

Synthesis, Properties and Performance of the High Explosive ANTA

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Synthese, Eigenschaften und Leistung des Hochleistungssprengstoffs ANTA

3-Amino-5-nitro-1,2,4-triazol (ANTA) wurde hergestellt und bewertet in Bezug auf seine Unempfindlichkeit und Leistung. Die Verbindung ist sehr unempfindlich gegen Stoß aber mäßiger gegenüber thermischen Einflüssen. Es wurde gefunden, daß die Leistung niedriger ist als die des 1,3,5-Triamino-2,4,6-trinitrobenzols (TATB). Die Synthese des ANTA erfolgt am besten über einen Dreistufenweg unter Verwendung des handelsüblichen 3,5-Diamino-1,2,4-triazols.

Synthèse, propriétés et performances de l'explosif énergétique ANTA

Le 3-amino-5-nitro-1,2,4-triazole (ANTA) a été synthétisé et évalué sur le plan de son insensibilité et de ses performances. La composition est très insensible aux chocs, mais ne l'est que moyennement aux influences thermiques. On a constaté que la performance était inférieure à celle du 1,3,5-triamino-2,4,6-trinitrobenzène (TATB). La meilleure méthode de synthèse de l'ANTA est une méthode en trois temps qui utilise le 3,5-diamino-1,2,4-triazole du commerce.

Summary

3-Amino-5-nitro-1,2,4-triazole (ANTA) was prepared and evaluated in terms of insensitivity and performance. The material is very insensitive to impact and moderately so to thermal stimuli. Performance was found to be inferior to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). The best synthesis of ANTA is a three-step route using commercially available 3,5-diamino-1,2,4-triazole.

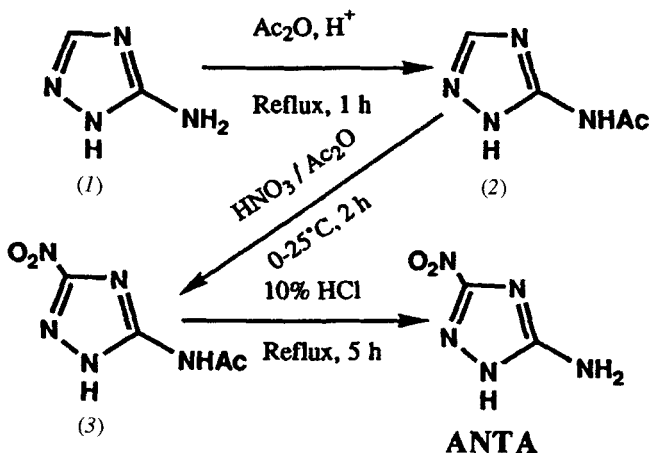
1. Introduction

Our interest in ANTA falls under our general interest in amino-nitro heterocyclic compounds as insensitive energetic materials. The substituent combination of amino and nitro groups provides the inter- and intramolecular hydrogen bonding that may stabilize the molecule and increase its crystal density. The heterocyclic substrates are included to add density compared to the corresponding carbocyclic materials, and, in many cases, contribute to a more positive heat of formation. ANTA was a known material⁽¹⁻³⁾ that met these criteria. Although it had received some interest as an energetic material, we felt it needed further investigation to more fully define its energetic properties.

2. Synthesis and Preparation

ANTA was first prepared by Pevzner, et al.⁽¹⁾ starting from commercially available 5-amino-1,2,4-triazole (1).

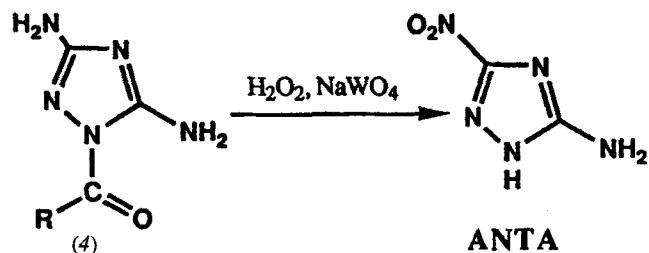
Compound (1) was converted to the 5-acetamido derivative (2) with acetic anhydride, and then nitrated with an acetic acid/nitric acid mixture to give 3-nitro-5-acetamido-1,2,4-triazole (3). ANTA was then obtained by hydrolysis with hydrochloric acid. This three-step synthesis is the most direct route to ANTA, but it suffers from variable and poor yields in the nitration step. The highest yield obtained in our laboratory, under a wide variety of nitration conditions, was about 20%. Yields were not consistent under identical conditions, and often no yield or only a trace of the desired nitrated material could be isolated.



