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Assessment of thermal stability and detonation performance of 4-amino-1,2,4-triazolium nitrate as comapred to 2,4,6-trinitrotluene for melt-cast explosives

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Abstract

4- Amino-1,2,4-triazolium nitrate (4-ATN) is an energetic and non-sensitive ionic liquid, which was introduced as a good candidate in previous works for the replacement of 2,4,6-trinitrotoluene (TNT) in melt-cast explosives. Since previous studies used pure nitric acid for nitration of 4-ATN, the effect of the use of low price industrial nitric acids (50%, 70% and 98%) is investigated on the percent yields of 4-ATN. The thermogravimetric and differential scanning calorimetry (TGA/DSC) are done on the synthesized 4-ATN with impure nitric acid at a heating rate of 10°C.min^{-1} by the vacuum system. The obtained TGA/DSC curves confirm decomposition of 4-ATN involving melting and dissociation. Derivative thermogravimetric (DTG) curves of 4-ATN at various heating rates are applied to obtain activation energy of thermolysis by several model-free techniques. The calculated activation energies are in the range 78.7-87.7 kJ.mol^{-1}, which are about 10 kJ.mol^{-1} more than the reported activation energy of industrial TNT (purity 98.2%), i.e. 66-70 kJ.mol^{-1}. Assessments of detonation performance of 4-ATN are also compared with TNT, which show higher detonation performance of 4-ATN. Thus, 4-ATN can be used with nitramine compounds as melt-cast explosives with higher thermal stability and detonation performance than corresponding nitramine compound/TNT explosives.

Keywords: 4-Amino-1,2,4-triazolium nitrate; Thermal stability; Activation energy; Detonation performance

Introduction

Energetic ion liquids (EILs) can be used in explosive and propellant formulations [1]. They may provide low sensitivity without adverse effects of the overall performance. Since energetic ionic liquids have a low melting point, they can be used as melt-cast, the same as 2,4,6-trinitrotoluene (TNT), in different molds. The presence of high contents of hydrogen and nitrogen atoms in EILs can reduce the amount of additional oxidant for their combustion. EILs have some further advantages with respect to non-ionic ones that include lower vapor pressure, lower melting point and higher density [1d]. Moreover, they are more environmentally friendly than TNT [2]. EILs based on azoles are very promising candidates for the replacement of TNT-based explosives because they can store a large amount of energy in N=N and N-N bonds [3]. The thermal stability of triazole ring can be increased by introducing the N-amino group. Furthermore, intra- and inter-molecular hydrogen bonding can improve structural stability [4]. Since combining oxygen-containing groups in heterocyclic anions may help to improve the density and oxygen balance, corresponding EILs are suitable candidates [5]. Thus, the synthesis of EILs with favorable physical properties as well as detonation and combustion performance is attractive [5]. Among a different kind of EILs, 4-amino-1,2,4-triazole nitrate (4-ATN) [2, 6] is a good candidate to use as 4-ANT-based explosives instead of TNT-based explosives. The pure nitric acid was used to synthesize 4-ATN in previous works [2, 6]. The purpose of this work is to study the effect of low price industrial nitric acids (50%, 70% and 98%) on the percent yields of 4-ATN. Since the use of energetic compounds with high thermal stability is essential for military and civilian applications, thermogravimetric and differential scanning calorimetry (TGA/DSC) is used to investigate some thermokinetic parameters of the synthesized 4-ATN with industrial nitric acid. Derivative thermogravimetric (DTG) curves of 4-ATN at various heating rates are

used to calculate the activation energy of the decomposition process because of the kinetic triplet (activation energy, pre-exponential factor and reaction model) is useful for assessment of the chemical lifetime of explosives. The calculated activation energy of the synthesized 4-ATN is compared with industrial TNT (purity 98.2%). Theoretical assessments of detonation performance (detonation velocity, detonation pressure and power) of 4-ATN are done and compared with corresponding data of TNT.

