



Explosive Properties of 4,4',5,5'-Tetranitro-2,2'-bi-1*H*-imidazole Dihydrate

Rafał LEWCZUK,^{1*} Mateusz SZALA,¹ Judyta REĆKO,¹
Stanisław CUDZIŁO,¹ Thomas M. K LAPÖTKE,²
Waldemar A. TRZCIŃSKI,¹ Leszek SZYMAŃCZYK¹

¹*Institute of Chemistry, Military University of Technology,
Kaliskiego 2, 00-908 Warsaw, Poland*

²*Department of Chemistry, Ludwig-Maximilian University
of Munich, Butenandtstr. 5-13, 81377 Munich, Germany*

**E-mail: rafal.lewczuk@wat.edu.pl*

Abstract. This paper reports measured explosive properties of 4,4',5,5'-tetranitro-2,2'-bi-1*H*-imidazole dihydrate (TNBI·2H₂O). Non-isothermal kinetics analysis, calorimetric measurements, detonability tests, small-scale shock reactivity tests (SSRT), detonation velocity measurements and cylinder tests were performed. The results of the cylinder tests were used to determine the acceleration ability of TNBI·2H₂O. Some experiments were conducted also with TNT, NTO, FOX-7 and RDX. Our experimental studies have shown that TNBI·2H₂O is a thermodynamically stable compound, surpassing TNT with regard to its energetic and detonation parameters. The results of the SSRT indicate that this material has better performance in small charges than RDX, FOX-7 and NTO.

Keywords: TNBI dihydrate, NTO, explosives, detonation properties, thermal analysis

1 Introduction

It is commonly accepted that good explosives should combine excellent performance characteristics with high stability and low sensitivity to accidental mechanical and thermal stimuli. Weapon systems containing such explosives are not only effective but also safe in handling, and comparatively cheap in utilization, because of low logistical requirements [1]. Possible candidates for

insensitive highly energetic explosives are sought in the group of heterocyclic compounds, especially among nitro- and amino-nitro-substituted azoles and azines. The density and enthalpy of formation, and consequently also the performance parameters of these compounds increase with the addition of each nitrogen atom in the heterocycles [2, 3]. Additionally, dinitrogen then becomes the main product of their combustion or detonation processes, and this finally causes the processes to proceed almost without flame and smoke generation. The lack of solid residue and the minimization of visual and thermal signatures make these compounds of interest as novel propellant components [2, 3].

Unfortunately the replacement of carbon atoms with nitrogen atoms in the structure-creating role usually results in high sensitivity and low stability, in extreme cases (very high- and all-nitrogen compounds) to a level that excludes any applications [4]. One of the methods used to improve the sensitivity and stability characteristics of nitrogen rich, nitro-substituted azoles and azines is amination on positions *ortho* to the nitro group. Strong intra- and inter-molecular hydrogen bonds stabilize such compounds. Extensive and three-dimensional hydrogen bonding increases the lattice energy as well as the melting and decomposition temperatures [5].

It has been known for many years that 1,2- and 1,3-diazoles (pyrazoles and imidazoles, which structures are shown in Figure 1) that have two or more nitro substituents are highly energetic explosives with detonation parameters comparable to those of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) [6]. Amino- and nitro-substituted diazoles are significantly less sensitive to mechanical and thermal stimuli. For example, 4-amino-3,5-dinitropyrazole (LLM-116), produced by amination of 3,5-dinitropyrazole, has been proposed as an insensitive alternative to RDX. 1,4-Diamino-3,6-dinitropyrazolo[4,3-*c*]pyrazole (LLM-119) is more energetic than HMX, but it also exhibits low sensitivity to mechanical stimuli and electrostatic discharge [6].

