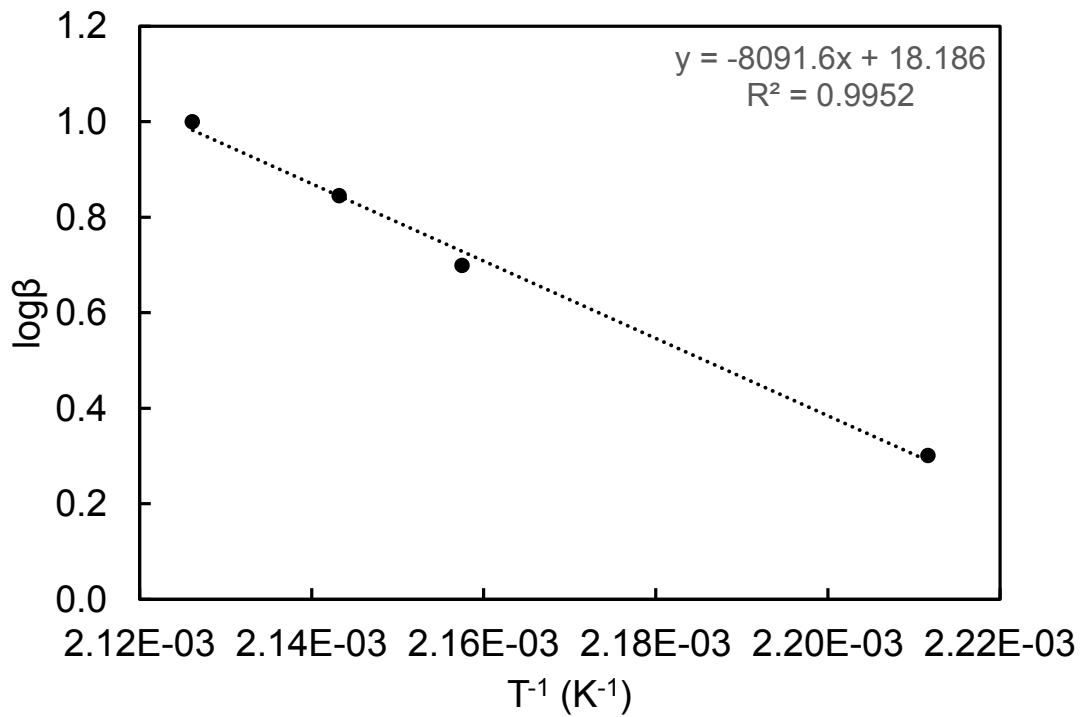
- measurements of HMX, TATB, DHT, DAAF, and BTATz *28th International Symposium on Combustion*, Edinburgh, UK July 30 - August 4, **2000**, p. 919-924.
- [5] D. E. Chavez and B. C. Tappan, Synthesis and Characteristics of Novel High-Nitrogen Material, *Int. J. Energ. Mater. Chem. Prop.* **2013**, 12, 173-182.
- [6] D. E. Chavez, B. C. Tappan, B. A. Mason, and D. Parrish, Synthesis and energetic properties of bis-(triaminoguanidinium) 3,3-dinitro-5,5-azo-1,2,4-triazolate (TAGDNAT): A new high-nitrogen material, *Propellants, Explos., Pyrotech.* **2009**, 34, 475-479
- [7] B. C. Tappan, S. F. Son, A. N. Ali, D. E. Chavez, and M. A. Hiskey, Decomposition and performance of new high nitrogen propellants and explosives, *6th International Symposium on Special Topics in Chemical Propulsion: Advancements in Energetic Materials and Chemical Propulsion*, Santiago, Chile, **2005**, p. .
- [8] R. S. Damse, N. H. Naik, M. Ghosh, and A. K. Sikder, Thermoanalytical screening of nitrogen-rich compounds for ballistic requirements of gun propellant, *J. Propul. Power* **2009**, 25, 249-256.