Experimental

Materials and method

Samples and instruments

4-ATN, methanol, acetone, isopropanol with synthetic grade were purchased from Merck Chemical Co. and industrial nitric acid with 98% purity from Iran's defense industries. Electrothermal digital melting point apparatus cat no8101 was used to determine the melting point of the product. A Bruker Avance 400 Ultrashield spectrometer (Bruker Biospin, Rheinstetten, Germany) was used to record ^{1}H-NMR. A Fourier transform infrared (FTIR) spectrometer (FT/IR 6300, JASCO, Japan) was also used to determine the FT-IR spectrum in the wavelength range 400-4000 cm^{-1}. Elemental analyses were performed with Leco-932 (C, H, N, S elemental analyzer, St. Joseph, USA). For analysis of the samples by TGA and DSC, Perkin Elmer (STA 6000) with alumina pans was used in open-cell under Ar atmosphere at a flow rate of 2 liters per hour. The DSC/TGA thermograms were simultaneously recorded at a temperature of 25-450 °C at a heating rate of 10 $°C.min^{-1}$ where the sample weights were 0.3 mg per test. Vyazovkin et al. [7] have recommended kinetic analysis according to recommendations of the ICTAC committee. The sample size and heating rates were adopted for kinetic analysis of

energetic materials, which have been used in previous studies [8] because the conditions should be chosen carefully.

Synthesis and characterization of 4-ATN

The method of Drake et al. [2] was used to synthesize 4-ATN, which is shown in Fig. 1. The melting point of 4-ATN is 69±2°C where it dissolves in water and methanol at room temperature. Meanwhile, 4-ATN is insoluble in a mixture of methanol and nitric acid (80% of nitric acid) at 0°C. The yield of 4-ATN depends on the concentration of nitric acid. For 50%, 70% and 98% of nitric acid, percent yields of 4-ATN were 25%, 62% and 88% for one hour at ambient temperature in methanol solvent. Thus, there is a direct relationship between the concentration of nitric acid and the amount of product. Elemental analysis of CHN, ^{1}H-NMR and FT-IR were used to control the 4-ATN quality (Supplementary Information).

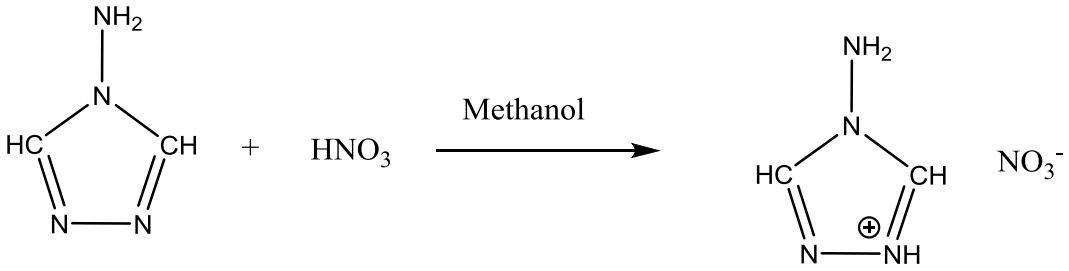

Figure 1. Synthesis of 4-ATN [2]

Results and Discussion

Thermal analysis of 4-ATN

The purpose of kinetic analysis of thermally stimulated processes is to establish

mathematical relationships between the process rate, the temperature, and the extent of conversion. According to ICTAC committee recommendations [7], the most straightforward way in determining a kinetic triplet, which is a term frequently used to describe a single set of pre-exponentional factor (A), activation energy (E), and kinetic models or mechanisms f(a) or g(a). For a single-step process, evaluating a single kinetic triplet according to Eq. (1) should be sufficient to predict the process kinetics for any desired temperature program:

$$\frac{da}{dt} = A\exp(-\frac{E_a}{RT})f_{(a)} \qquad (1)$$

TGA/DSC curves of 4-ATN at a heating rate of 10°C.min^{-1} by vacuum system is shown in Fig. 2. As seen in Fig. 2, there is a two-step process for melting and decomposition of 4-ATN. In the first stage, an endothermic peak is observed at 68.41°C, which is caused by the melting of 4-ATN. The second step appears at 264.19°C, which is due to the decomposition of 4-ATN and the formation of gaseous products. Onset temperature and end-point temperature for the second step are 249.50 and 281.03°C, respectively. Since the initial exothermal decomposition temperature of TNT is 253°C [9], the thermal stability of 4-ATN is good as compared to TNT.