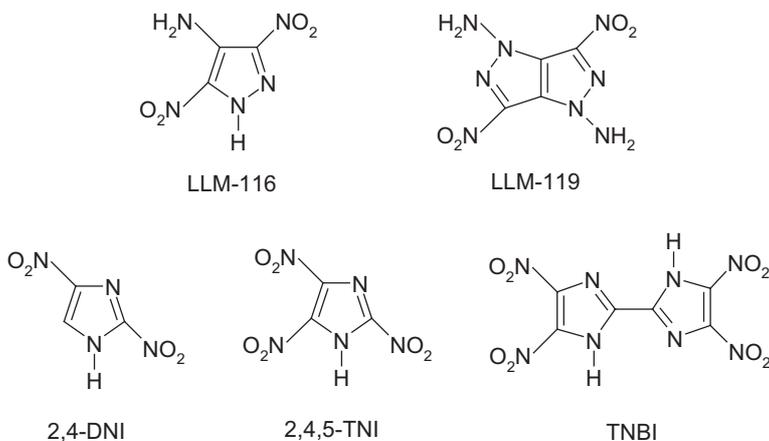


Figure 1. Chemical structures of the known nitro- and amino-substituted diazoles.

Various nitrated imidazoles, including 2,4-dinitroimidazole (2,4-DNI) [7], 4,5-dinitroimidazole (4,5-DNI) [8], 2,4,5-trinitroimidazole (2,4,5-TNI) [9], and 4,4',5,5'-tetranitro-2,2'-bi-imidazole (TNBI) [10] have also been synthesized and investigated. All of these are highly energetic explosives, but they suffer from hygroscopic properties and lack of chemical stability (they show nucleophilic properties), because of the presence of the labile N–H hydrogen at position 1 [11, 12]. On the other hand, the quite strong acidity of the nitro-substituted imidazoles facilitates the formation of stable ionic compounds. Organic salts in which both the cation and the anion belong to high-nitrogen molecules are of increasing interest, as they have very high enthalpies of formation that are directly attributed to the large number of single and double N–N and N–C bonds in the structures. Additionally such compounds also have high density and stability, low sensitivity and vapor pressure, as well as a good oxygen balance [3].

Recently, organic salts containing the doubly deprotonated, bicyclic anion of 4,4',5,5'-tetranitro-2,2'-bi-imidazole (TNBI) have attracted considerable interest [13–19]. After the addition of two large high-nitrogen cations, extensive molecules are formed, and this mostly results in a higher enthalpy of formation, lower sensitivity and high stability. In spite of the fact that many TNBI salts have been characterized in detail as promising explosives, the explosive properties of TNBI are not so well known.

In 2005, Cho *et al.* described the results of a thermal analysis of TNBI, and its sensitivity to impact, friction and electric spark [11]. They stated that pure TNBI is almost as sensitive to mechanical stimuli as RDX and HMX. Samples of pure TNBI exposed to the atmosphere absorb water forming the stable TNBI

dihydrate (TNBI·2H₂O), which is a less sensitive explosive. TNBI prepared by nitration of 2,2'-bi-imidazole with a NaNO₃/H₂SO₄ mixture may contain sulfate impurities, and this increases the hygroscopicity of TNBI samples [11].

A year later the same authors published a paper on the theoretical molecular and explosive properties of TNBI [12]. The heat of formation of TNBI in the solid phase was computed to be 207.3 kJ·mol⁻¹. Its density was estimated as 1.92-1.96 g·cm⁻³, and the calculated explosive performance (at a density of 97% TMD) was a bit better than that of RDX, with the velocity and pressure of detonation of approx. 8800 m·s⁻¹ and 35 GPa, respectively [12]. An experimental study of the parameters of blast waves in air generated by the detonation of TNBI dihydrate was performed by Szala *et al.* [20].

In the present work, the results of an experimental investigation of the explosive properties of 4,4',5,5'-tetranitro-2,2'-bi-imidazole dihydrate (TNBI·2H₂O) are presented. Non-isothermal kinetics analysis, calorimetric measurements, detonability tests, small-scale shock reactivity tests, detonation velocity measurements and cylinder tests were performed. The results of the cylinder tests were used to determine the acceleration ability of TNBI·2H₂O detonation products.