- [9] J.-H. Yi, F.-Q. Zhao, Y.-H. Ren, B.-Z. Wang, C. Zhou, X.-N. Ren, et al., "BTATz-CMDB propellants: High-pressure thermal properties and their correlation with burning rates," *J. of Therm. Anal. and Calorim.* **2011**, 104, 1029-1036.
- [10] J.-H. Yi, F.-Q. Zhao, B.-Z. Wang, Q. Liu, C. Zhou, R.-Z. Hu, et al., Thermal behaviors, nonisothermal decomposition reaction kinetics, thermal safety and burning rates of BTATz-CMDB propellant, *J. Hazard. Mater.* **2010**, 181, 432-439.
- [11] N. Kumbhakarna, S. T. Thynell, A. Chowdhury, and P. Lin, Analysis of RDX-TAGzT pseudo-propellant combustion with detailed chemical kinetics, *Combust. Theory Modell.* **2011**, 15, 933-956.
- [12] B. A. Mason, J. M. Lloyd, S. F. Son, and B. C. Tappan, Burning rate studies of bis-triaminoguanidinium azotetrazolate (TAGzT) and hexahydro-1,3,5-trinitro-1,3,5-triazave (RDX) mixtures, *Int. J. Energ. Mater. Chem. Prop.* **2009**, 8, 31-8.
- [13] A. N. Ali, S. F. Son, M. A. Hiskey, and D. L. Naud, Novel High Nitrogen Propellant Use in Solid Fuel Micropropulsion, *J. Propul. Power* **2004**, 20, 120-126.
- [14] C. Radack, J. Salan, and L. Shelly, Bis Triaminoguanidinium Azotetrazolate (TAGzT) Scale Up And Production, *AIChE 2007 Annual Meeting*, Salt Lake city, UT, USA, November 4-9 **2007**.
- [15] C. F. Petre, F. Paquet, C. Nicole, and S. Brochu, Optimization of the Mechanical and Combustion Properties of a New Green and Insensitive Gun Propellant Using Design of Experiments, *Int. J. Energ. Mater. Chem. Prop.* **2011**, 10, 437-453.
- [16] I. A. Johnston, *Understanding and Predicting Gun Barrel Erosion*, Report DSTO-TR-1757, Weapons Systems Division - Defence Science and Technology Organisation, Edinburgh, Australia, **2005**.
- [17] N. Kubota, *Propellants and Explosives Thermochemical Aspects of Combustion*: Wiley-VCH, **2007**.
- [18] R. S. Damse and A. K. Sikder, Suitability of nitrogen rich compounds for gun propellant formulations, *J. Hazard. Mater.* **2009**, 166, 967-971.
- [19] U. S. Department of Defense, "MIL-STD-286C," ed, **1991**.
- [20] J. H. Flynn and L. A. Wall, General Treatment of the Thermogravimetry of Polymers, *J. Res. Natl. Bur. Stand. (U. S.)* **1966**, 70A, 487-523.
- [21] ASTM, Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method Standard E698-11, Conshohocken, PA: ASTM International, **2011**.