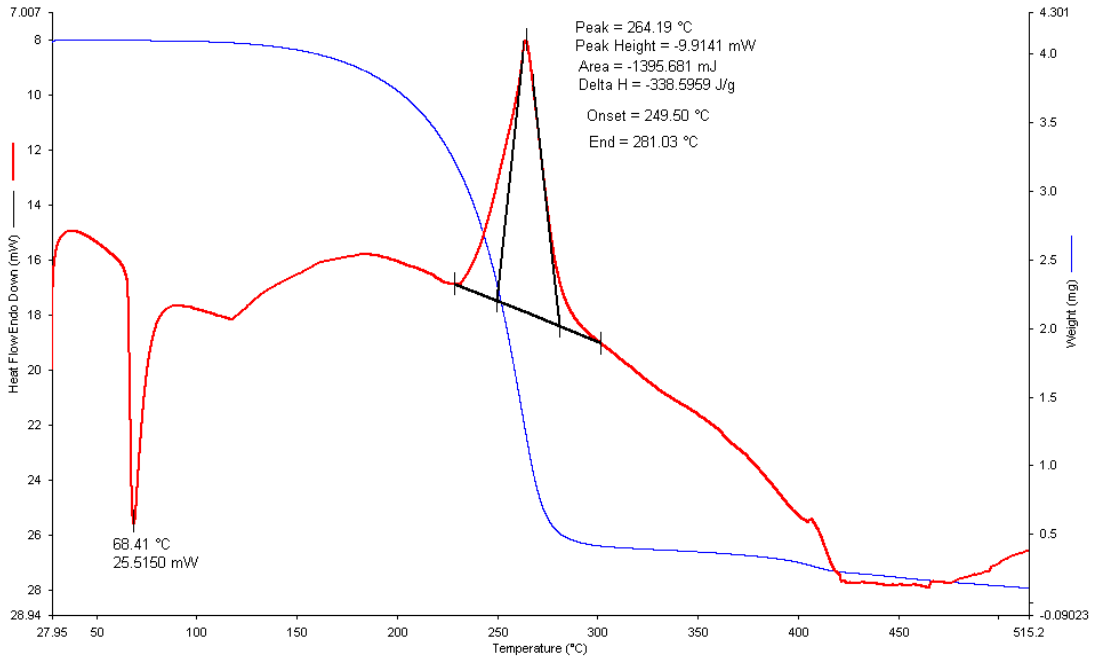

Figure 1. TGA and DSC curves of 4-ATN at a heating rate of 10°C.min^{-1}

Derivative thermogravimetric (DTG) curves of 4-ATN at various heating rates are presented in Fig. 3. As indicated in Fig. 3, the exothermic peaks are shifted to higher temperatures with increasing heating rate. These data allow one to obtain the activation energy of the decomposition process, which is independent of the reaction model or, in other words, single-valued. At the heating rate of 10°C.min^{-1}, there is a weight loss associated with the 4-ATN degradation reaction in the temperature range of 121.04 to 266.2°C.

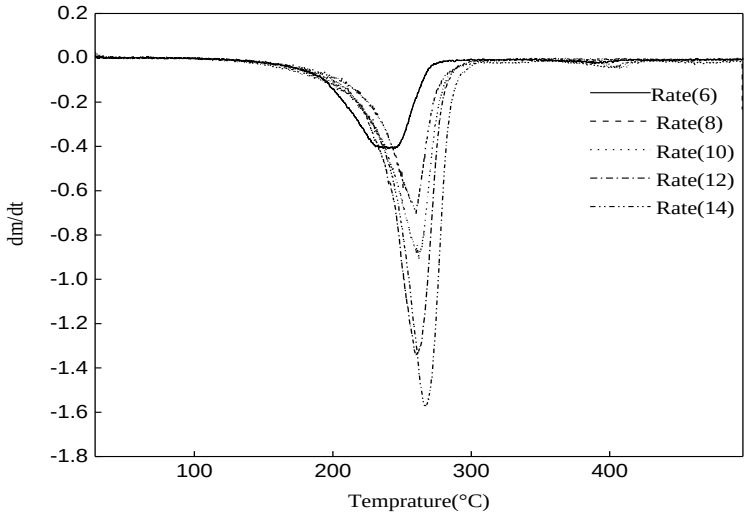

Figure 3. DTG thermal analysis curves for 4-ATN combinations at 6, 8, 10, 12 and 14°C.min^{-1}

