Synthesis and Characterization of the Guanidine Salt Based on 1,1,2,2-Tetranitraminoethane (TNAE)

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Abstract: A novel method has been successfully developed to synthesize the guanidine salt of 1,1,2,2-tetranitraminoethane (TNAE). By the use of IR, ^{1}H and ^{13}C NMR spectroscopy, the structure of the guanidine salt of TNAE was thoroughly characterized. In addition to the thermal stability investigated by TG-DSC, the kinetic parameters of this kind of material including activation energy and the pro-exponential factor were also calculated by Kissinger equation. The measurements of impact and friction sensitivity were carried out respectively. According to the theoretical performance calculations, the guanidine salt of TNAE exhibited the excellent detonation pressures and velocities. The solubility analysis for guanidine salt of TNAE by HPLC was performed at different temperatures, revealing the solubility increased with the increasing of temperature. And its solubility was proved to be the best in water among all the experimented solvents, ethyl acetate, dichloromethane and acetone followed up. With the great potential in practical application, the guanidine salt of TNAE is of significant value being employed as environmentally friendly gas generant, insensitive explosive and solid propellant.

Keywords: 1,1,2,2-tetranitraminoethane · Safety performances · Apparent activation energy · Solubility

1 Introduction

In 1980, Peng et al. first reported the synthesis of 1,1,2,2-tetranitraminoethane (TNAE) [1], which is an oxygen-rich explosive that can be readily synthesized from the hydrolysis reaction of tetranitroglycoluril (TNGU) or octahydro-1,3,4,5,7,8-hexanitrodiimidazo [4,5-b:4′,5′-e] pyrazine-2,6(1H,3H)-dione (HHTDD) in the presence of base [2]. However, due to the active acidic hydrogen of this compound, slowly hydrolyzation was inevitably happened. In order to solve this problem, many TNAE derivatives have been synthesized by using simple acid-base or metathesis reactions. Wan et al. reported the synthesis and properties of sodium salt [3]. Lee et al. reported potassium salt, amine salt, and guanidine salt [2a]. Then, ammonium, hydroxylammonium, guanidinium, triaminoguanidinium, carbamylguanidinium, and hydrazinium salt were synthesized by Goede et al [4]. Most of the above salts exhibited better thermal stability and lower mechanical stimulation sensitivity than TNAE. Among them, the Na salt has gained great interests because of its high detonation pressure (42.7 GPa) and velocity (10900 m·s^{-1}) at a density of 2.11 g·cm^{-3} in theory [2b, 5]. Born et al. reported the single crystal structure of Na salt and K salt [6]. All the results indicated the Na salt is very likely to become an alternative to RDX on account of its good coordination of energy and sensitivity as well as simple and convenient preparation.

With the constant pursuit of new high energy density materials, great progress has been made in nitrogen-rich energetic ionic salts with complex ions such as guanidinium, hydrazonium, and nitrogen heterocycles [7]. These salts are ideal high energy density materials owning to the advantages of high heat of formation, high crystal density, good oxygen balance, and clean products [8]. For example, 1,1,2,2-tetranitroethane is highly unstable at room temperature, whose structure is similar to that of TNAE, but its nitrogen-rich ionic derivatives exhibit greater stabilities and detonation performance [9]. Compared to the metal salt of TNAE, guanidine salt of TNAE has a lower sensitivity, and higher nitrogen content, and is much likely to be a candidate for high-energy, low-sensitivity materials. But so far, there are only few reports on the synthesis methods and properties of TNAE guanidine salt. In the present work, the guanidinium salt of TNAE was prepared by deprotonation of TNAE, in the meantime its thermodynamic properties, mechanical sensitivity, detonation parameters, dissolution properties, and kinetic parameters of thermal decomposition were also investigated.