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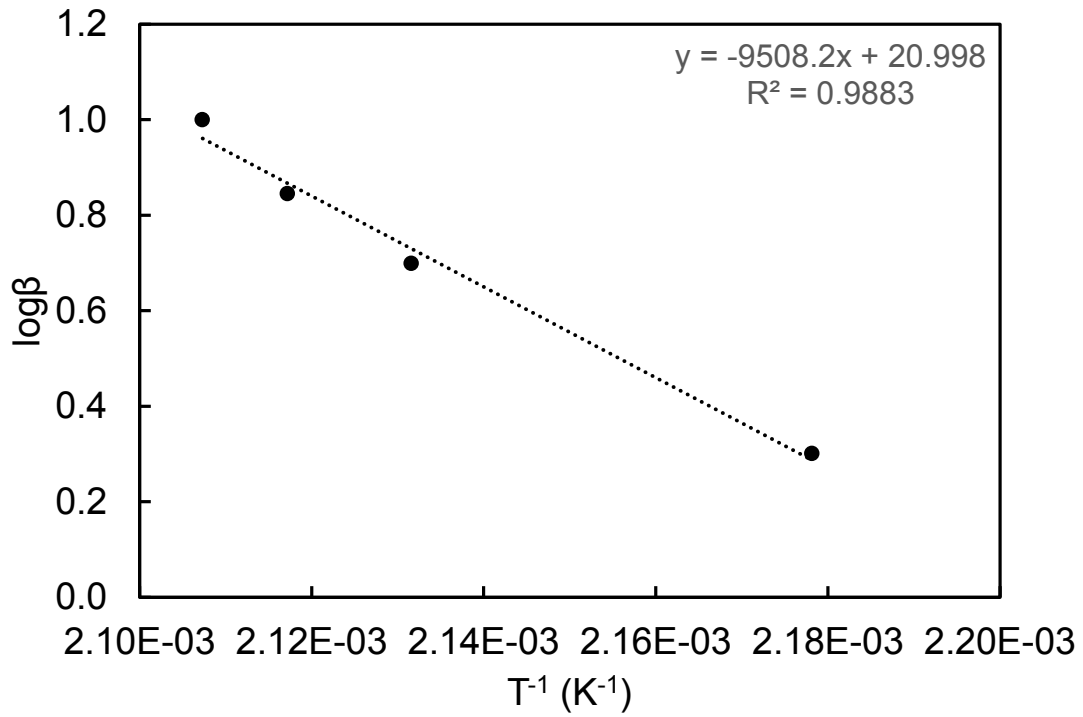
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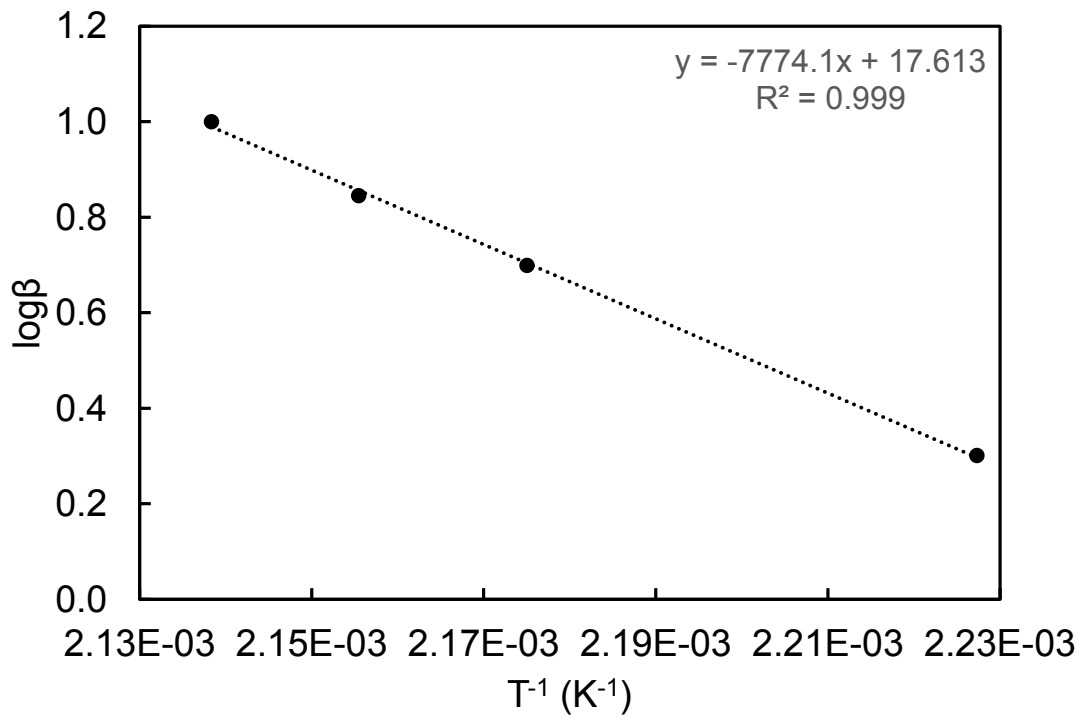
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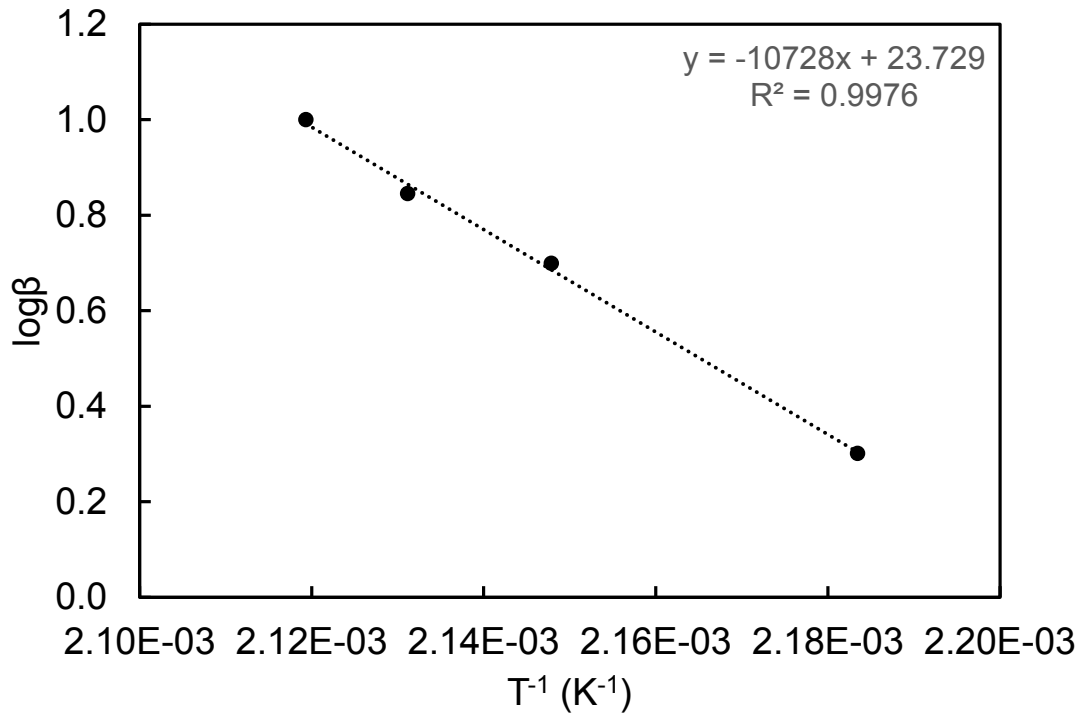
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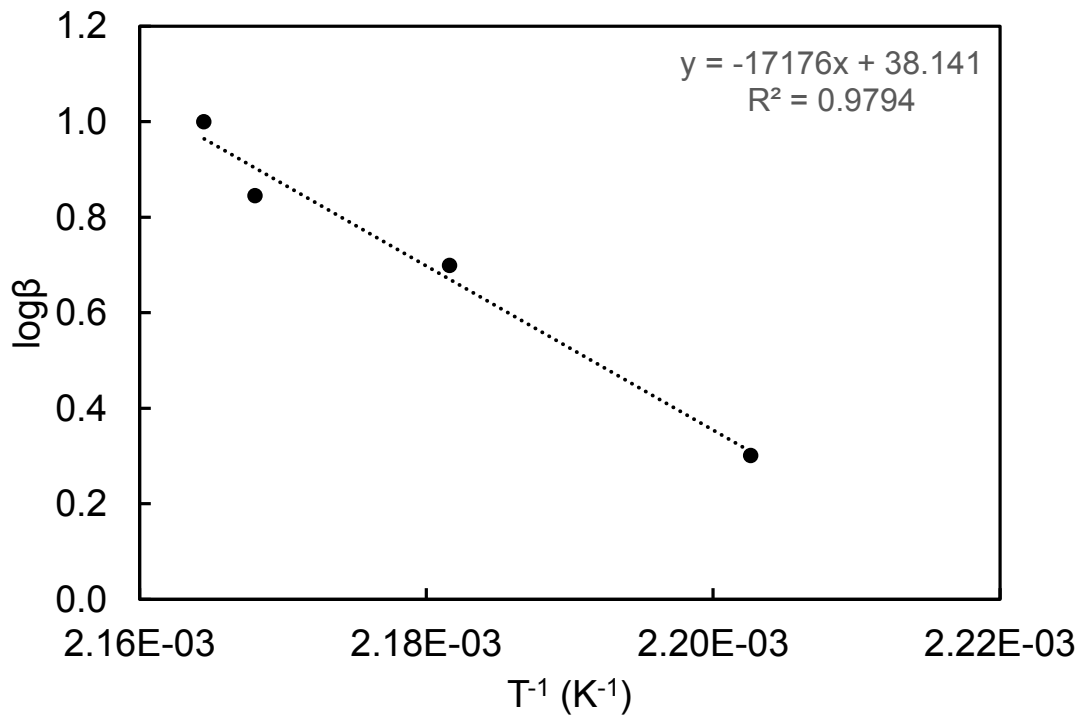
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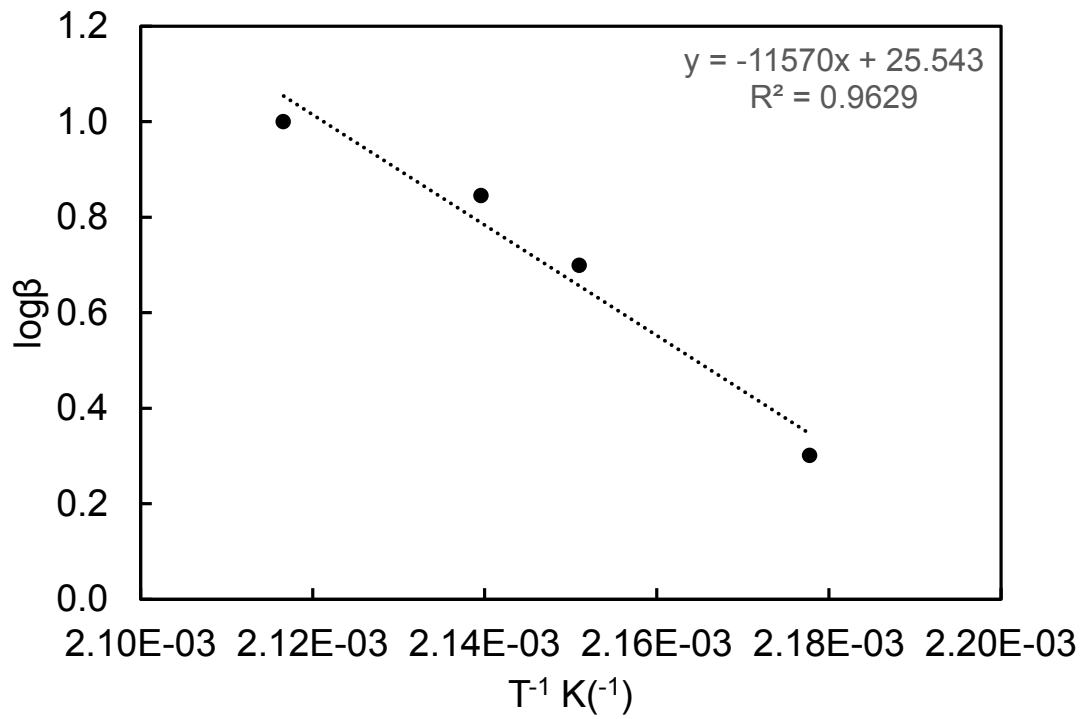
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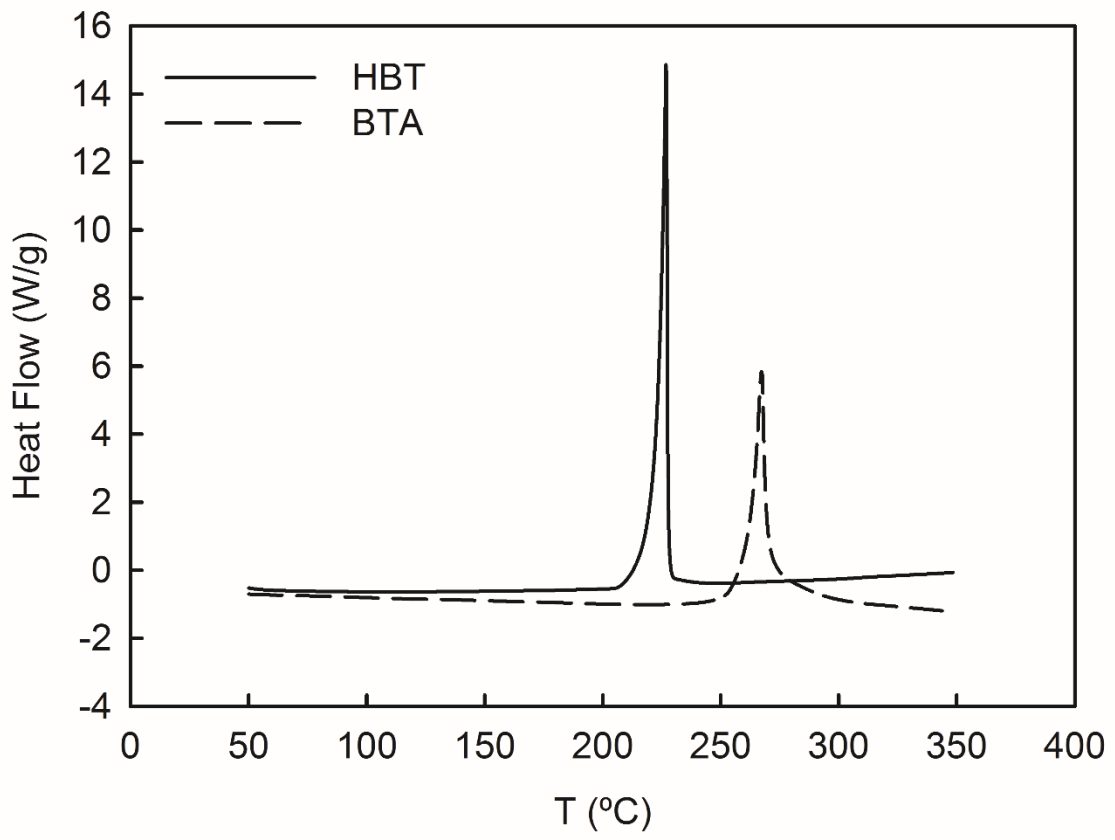