Calculation of activation energy of 4-ATN

For a one-step decomposition process of 4-ATN, model-free techniques like Ozawa, Kissinger, Ozawa-Flynn-Wall (OFW), and Kissinger-Akahira-Sunrose (KAS) methods can be used to determine activation energy as follows [10]:

Ozawa $$ln(\beta_i) = Constant - 1.0516\left(\frac{E_a}{RT_a}\right) \quad (2)$$

Kissinger $$ln\left(\frac{\beta_i}{T_m^2}\right) = ln\left(-\frac{AR}{T}\right) - \left(\frac{E_a}{RT_m}\right) \quad (3)$$

OFW $$ln(\beta_i) = Constant - 1.052\left(\frac{E_a}{RT_a}\right) \quad (4)$$

KAS $$ln\left(\frac{\beta}{T^2}\right) = Constant - \left(\frac{E_a}{RT_a}\right) \quad (5)$$

where β is heating rate (K.min^{-1}); E_a is activation energy (kJ.mol^{-1}); T_a is the temperature in each extent of conversion (α), T_m is the maximum temperature or peak temperature of DTG curves (K), A is Arrhenius constant, g(α) is a function that represents the mechanism involved in the thermal transformation and R is gas constant (8.314 J·K^{-1}·mol^{-1}). The value of E_a can be evaluated from the slope of the straight line, which gives the best regression coefficients (R^2). For heating rates 6, 8, 10, 12 and 14 °C.min^{-1}, calculation of the activation energy of the 4-ATN sample decomposition reaction is done based on Eqs. 1 to 4 where the results are given in Table 1.

Table 1. The calculated activation energies obtained from Ozawa, Kissinger, OFW and KAS for 4-ATN and their comparisons with industrial TNT (purity 98.2%)

E_a(kJ.mol^{-1}), 4-ATN	The method of calculation	R^2	E_a (kJ.mol^{-1}), TNT [10a]
83.4	Ozawa	0.9994	70.2
78.7	Kissinger	0.9995	66.2
83.4	OFW	0.9994	70.2
87.7	KAS	0.9995	-

As seen in Table 1, the predicted values of R^2 values of four models are good. The calculated activation energies of 4-ATN are also compared with the reported data for industrial TNT (purity 98.2%) in Table 1 by three models of Ozawa, Kissinger, and OFW. As indicated, the activation energies of both models Ozawa and OFW are the same for both 4-ATN and TNT, i.e. 83.4 and 70.2 $kJ.mol^{-1}$, respectively. The model of Kissinger predicts the values of 78.7 and 66.2 $kJ.mol^{-1}$, respectively, which are less than those predicted by the other methods. Since all methods confirm the higher value of activation energy for 4-ATN as compared to industrial TNT, it can be expected that 4-ATN has higher thermal stability.

Calculation of the changes of activation energy with α by KAS model

The changes in activation energy at a different extent of conversion (α) show a single-step or multiple steps thermal decomposition. For single-step decompositions, the changes of activation energies with α are nearly constant because the value of α at different peak temperatures of heating rates is the same. According to the model of KAS, the activation energy of thermal decomposition of 4-ATN at different values of α can be calculated. As shown in Fig. 4, the activation energy of 4-ATN decomposition is nearly constant up to $\alpha=0.5$ and shows slightly changes for $\alpha>0.5$. For the assessment of shelf-life energetic compounds, the study of thermal decomposition at low values of α is appreciable.