2 Methods, Results and Discussion

2.1 Synthesis of TNBI dihydrate

TNBI dihydrate was synthesized according to the previously published procedure by nitration of 2,2'-bi-imidazole (BI) with nitric acid in polyphosphoric acid, the latter prepared using phosphoric acid and phosphorus pentoxide [21]. The quality of the product depended on various parameters, *e.g.* purity of BI and concentration of the acids, so the yield was not reproducible in the series of experiments performed under the same conditions. The raw product was purified by recrystallization from water or solvents containing acetone, ethanol and water. The high purity of the TNBI·2H₂O samples prepared (above 99.5%) was demonstrated by TG/DTA plots, elemental analysis and ¹H, ¹³C, and ¹⁵N NMR spectra.

2.2 Non-isothermal kinetics analysis

The non-isothermal analysis method developed by Kissinger [22] has been applied many times to study the decomposition kinetics of energetic materials [23-25]. This method allows the kinetic parameters of a solid-state reaction to be calculated when the mechanism is unknown. The value of the activation

energy E_a can be obtained from a plot of $\ln(\beta/T_m^2)$ against $1000/T_m$ for a series of experiments at different heating rates (β), where T_m is the peak temperature on the DSC curve. The equation is:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_m}\right) \quad (1)$$

where A is the pre-exponential factor and R is the universal gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The activation energy can be calculated from the slope of the plot, which is equal to $-E_a/R$.

Differential scanning calorimetry (DSC) measurements ($2.00 \pm 0.05 \text{ mg}$ of each sample) were performed in covered Al-containers containing a hole (0.1 mm) in the lid for gas release and a nitrogen flow of $20 \text{ mL}\cdot\text{min}^{-1}$ on a Linseis DSC PT10, calibrated with standard pure indium and zinc.

The DSC thermograms of TNBI·2H₂O at different heating rates ($\beta = 2, 5, 10$ and $15 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) are presented in Figure 2 (left). To compare the results with another material, a series of experiments was also performed for 3-nitro-1,2,4-triazol-5-one (NTO) which has a similar decomposition temperature to TNBI dihydrate and low sensitivity to mechanical stimuli [26]. The DSC thermograms of NTO are presented in Figure 2 (right).

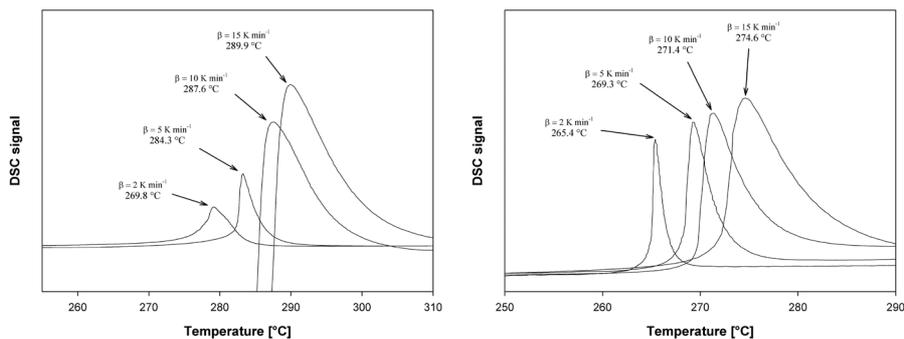


Figure 2. DSC curves of TNBI·2H₂O (left) and NTO (right) at different heating rates.

For Equation 1, straight lines were obtained when $\ln(\beta/T_m^2)$ was plotted against $1000/T_m$, and these are shown in Figure 3. Symbol r is the linear correlation coefficient for $\ln(\beta/T_m^2)$ vs. $1000/T_m$.