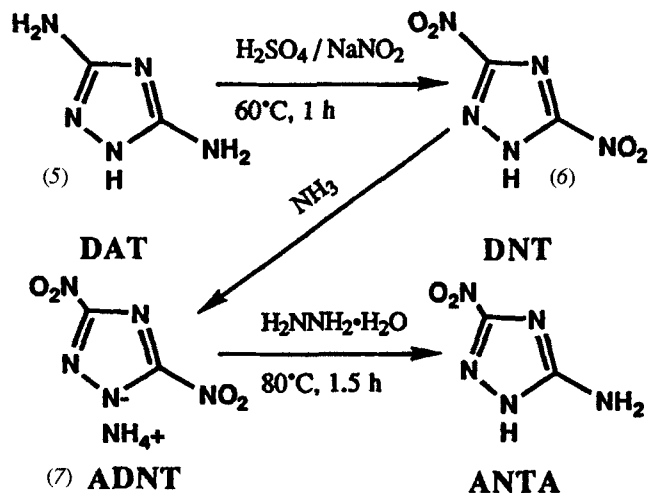
A second route to ANTA, reported by Namestnikov, Kofman, and Pevzner⁽²⁾ in 1982, involves the oxidation of 1-acyl-3,5-diamino-1,2,4-triazole (4) with hydrogen perox-

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ide in the presence of sodium tungstate to give ANTA. The route does not appear to offer any advantage over the first and third routes discussed in this section in that it involves an acetylation step and the use of hydrogen peroxide. It has not been investigated in this laboratory.



An alternative route to ANTA was developed by Lee, Storm and Stinecpher^(3,4) starting with commercially available 3,5-diaminotriazole (5). In this two-step process, (5) is converted to 3,5-dinitrotriazole (6) by a diazotization reaction using sodium nitrite in sulfuric acid. Although yields from this reaction are moderate (70%-80%), the reaction is time-consuming and requires constant monitoring. Foaming can also be a problem. Further scale-up of this reaction to multi-pound quantities should be of some concern, since unstable diazonium salts are present. The procedure we developed for the synthesis of (6) is essentially the same as that of Stinecpher⁽³⁾ except that the reaction temperature was maintained at -15°C to -10°C to control foaming and any exotherm that might occur and to permit more rapid addition of the sodium nitrite solution.



Compound (6) is soluble in the aqueous reaction mixture but may be extracted by multiple extractions with ethyl ether. Treatment of the ether solution with ammonium bicarbonate gave a stable, easily isolable yellow solid, ammonium 3,5-dinitro-1,2,4-triazole (ADNT). A method for extraction of (6) from the aqueous reaction mixture with a solution of tridodecylamine in toluene was also investigated⁽⁴⁾. This method avoids the multiple extraction steps the first entails, making it more amenable to scale-up. The extraction with tridodecylamine yields a toluene-soluble tri-

dodecylammonium 3,5-dinitro-1,2,4-triazolate. This was converted to ADNT by bubbling anhydrous ammonia through the toluene solution to precipitate the ADNT and regenerate the tridodecylamine/toluene solution. ADNT may be purified by dissolution in a 9:1 EtOAc/acetone solution, removal of insoluble inorganic material by filtration, and partial evaporation of the solvent. This precipitates ADNT in 81% yield and in pure enough form to use in subsequent steps.

The next step in the synthesis of ANTA involves the reduction of one of the nitro groups of (7) to an amino group and is essentially the same as that described in Ref. 3. This reduction is accomplished in 95% yield by simply stirring (7) with 4 molar equivalents of hydrazine hydrate at 80°C to 85°C for 90 min. Upon cooling and neutralization with 10% HCl, ANTA separates as a yellow, crystalline solid. ANTA is essentially pure at this point but can be recrystallized from water, which also serves to remove any residual hydrazine hydrochloride side-product.