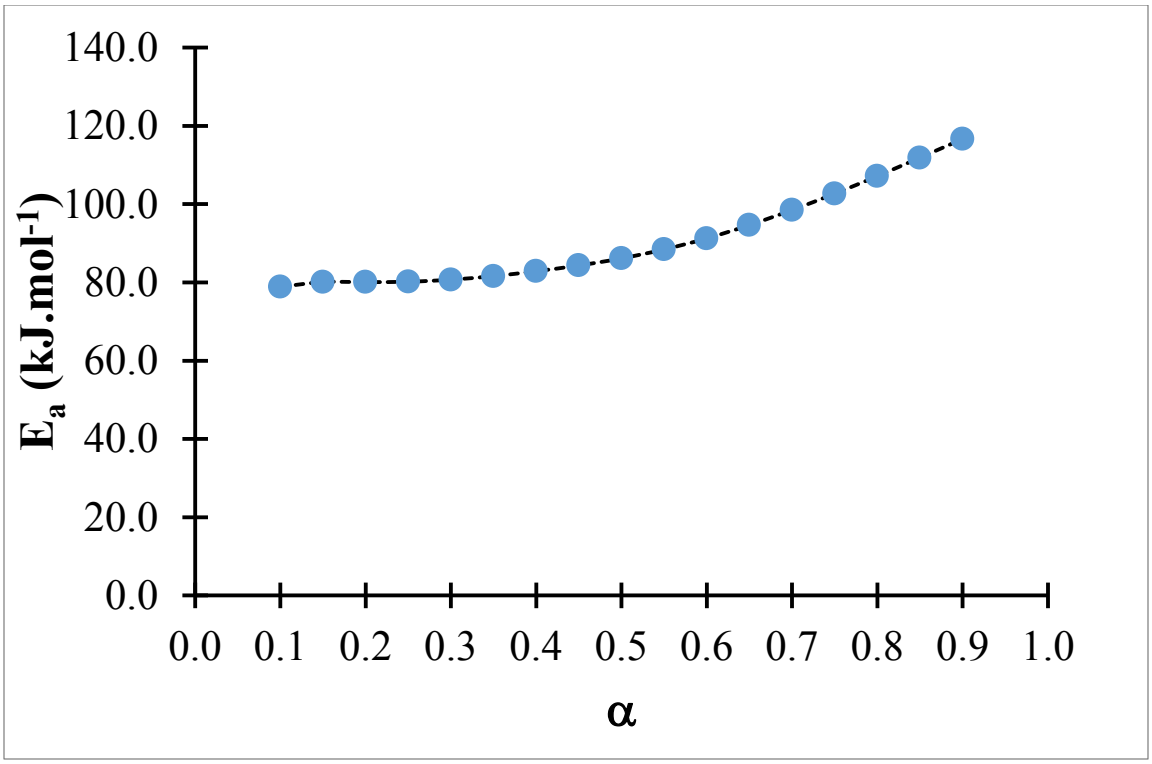

Figure 4. The curve of activation energy versus α for 4-ATN

Determination of kinetic triplet

According to suggestions of the ICTAC committee [7], various kinetics models are fitted by experimental data to obtain the best model as a reaction mechanism. At first, the measured parameter z(α) is determined. Then, the kinetic model and pre-exponential factor are calculated. Moreover, the estimated activation energy, by the KAS method based on ICTAC comments for one-step reactions, is taken as 87.8 kJ mol^{-1}. Different values of α are substituted in $f(\alpha)$ and g(α) to calculate the theoretical value of z(α) as:

$$z(\alpha)_{Theoretical} = f(\alpha) \times g(\alpha) \quad (6)$$

The experimental value of z(α) is calculated as:

$$z(\alpha)_{Experimental} = \beta(d\alpha/dT)_a T_a^2 [\frac{\pi(x)}{RT_a}] \quad (7)$$

where $\pi(x)$ and x are defined as:

$$\pi(x) = \frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \quad (8)$$

$$x = \frac{E_{a,\alpha}}{RT_\alpha} \quad (9)$$

The parameter $E_{a,\alpha}$ in Eq. (9) is the calculated activation energy by the KAS method. In Eq. (7), β is heating rate; T_α is the related temperature of the desired α; dα/dT shows the ratio of conversion with temperature. A suitable $z(\alpha)_{Experimental}$, which has good matching with $z(\alpha)_{Theoretical}$, is selected by drawing $z(\alpha)_{Experimental}$ and $z(\alpha)_{Theoretical}$ versus α. The model $A_{3/2}$, $f(\alpha)=(3/2(1-\alpha)[-Ln(1-\alpha)]^{1/3}$, which belongs to Avrami–Erofeev models, was taken as a suitable model for 4-ATN. Fig. 5 shows the curve of $z(\alpha)_{Experimental}$ and $z(\alpha)_{Theoretical}$ versus α for the selected model. As seen, different curves and maximum of α have nearly the same trend for $z(\alpha)_{Experimental}$ versus the selected model of $z(\alpha)_{Theoretical}$.