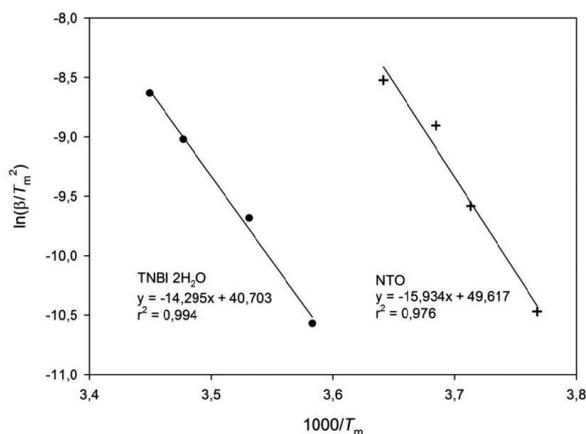


Figure 3. Kissinger plots for TNBI·2H₂O and NTO.

As can be seen, when the heating rate increases, the temperature of the exothermic peak maximum also increases, and this enables the kinetic parameters of thermal decomposition to be determined. Using the main exothermic peak temperatures, the apparent activation energy E_a of TNBI·2H₂O and the pre-exponential factor A were estimated to be 118.5 kJ·mol⁻¹ and 5.8449·10²¹ s⁻¹, respectively, with a correlation coefficient $r^2 = 0.994$. The activation energy E_a of NTO and the pre-exponential factor A were estimated to be 132.5 kJ·mol⁻¹ and 5.6327·10²² s⁻¹, respectively, with a correlation coefficient $r^2 = 0.976$. The Arrhenius equation can be expressed in E_a and $\ln A$ as follows:

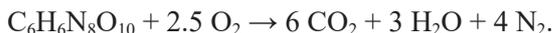
$$\begin{aligned} \text{TNBI}\cdot 2\text{H}_2\text{O}: & \quad \ln k = 50.12 - 118516 (RT)^{-1} \\ \text{NTO}: & \quad \ln k = 52.39 - 132475 (RT)^{-1} \end{aligned}$$

These equations can be used to calculate rate constant k at different temperatures T and thus assess the potential of the materials for thermal explosion. The activation energy for TNBI dihydrate decomposition is lower than that of NTO by ~14 kJ·mol⁻¹, but still indicates quite good thermal stability of dehydrated TNBI (TNBI·2H₂O loses crystal water in the temperature range 80-125 °C, [21]).

2.3 Thermodynamic aspects

A water calorimeter (static jacket) KL-12Mn, PRECYZJA-BIT, equipped with an oxygen bomb was used for the calorimetric measurements. Pressed samples of approx. 2.0 g in mass, and density 1.73 g·cm⁻³, were loaded into open quartz crucibles and initiated with an electrically heated wire. The calorimeter was

calibrated by combusting a benzoic acid standard in an oxygen atmosphere at a pressure of 3.0 MPa just prior to the measurement. The reported values are the average of three single measurements. The enthalpy of formation was calculated at 298.15 K using a Hess thermochemical cycle with the assumption that the combustion products contained only carbon dioxide, water and nitrogen:



The test and calculation results are summarized in Table 1.

Table 1. Physical properties of TNBI·2H₂O

Formula	C ₆ H ₆ N ₈ O ₁₀
Molecular mass [g·mol ⁻¹]	350.16
Nitrogen content [%]	32.0
Oxygen balance [%]	-22.8
Heat of combustion [J·g ⁻¹]	8765 ±80
Standard enthalpy of formation [kJ·mol ⁻¹]	-149.3

Cho *et al.* reported that pure TNBI had a positive value of the theoretically estimated enthalpy of formation (270.3 kJ·mol⁻¹) [12]. From our calorimetric measurements it follows that TNBI·2H₂O is a thermodynamically stable compound with a negative value of -149.3 kJ·mol⁻¹. This is a result of the inclusion of two molecules of crystal water on each TNBI molecule, stabilizing the structure by the creation of strong hydrogen bonds NH...O.