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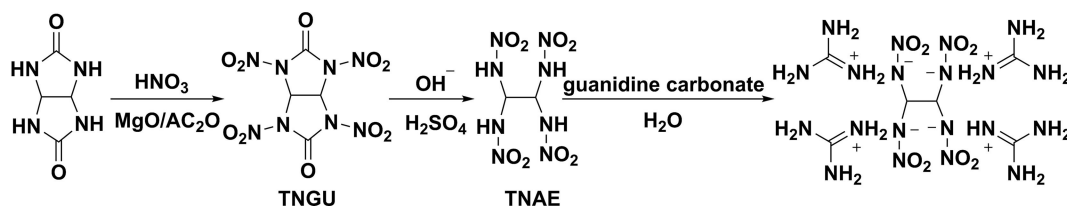
Scheme 1. Synthesis of TNAE and the guanidine salt of TNAE.

2 Experimental Section

Caution! Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged.

2.1 General Methods

Glycoluril was prepared according to literature methods [10], while the other reagents were purchased from local commercial suppliers and used without any further purification. NMR spectra were recorded on an Agilent VNS-600. IR spectra were recorded using a Thermo Nicolet with Nexus 870 device. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyzer. DSC measurements were performed on a Thermo Plus EVO DSC-8230 under a nitrogen atmosphere at a flow rate of 50 mL·min^{-1}, and the sample weight was about 0.7 mg and heating rates used were 5, 10, 15, 20 and 25 °C·min^{-1} from ambient temperature to 500 °C. Thermogravimetric measurements were performed with a SHIMADZU DTG-60 apparatus using a heating rate of 10 °C·min^{-1} from ambient temperature to 500 °C with a sample weighs about 0.6 mg under a nitrogen atmosphere. HPLC analyses were performed using a Shimadzu LC-20 system equipped with an auto sampler and diode array detector, and carried out on the following conditions: Agela Venusil XBP Si (4.6 mm × 250 mm, 5 μm); Injection volume: 10 μL; Mobile phase: MeOH/Isopropanol (7:3) with a flow rate of 1.0 mL min^{-1}; detection wavelength: 238 nm. The sensitivities to impact and friction stimuli were tested by standard procedures using a BAM Fall Hammer BFH-10 and a BAM Friction Apparatus FSKM-10, respectively.

2.2 Materials

Tetranitroglycoluril (TNGU): To a mechanically stirred solution of MgO (1.0 g, 25 mmol) in fuming nitric acid (98%) (180 mL) was slowly added glycoluril (10 g, 70 mmol), and a room temperature water bath was used to keep the temperature below 40 °C. After the solids were completely dissolved, 90 mL acetic anhydride was slowly added dropwise below 40 °C. The reaction solution was cooled to room tem-

perature and reacted at room temperature for 6 h. After filtration, the filtrate was collected and washed with 200 ml of water and dried to give the target product. After filtration, the filtrate was collected and washed with water to neutral and dried to give a white solid (12.17 g, 53.7%). IR (KBr): 3417, 3009, 2889, 1813, 1622, 1368, 1261, 1148, 1098, 936, 813, 734 cm^{-1}.

TNAE: To a 30 mL of NaOH aqueous solution (0.1 mol/L) with magnetic stirring at 0–5 °C was slowly added tetranitroglycoluril (2 g, 6.2 mmol). After reacting for 2 h at temperature lower than 10 °C, acidified with concentrated H$_2$SO$_4$ to pH = 1 below 5 °C. Anhydrous ether (5 × 15 mL) were being used to extract the neutralization solution, and ether layer was collected and dried over anhydrous sodium sulfate. The mixture was evacuated under vacuum until solid appeared, and 2 to 3 volumes of methylene chloride was added. A large amount of solid was precipitated, filtered, and dried to give a white solid (1.17 g, 69.8%). IR (KBr): 3245, 3008, 1579, 1452, 1347, 1234, 1163, 1096, 1064, 933, 835 cm^{-1}.