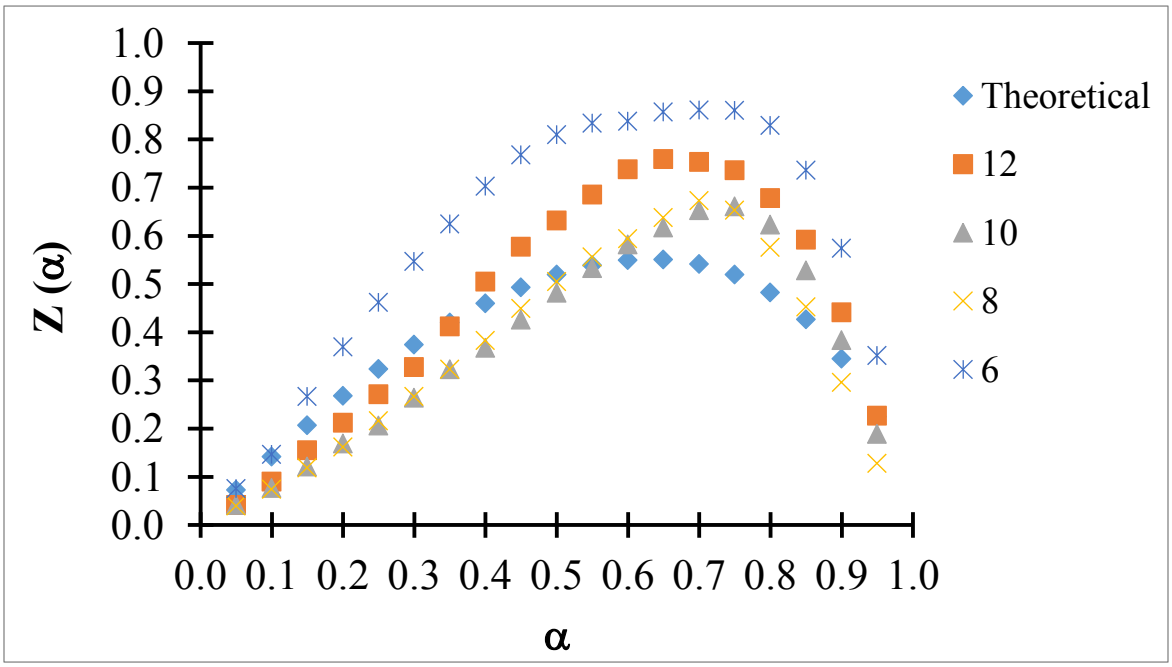

Figure 5- The curves of the model $A_{3/2}$ of $z(\alpha)_{Theoretical}$ and $z(\alpha)_{Experimental}$ versus α at four heating rates for 4-ATN

For assessment of the reliability of the selected model, the values of the Residual Sum of Squares (RSS) and S^2 at various heating were calculated for the difference between $z(\alpha)_{Experimental}$ and $z(\alpha)_{Theoretical}$ by Eqs. (10) and (11) as:

$$RSS = \Sigma(z(\alpha)_{exp} - z(\alpha)_{theor})^2 \quad (10)$$

$$S^2 = \frac{RSS}{\mathrm{n}-1} \quad (11)$$

Eq. (12) can predict pre-exponential through distinguishing the reaction model and the use of derivatives of $f(\alpha)$ as:

$$A = \frac{-\beta E_0}{R\, T_{max}^2 f'(\alpha_{max})} \exp(\frac{E_0}{R\, T_{max}}) \quad (12)$$

where β is heating rate, T_{max} is the peak maximum temperature, α_{max} is the value of α at the peak maximum, E_0 is the average value of the predicted activation energies by model-free methods. The predicted value of log A is 17.81.