2.4 Detonability of TNBI·2H₂O

The detonability of TNBI·2H₂O was checked in a steel plate test. Pressed, unconfined, cylindrical charges with a mass of 6.0 g and diameter 16 mm were initiated with a commercially available detonator (containing ~0.8 g of PETN). The charges were placed on a 2-mm thick steel plate that served as a witness plate. A sketch of the test setup and a photograph of the witness plate after the test are presented in Figure 4.

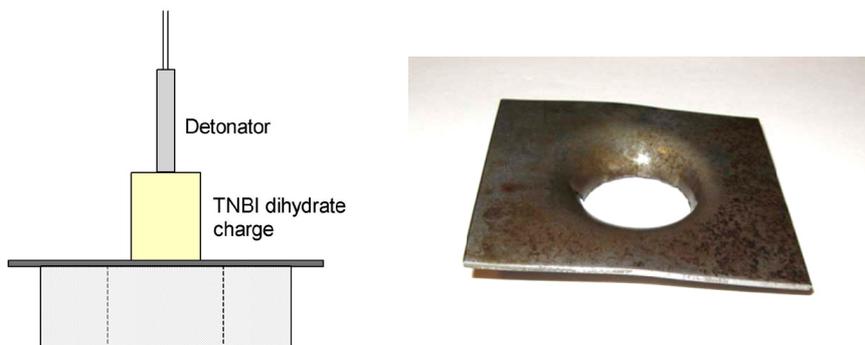


Figure 4. Sketch of the test setup and the holed witness plate.

Initiation of the tested explosive resulted in a hole being cut in the witness plate with a diameter equal to that of the charge, clearly indicating detonation of the $\text{TNBI} \cdot 2\text{H}_2\text{O}$ charge.

2.5 Detonation properties of $\text{TNBI} \cdot 2\text{H}_2\text{O}$

The Cheetah code [27] was used to estimate the theoretical detonation parameters of the tested explosive. The Becker-Kistiakowsky-Wilson equation of state (BKW EOS) was assumed to characterize the physical properties of the gaseous products. The BKWC set of parameters, $\alpha = 0.5$, $\beta = 0.403$, $\kappa = 10.86$, and $\Theta = 5441$ [28], as well as the experimental density ($1.73 \text{ g} \cdot \text{cm}^{-3}$) and the value of the enthalpy of formation ($-149.3 \text{ kJ} \cdot \text{mol}^{-1}$) were used in the calculations.

The performance data were also calculated using the computer code EXPLO5_V6.01 [29]. EXPLO5_V6.01 is based on chemical equilibrium and a steady state model of detonation. It uses the BKW EOS for the gaseous detonation products and the Cowan-Fickett equation of state for solid carbon. The BKWG-S set of parameters, $\alpha = 0.5$, $\beta = 0.29$, $\kappa = 10.45$, and $\Theta = 4120$, was used in the calculations. The input was based on the sum formula, the measured enthalpy of formation and the experimental density.

The detonation velocity was measured using short circuit sensors in unconfined charges of diameter 16 mm, pressed to a density of $1.73 \text{ g} \cdot \text{cm}^{-3}$. The length of the measuring distances was 18.0 mm. The first sensor was located at a distance of 54.0 mm from the booster. The charges were initiated with a pressed HMX/wax charge of mass 6.7 g.

The calculated and measured detonation properties are listed in Table 2.

Table 2. Detonation parameters of TNBI·2H₂O

Parameter	CHEETAH	EXPLO5	Measured
Detonation velocity [m·s ⁻¹]	8182	8125	7940 ±80
Detonation pressure [GPa]	27.86	28.30	-
Detonation energy [J·g ⁻¹]	4997	5003	-
Detonation temperature [K]	4105	3702	-

The detonation energy calculated with the Cheetah code is the sum of the mechanical and thermal energies. The mechanical energy represents the amount of energy available to do mechanical work and is equal to the expansion work of the detonation products. It is determined for the volume of the detonation products corresponding to a pressure of $p = 1$ atm. The thermal energy represents the heat content in the detonation products at $p = 1$ atm. In these calculations, the composition of the detonation products was frozen at a temperature of 1800 K on the isentrope starting at the CJ point. For ideal explosives the Cheetah detonation energy is close to the calorimetric heat of detonation.