Arrhenius plot of the propellant containing 15% HBT



Arrhenius plot of the propellant containing 25% BTA



Arrhenius plot of the propellant containing 25% HBT



DSC of the pure nitrogen rich materials

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The influence of two selected bistetrazoles, 5,5'-bis-(1H-tetrazolyl)-amine (BTA) and 5,5'-hydrazinebistetrazole (HBT), on the combustion behaviour of a typical triple-base propellant was investigated. Seven propellant formulations, one reference and six others incorporating respectively, 5%, 15% and 25% of either HBT or BTA compounds were mixed and extruded into a cylindrical, no perforations, geometry. The resulting propellants showed high burning rates, up to 93% higher than the reference formulation at 100 MPa. However, the increase in burning rates came at the cost of higher burning rate dependency on pressure, with a pressure exponent as high as 1.4 for certain formulations. HBT-containing propellants showed notably lower flame temperature when compared to the reference formulation, with a flame temperature reduction of up to 461 K for the propellant containing 25% HBT. The thermal behaviour of the propellants was also investigated through DSC experiments. The addition of bistetrazoles provided lower decomposition temperatures than the pure nitrogen-rich materials, indicating that the two compounds probably react readily with the -ONO₂ groups present in the nitrocellulose and the plasticizers used in the formulation. The onset temperature of all propellants remained within acceptable ranges despite the observed decrease caused by the addition of the bistetrazole compounds.

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