Assessment of detonation performance

Detonation velocity and pressure are two important parameters for the assessment of the detonation performance of high explosives [11]. Detonation velocity is defined as the velocity with which detonation wave travels through an explosive. Detonation pressure is the pressure produced in the reaction zone of a detonating explosive and is a function of explosive density and detonation velocity. These parameters can be calculated by the following correlations [12]:

$$D_{\mathrm{det}} = 5.5204(n'_{gas})^{0.5}\left(\overline{Mw}_{gas} Q_{\mathrm{det}}\left[H_2O(g)\right]\right)^{0.25}\rho_0 + 1.97 \quad (13)$$

$$P_{\det} = 245.5(n'_{gas})\left(\overline{Mw}_{gas} Q_{\det}\left[H_2O(g)\right]\right)^{0.5} \rho_0^2 - 11.2 \quad (14)$$

where $D_{\det}$ and $P_{\det}$ are detonation velocity and pressure in km/s and kbar, respectively, n'_{gas} is the number of moles of gaseous detonation products per gram of explosive, $\overline{Mw}_{gas}$ is the average molecular weight of the gaseous products in g/mol, $Q_{\det}\left[H_2O(g)\right]$ is in kJ.mol^{-1} and ρ_0 is the initial density in g.cm^{-3}. The calculated values of n'_{gas}, $\overline{Mw}_{gas}$ and $Q_{\det}\left[H_2O(g)\right]$ are given in Table 2. The computer code EMDB 1.0 [13] can also be used to assess detonation performance based on Eqs. (13) and (14). The necessary data for calculation of detonation performance based on Eqs. (13) and (14) are crystal densities and the condensed phase heats of formation of 4-ATN and TNT. The predicted detonation performance, as well as crystal densities and the condensed phase heats of formation of 4-ATN and TNT, are given in Table 2. As seen, detonation velocity and pressure of 4-ATN are higher than TNT. The Trauzl lead block test is one of the conventional laboratory tests for assessment of the power of an explosive [11]. The calculated value of the Trauzl lead block test for 4-ATN by EMDB 1.0 [13] is also given in Table 2. As seen, the relative power of 4-ATN with respect to TNT (%$f_{\text{Trauzl, TNT}}$) [11] is slightly higher. Thus, it can be expected that 4-ATN is suitable for RDX/4-ATN or HMX/4-ATN, the same as corresponding RDX/TNT or HMX/TNT, where they are melt-cast although the process is not as simple as it sounds. Details of the sensitivity of 4-ATN to different stimuli were reported elsewhere [6a] that confirm the high safety assessment of 4-ATN.

Table 2. Comparison of the various properties of 4-ATN with TNT

Property	**4-ATN**	**TNT**
Molecular formula	$C_2H_5N_5O_3$	$C_7H_5N_3O_6$
ρ (g.cm^{-3})	1.62 [2]	1.64 [14]
T_m (K)	343.1 [2]	354 [14]
$\Delta_f H^{\theta}$(c) (kJ.mol^{-1})	-41.84 [6a]	-66.94 [14]
n'_{gas} (mol.g^{-1})	0.048	0.044
$\overline{Mw_{gas}}$ (g.mol^{-1})	21.02	21.51
$Q_{det}\left[H_2O(g)\right]$ (kJ.g^{-1})	-2.86	-2.62
D (km.s^{-1})	7.46	7.26 (6.93 [14]) [a]
P (kbar)	228	209 (210 [14]) [a]
$\%f_{\text{Trauzl, TNT}}$	105	100

[a] Experimental values and corresponding reference of TNT are given in parentheses.

Conclusion

In this work, it was shown that 4-ATN can be introduced as a good candidate for the replacement of TNT. Synthesis and characterization of 4-ATN were investigated under different conditions. Industrial nitric acid with 98% purity was used to prepare 4-ATN. For this purpose, thermal stability and performance assessment of 4-ATN have been compared with TNT. Four model-free techniques including Ozawa, Kissinger, OFW, and KAS methods were used to calculate the activation energy of thermolysis. The calculated activation energies are in the range of 78.7-87.7 kJ.mol^{-1}. Since these activation energies are about more than 10 kJ.mol^{-1} more than industrial TNT (purity 98.2%), the thermal stability of 4-ATN is higher than industrial TNT. Assessment of detonation performance of 4-ATN shows that detonation pressure and velocity of 4-ATN are higher than TNT. Thus, 4-ATN is suitable for nitramine compound/4-ATN explosives with higher detonation performance than corresponding nitramine compound/TNT explosives as melt-cast.

Supplementary Information

The requested data of FTIR, NMR, and CHN techniques are given in Supplementary Information.

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