The detonation parameters calculated using EXPLO5_V6.01 are similar to those from CHEETAH. A difference in the detonation temperature is mainly caused by the use of another set of parameters.

As a result of the lower density and the negative value of the enthalpy of formation, TNBI dihydrate has lower detonation parameters than those calculated for pure TNBI – detonation velocity of 8800 m·s⁻¹ at density 1.95 g·cm⁻³ [12]. In spite of this, TNBI·2H₂O is a good explosive in terms of performance as it detonates at a velocity of 7940 m·s⁻¹ when pressed to a density of 1.73 g·cm⁻³.

2.6 Small-scale shock reactivity test (SSRT)

To assess the explosive performance of TNBI·2H₂O on a small laboratory scale, a small-scale shock reactivity test (SSRT) [30] was carried out. Here, a defined volume of the explosive is pressed into a perforated steel block, which is topped with a commercially available detonator (Orica, DYNADET-C2-0ms). Initiation of the tested explosive results in a dent in a separate aluminium block, which is placed directly underneath the steel block. The used sample weight m_s was calculated using the formula $m_s = V_s \cdot \rho_{x\text{-ray}} \cdot 0.95$, where V_s is a volume equal to 0.284 mL and $\rho_{x\text{-ray}}$ is the crystal density from the single crystal X-ray diffraction measurement. For TNBI dihydrate $\rho_{x\text{-ray}} = 1.79$ g·cm⁻³ [10].

Several tests with explosives such as NTO, 1,1-diamino-2,2-dinitroethene (FOX-7) and RDX were performed in order to obtain different dents within the aluminum plate. The dent sizes were measured by filling them with powdered SiO₂ and measuring the resulting weight increase. The results are shown in Table 3.

NTO created the smallest dent, obviously because of the high critical diameter, $d_{cr} = 16$ mm [31], which exceeds the diameter of the charge. The performance of FOX-7 is comparable to RDX and so the results of the SSRT of those materials are similar to each other. Surprisingly, TNBI·2H₂O shows the highest value of the dent. A possible explanation for this fact is that TNBI dihydrate has a very short distance from the initiation by the shockwave to the point with a stable detonation.

It may be concluded that the small scale explosive performance of TNBI·2H₂O exceeds the performance of the commonly used RDX, and modern low-vulnerability RDX replacements – NTO and FOX-7.

Table 3. Results from the small-scale shock reactivity test

Material	Weight, [mg]	Dent, [mg SiO ₂]
NTO	520	455
FOX-7	503	579
RDX	504	589
TNBI·2H ₂ O	483	664

2.7 Acceleration capability of TNBI·2H₂O

A cylinder expansion test was performed to estimate the acceleration capability of the tested explosive. The explosive charge was placed inside a copper tube 200 mm long with an inner diameter and wall thickness of 13 and 1 mm, respectively. The expansion of the tube, driven by the detonation products, was recorded using a SCANDIFLASH XR 450 apparatus. Images were recorded when the detonation front was approx. 10 mm from the end of the charge. The detonation velocity of the charges was simultaneously measured using short circuit sensors. For comparison, the test was repeated under the same conditions for TNT (detonation velocity of 6790 m·s⁻¹ at density 1.58 g·cm⁻³) and RDX/wax (detonation velocity of 8390 m·s⁻¹ at density 1.67 g·cm⁻³).