2.1 Synthesis of ammonium 3,5-dinitro-1,2,4-triazole (ADNT)

A solution of 3,5-diamino-1,2,4-triazole (DAT) (8.0 g, 80.8 mmol) in 0.68M sulfuric acid (294 ml, 0.2 mol) was added dropwise over 2-3 h to a solution of sodium nitrite (53.3 g, 0.74 mol) in water (55 ml). This reaction can be carried out in an open 3-necked flask, and care should be taken so that the nitrogen oxide gases evolved do not come in contact with the DAT solution. This causes solids to form in the addition funnel, and makes the addition of the DAT solution difficult. Best mixing is achieved with a mechanical stirrer. After the addition is complete, the orange mixture is heated at 60°C for about 1 h, or until all solids in the reaction are dissolved. The reaction mixture is then cooled to $0-5^\circ\text{C}$ and 26.5 ml of 6M sulfuric acid (0.16 mol) is added to acidify the mixture. A 4-g sample of urea is added which may cause some foaming. The mixture is treated with activated charcoal for 0.5 h, filtered, and the light yellow solution is extracted six times with 250 ml portion of diethyl ether. These extracts are combined and dried over magnesium sulfate, the solution is reduced to about 30 ml with a rotary evaporator, and 100 ml of acetone is added. This solution is stirred with finely ground ammonium carbonate (30 g) until it is basic to moist litmus paper. The excess ammonium bicarbonate is filtered off, and the solvent is removed under vacuum to yield a light yellow solid. Occasionally this product is an oil which must be placed under vacuum in a desiccator to solidify. Addition of 30 ml of a 9:1 mixture of ethyl acetate to acetone allows the collection of a light yellow solid by suction filtration. Weight, 11.4 g (80% yield).

2.2 Synthesis of ANTA by procedure 1

The following reaction is typical of the preparation of ANTA from 3-acetamido-5-nitro-1,2,4-triazole. Scale-up does not appear to cause any problems.

A 16.0-g sample of 3-acetamido-5-nitro-1,2,4-triazole is stirred in 340 ml of 10% aqueous HCl. The mixture is refluxed for 4.5 h during which time the solid dissolves giving a yellow solution. This solution is then cooled with an ice bath for one hour causing the precipitation of ANTA. The product is collected by filtration and dried overnight under high vacuum. Weight, 4.82 g; yield, 40%. ANTA is sufficiently pure at this point to use for further reactions.

2.3 Synthesis of ANTA by procedure 2

The following reaction is typical of the preparation of ANTA from the ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT). It may be scaled up so that the quantity of ANTA produced is 50 g. The reaction is easily scaled up with no apparent problems.

A 5 ml (5.16 g, 103 mmol) sample of hydrazine monohydrate is placed in a 25 ml round-bottomed flask. To this is added in small portions 7.05 g (40 mmol) of ADNT, and the resulting mixture is refluxed for 2.5 h. This mixture must be heated slowly to reflux temperature, since there is a vigorous gas release during the first phase of this reaction. After refluxing, the solution is immediately added to 50 ml of cold 20% hydrochloric acid (if the reaction is allowed to cool to ambient temperature solidification can occur). This mixture is stirred for 15 min and placed in freezer overnight. The precipitated product was collected by suction filtration, washed with a small amount of cold water, and dried under vacuum. Weight, 4.65 g (90% yield). Recrystallization from ethanol yielded 4.04 g (87% recovery, 78% yield) of needles; mp 238°C-241°C.

All reaction pathways yielded material with similar sensitivity characteristics. The material used for small scale characterization and performance evaluation was synthesized by procedure 1.

3. Properties

The nuclear magnetic resonance and infrared spectral peaks of pure ANTA are shown in Tables 1 and 2.

Table 1. $^1\text{H-NMR}$ Peaks of ANTA in DMSO-d_6

δ [ppm]	Integration	Proton
6.85	S (5,2 H)	$-\text{NH}_2$
3.31	S (5,1 H)	$>\text{NH}$

Table 2. Infrared Absorption Peaks of ANTA in KBr [cm^{-1}]

3443 (s) ^(a) ,	3331 (m),	3237 (w),	3172 (w),
1656 (m),	1638 (m),	1588 (w),	1515 (s),
1399 (m),	1385 (m),	1312 (m),	1127 (w),
1038 (w),	849 (w),	754 (w),	645 (w)

(a) Peak strength.