Figure 5 shows a photograph of the copper tube driven by the detonation products of TNBI·2H₂O. The dependence of the outer radius of the tube on the axial coordinate was determined from the photograph using graphical computer processing. The examined range of the axial coordinate was limited to those locations where the volume of the detonation products was 9-10 times larger than the initial volume. These dependences, along with the values of the detonation velocity of TNBI·2H₂O (7750 m·s⁻¹ at density 1.72 g·cm⁻³), were used to determine the explosive performance. A detailed procedure for determining the cylinder velocity and energy is given in [32].

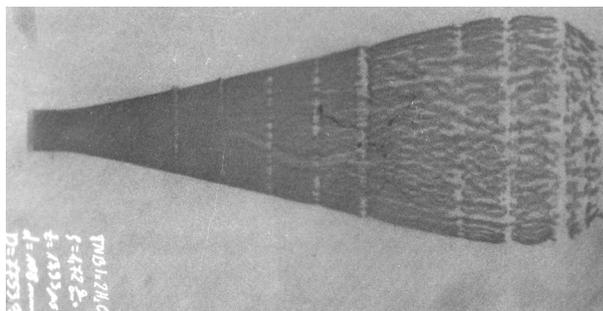


Figure 5. X-ray photograph of the copper tube driven by the detonation products of $\text{TNBI}\cdot 2\text{H}_2\text{O}$.

The calculated dependencies of the Gurney energies on the relative volume of the detonation products are presented in Figure 6. For comparison, the figure also shows the Gurney energies of TNT and RDX/wax determined from the same arrangement.

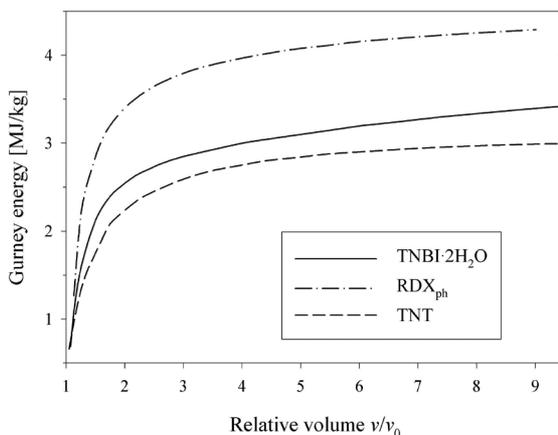


Figure 6. Gurney energy versus the relative volume of detonation products.

The final value of the Gurney energy for $\text{TNBI}\cdot 2\text{H}_2\text{O}$ is approx. $3430 \text{ J}\cdot\text{g}^{-1}$. Under the same conditions the performance of RDX/wax is considerably higher ($4290 \text{ J}\cdot\text{g}^{-1}$). However, $\text{TNBI}\cdot 2\text{H}_2\text{O}$ still performs better in the cylinder expansion test than TNT ($2990 \text{ J}\cdot\text{g}^{-1}$).

3 Conclusions

From this experimental study the following conclusions can be drawn:

1. The activation energy for the thermal decomposition of TNBI·2H₂O is equal to 118.5 kJ·mol⁻¹, which is a bit lower than the activation energy of NTO (132.5 kJ·mol⁻¹) – a low-sensitivity explosive with a similar decomposition temperature.
2. TNBI dihydrate is a thermodynamically stable energetic compound (standard enthalpy of formation is -149.3 kJ·mol⁻¹), with comparatively high detonation parameters. TNBI·2H₂O pressed to a density of 1.73 g·cm⁻³ can be initiated with a standard detonator and detonates at a velocity of 7940 m·s⁻¹ in unconfined charges of diameter 16 mm.
3. Small-scale shock reactivity test results show that this material has better performance in small charges than RDX, FOX-7 and NTO. Also it has a critical diameter probably lower than 10 mm.
4. Results of the cylinder test indicates that TNBI·2H₂O surpasses pressed TNT with regard to acceleration capability, but performs much worse than RDX/wax. The Gurney energies for the explosives (determined under the same conditions) are as follows: 3430, 2990 and 4290 J·g⁻¹, respectively.

Acknowledgments

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