Two crystal structures of ANTA have been identified. Garcia and Lee⁽⁵⁾ identified a monoclinic crystal, having a C2/c space group, and a density of 1.819 g/cm³. The nitro

group, in this α -polymorph, has a 10.5° out of plane twist. Gilardi⁽⁶⁾ discovered a β -polymorph when the material was recrystallized from 2-butanone. This phase is monoclinic, P2₁/n, and has a density of 1.730 g/cm³. The β -polymorph forms hydrogen bonded sheets which are planar to within 0.006 Å. The material used in this work was inferred to consist of mainly the α -polymorph as all of the pressed parts exceeded the theoretical maximum density of the β -polymorph.

The heat of formation of ANTA was determined using a Parr, isothermally jacketed, calorimeter. Temperature resolution to 0.0001°C was obtained with a quartz thermometer. The sample was recrystallized from water and dried under vacuum. The heat of combustion was found to be -9.891 ± 0.008 kJ/g. Using this value the heat of formation was calculated to be 61.1 ± 4 kJ/mol.

Thermal stability was examined by: differential scanning calorimetry (DSC), the chemical reactivity test (CRT), and one-dimensional-time-to-explosion measurements. Figure 1 shows the DSC trace obtained with pure ANTA at 10°C/min. A significant exotherm, attributed to chemical decomposition, begins at 227°C. The principal exotherm occurs at 243°C. This value corresponds to the observed melting point of 238°C-241°C. Phase interconversion, suggested by the X-ray results, is not indicated at temperature below decomposition.

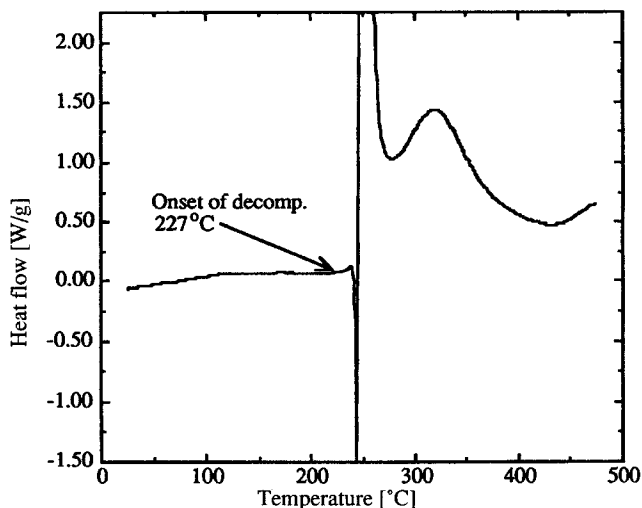


Figure 1. Differential scanning calorimetric trace obtained with pure ANTA. (Scan rate was 10°C/min)

The CRT measurement consists of heating samples to 120°C for 22 h under 1 atm of He. Total volume of gas evolved is measured and compositional analyses are made with gas chromatography. Total gas evolved was low and near the limits of instrument resolution. Decomposition products consisted mainly of N_2 , CO_2 and H_2O . The addition of a chlorofluoro-binder ($[\text{C}_8\text{H}_2\text{Cl}_3\text{F}_{11}]_n$) resulted in similar levels of gas evolved although there were trace amounts of NO and N_2O produced. These results are summarized in Table 3.

Other small-scale tests showed ANTA to be very insensitive. In particular the impact response was too low to be

determined with a 177 cm impactor height limit. This result, along with friction and spark sensitivity data, are given in Table 3.

Table 3. Small Scale Safety Test Results.

Material	Impact ^(a) [cm]	Friction ^(b) [kg]	Spark ^(c)	CRT ^(d) [cm ³ /g]
ANTA	>177	16.8	no rxn	0.24
RX-45-AA ^(e)	>177	14.4	no rxn	0.16
PETN ref.	13-16	8.0	no rxn	0.4-0.56
HMX ref.	32	11.6	no rxn	≤0.1

(a) 2.5 kg Type 12 tool with 35 mg pressed samples.

(b) Julius-Peters-Berlin 21 friction machine. One reaction in ten tries.

(c) Ten tries at 1 J with 510 Ω in line resistance.

(d) 22 h at 120°C under 1 atm He.

(e) RX-45-AA is 95wt% ANTA/5wt% KelF-800. KelF-800 is (C₈H₂Cl₃F₁₁)_n.

The thermal decomposition of ANTA with full mechanical and inertial confinement was studied by the one-dimensional-time-to-explosion method (ODTX)^(7,8). In this experiment a 1.27-cm diameter sphere is rapidly inserted between isothermally heated anvils. The time-to-explosion is measured while the anvils are held at a constant temperature. Mechanical confinement of the system is 10 MPa.

Figure 2 shows the results obtained with ANTA between 205°C and 305°C plotted as the logarithm of time versus inverse temperature. The material shows response times similar to HMX at low and high temperatures. At intermediate temperatures the time-to-explosion is less than HMX. Double explosions were obtained at 256°C and 275°C. This type of response is common with nitramines. At low temperatures pressure builds up slowly rupturing the cell non-violently. When the cell wall temperature is very hot, thermal transport limitations result in decomposition which is limited to the outer sample shell. At intermediate temperature an early mild reaction can vent the cell with a second explosion following. All explosions were considered mild with ANTA.

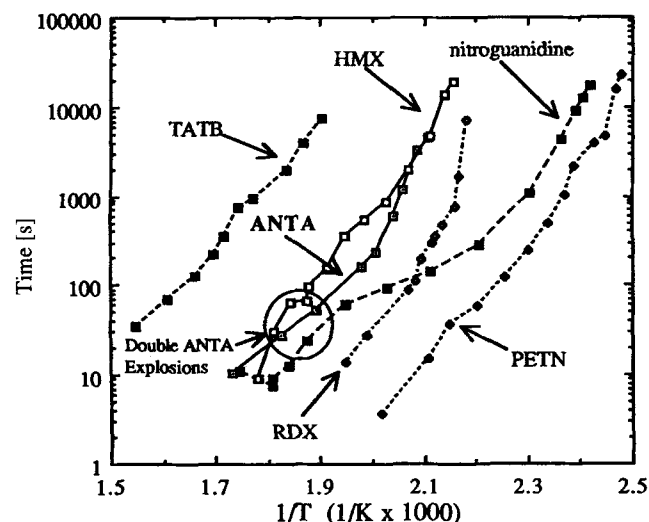


Figure 2. One-dimensional-time-to-explosion results for ANTA and common pure explosives.

4. Performance

To obtain large-scale performance properties an ANTA based molding powder was first developed. The chlorofluoro-binder KelF-800 was dissolved in a solution consisting of equal volumes of acetone and ethyl acetate. The ANTA was then slurry coated by adding it to the lacquer and removing the solvent at 80°C under vacuum producing a 95wt% ANTA/5wt% KelF-800 formulation. This formulation is designated RX-45-AA. Parts were ram-pressed at 100°C and 200 MPa. The nominal density of parts so obtained was 95.8% of theoretical maximum density (TMD).

4.1 Cylinder expansion test results

A cylinder expansion experiment⁽⁹⁾ was carried out on RX-45-AA. The experimental configuration is shown in Fig. 3. A rotating mirror streak camera was used to determine wall position as a function of time. To obtain high wall velocity resolution at small expansions of the detonation products, a two-legged Fabry-Perot interferometer was used. Three shorting pin rings were used to determine detonation velocity and whether a steady wave velocity was attained. A framing camera was also used to examine the quality of the cylinder expansion and the expansion volume at cylinder rupture.

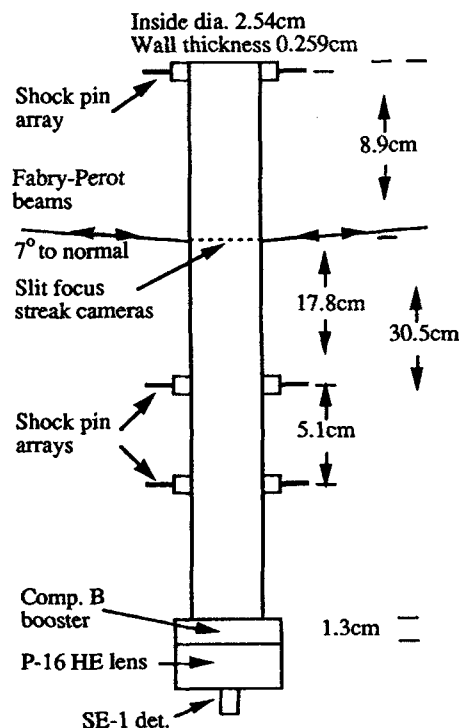


Figure 3. Experimental configuration for copper cylinder expansion.

4.2 Equation of state and comparison to predicted performance

The detonation velocity of RX-45-AA, at a density of 1.752 g/cm³, was measured at 7.71 mm/ μ s (\pm 0.03 mm/ μ s).

at 99% confidence). Early-time wall motion, as determined by Fabry-Perot velocimetry, is given in Fig. 4. The trace is consistent with spallation of the cylinder wall. After the second jump in surface velocity, the deceleration normally seen, which results because the strength of the copper wall exceeds the tensile forces caused by the shock reflection at the cylinder-air interface, is not apparent. This spallation is common with materials having large reaction zones, such as TATB. Hence, it is likely that ANTA reaction chemistry is similarly slow.

Figure 5 shows the radial wall velocity as a function of cylinder radius as determined by streak photography.

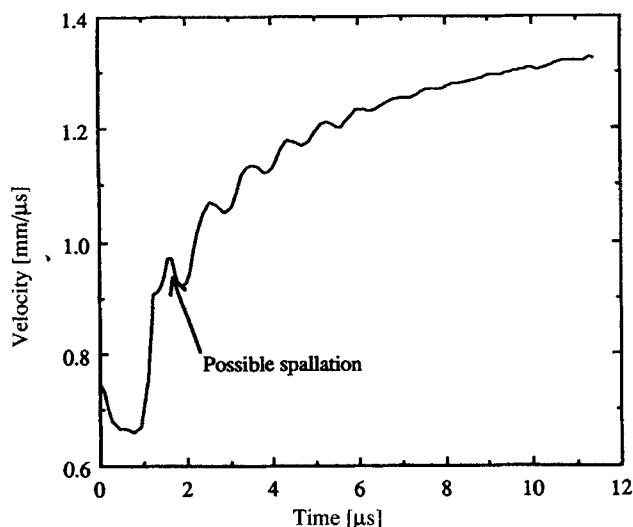


Figure 4. Fabry-Perot interferometric results on the early cylinder wall expansion of RX-45-AA. (Side-to-side velocity differences were negligible)

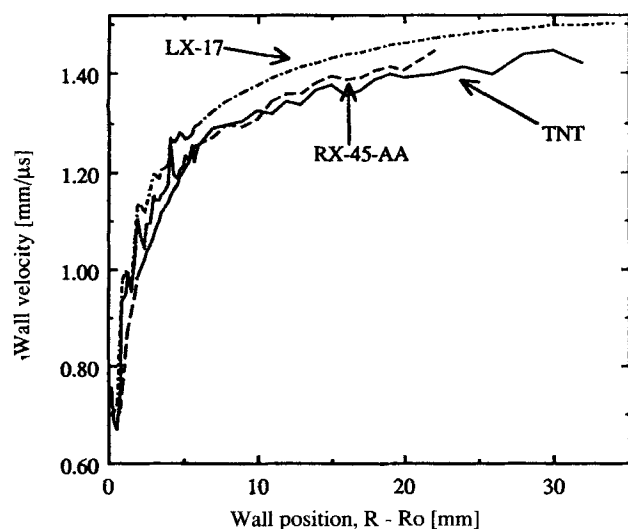


Figure 5. Wall velocity versus radial position for RX-45-AA, LX-17 (92.5 wt% TATB/7.5 wt% KelF-800), and pure TNT as determined by streak photography.

A summary of RX-45-AA performance is tabulated in Table 4. Wall velocity is given at cylinder expansions of: 6.5 mm, 12 mm, and 19 mm. These wall positions correspond to detonation product expansions of 2.2, 4.1 and 6.5,

Table 4. Detonation Velocity and Wall Velocity of RX-45-AA at Radial Expansions Corresponding to 2.2, 4.1 and 6.5 V/Vo. TATB Based Explosives are Included for Comparison.

	D [mm/μs]	Cylinder Wall Velocity [mm/μs]		
		R-R ₀ = 6.5 mm	R-R ₀ = 12 mm	R-R ₀ = 19 mm
RX-45-AA ρ ₀ = 1.752 g/cm ³ 95.8% TMD	7.71 ± 0.03 ^(b)	1.245	1.340	1.385
LX-17 ^(a) ρ ₀ = 1.875 g/cm ³ 96.5% TMD	7.54	1.305	1.405	1.455
LX-17 ^(a) ρ ₀ = 1.900 g/cm ³ 97.7% TMD	7.60	1.290	1.405	1.455

(a) Velocity data scaled down from 50 mm dia. experiments.

(b) 99% confidence.

as determined through numerical hydrodynamic calculations. For comparison, performance values of two densities of the insensitive high explosive LX-17 are also given. The relative energy of ANTA (RX-45-AA), at three volume expansions, is given in Table 5 as fraction of LX-17 energy. It can be seen that RX-45-AA performance is below that of TATB. Calculated performance of pure ANTA and TATB, supported by these experimental results, indicate that ANTA is slightly less energetic than TATB.

The elemental composition of ANTA is unusual in that it consists of a large amount of nitrogen. Performance data on ANTA, therefore, provides a valuable test of thermochemical approaches to predicting performance. The renormalized BKW equation of state⁽¹⁰⁾ (BKWR) was used to compare with the experimental results. These calculations were made by allowing chemical equilibration to occur until a volume expansion at which the detonation products are 1800 K is reached. At 1800 K the chemical composition is fixed and the products expand isentropically. This calculational method is based on comparison with experimental detonation calorimeter results⁽¹¹⁾. A large number of hydrodynamic experiments, on materials of significantly different elemental make-up, have been examined in this fashion and the results agree quite closely with predicted values.

In the case of RX-45-AA, BKWR underpredicts performance by about 2%. As ANTA is a low-energy, insensitive explosive, diameter effects in the 25-mm cylinder expansion cannot be ruled out. That is, somewhat greater performance may be seen at larger charge size.

5. Conclusions

ANTA has been synthesized by three routes, the best of which involves the diazotization of 3,5-diaminotriazole followed by reduction with hydrazine. The material has been found to be generally insensitive but of low energy. Performance of this high nitrogen material was overpredicted by several percent using the renormalized version of the BKW equation of state.

Table 5. Relative Energy of RX-45-AA Compared with LX-17 and Performance Prediction Based on Thermochemical Calculations Using the Renormalized BKWR Equation of State. (Based on these results BKWR was used to estimate performance of pure ANTA and TATB at crystal density.)

Material	Experimental Cylinder Wall Energy				BKWR Isentropic Energy	
	$(V_{\text{sample}}/V_{\text{ref}})^2$				Release - $\Delta E_{\text{sample}}/\Delta E_{\text{ref}}$	
	R-R ₀ = 6.5 mm	R-R ₀ = 12 mm	R-R ₀ = 19 mm	V/V ₀ = 2.2	V/V ₀ = 4.1	V/V ₀ = 6.5
RX-45-AA $\rho_0 = 1.752 \text{ g/cm}^3$ 95.8 % TMD	- 7%(b)	- 9%(b)	- 8%(b)	- 9%(b)	- 10%(b)	- 10%(b)
LX-17 ^(a) $\rho_0 = 1.900 \text{ g/cm}^3$ 97.7 % TMD	ref.	ref.	ref.	ref.	ref.	ref.
ANTA $\rho_0 = 1.819 \text{ g/cm}^3$ 100 % TMD	-	-	-	- 8.2%(c)	- 4.8%(c)	- 9.2%(c)
TATB $\rho_0 = 1.938 \text{ g/cm}^3$ 100 % TMD	-	-	-	ref.	ref.	ref.

(a) Velocity data scaled down from 50 mm dia. experiments. (b) Referenced to LX-17. (c) Referenced to TATB.

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