TNAE-guanidine: To a stirred solution of guanidine carbonate (2.42 g, 13.45 mmol) in water (60 mL) was slowly added with TNAE (2.7 g, 10 mmol). After stirring for 2 h at room temperature, a white suspension was obtained, which was filtered, washed with water to neutral, and dried in vacuum to give a white powder (2.81 g, 55.65%). IR (KBr): 3397, 3154, 1672, 1657, 1571, 1401, 1374, 1293, 1249, 1108, 977 cm^{-1}; ^{1}H NMR (600 MHz, D$_2$O): δ: 5.91 ppm (s); ^{13}C NMR (150 MHz, D$_2$O): δ: 188.69, 77.48 ppm. Elemental analysis for C$_6$H$_{26}$N$_{20}$O$_8$: calcd. C 14.23, H 5.18, N 55.32%; found: C 14.24, H 5.02, N 55.90%.

3 Results and Discussion

3.1 Synthesis

The synthetic pathway to TNAE and its guanidine salt is depicted in Scheme 1. TNGU, TNAE were prepared based on methods in the literature [1,2b,11]. Guanidine salt of TNAE was obtained as a white power in a yield of 56% from the anion exchange of guanidine carbonate with TNAE in H$_2$O, and confirmed by NMR and IR spectra. In ^{1}H NMR spectra, there is only a singlet at 5.91 ppm corresponding to the C—H functionality. In ^{13}C NMR spectra, there are two signals

($\delta = 77.5$, 188.7 ppm) assigned to the TNAE and the guanidine cation, respectively.

3.2 Thermal Property

Thermal analysis by TG and DSC revealed some phenomena, as depicted in Figure 1, Figure 2, Figure 3 and Table 1, Table 2. DSC curves (Figure 1) of TNAE-guanidine show an exothermic peak. It can be seen from the figure that the decomposition temperature of the TNAE guanidinium salt at the heating rate of 5–25 K/min are 224.33 °C, 228.96 °C, 233.00 °C, 234.75 °C and 237.28 °C, respectively. With the increasing of heating rate, the decomposition temperature increases and decomposition of exothermic peaks expands. In addition, TNAE-guanidine has a significant weight loss peak near 225 °C with energy release during weight loss is evident from the TG results (Figure 2), which is consistent with the DSC result. DSC and TG results show that TNAE-guanidine contains a high-energy exothermic process in line with the exothermic nature of the energetic material. Thermal decomposition peak temperature of 223.71 °C shows a good thermal stability, close to RDX [12], which can be classified as a heat-resistant explosive.
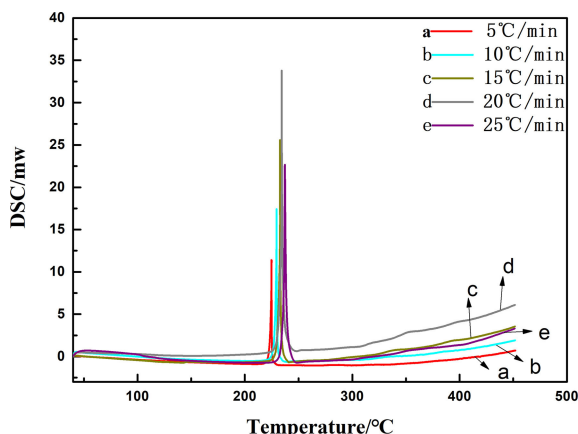

Figure 2. TG curves of TNAE-guanidine.

Figure 1. DSC curves of TNAE-guanidine at different heating rates.

The linear regression equation of $\ln(\beta/T_p^2)$ and $1000/T_p$ was obtained by Kissinger method [13]. Figure 3 shows that the linear equation fitted by Kissinger method is $y = -30.52x + 50.59$ with $r^2 = 0.9906$, and the correlation is satisfactory. The thermal decomposition activation energy of TNAE-guanidine was 253.74 kJ/mol and the pre-factor $\ln(A/s^{-1})$ was 60.92. The kinetic parameters of TNAE-guanidine are shown in Table 1.

The value of the thermal decomposition extrapolation temperature (T_{p0}) is 495.78 K, which is a good proof to excellent thermal stability. $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ are all positive, indicating that the decomposition of TNAE-guanidine is a exothermic and entropy increase reaction.

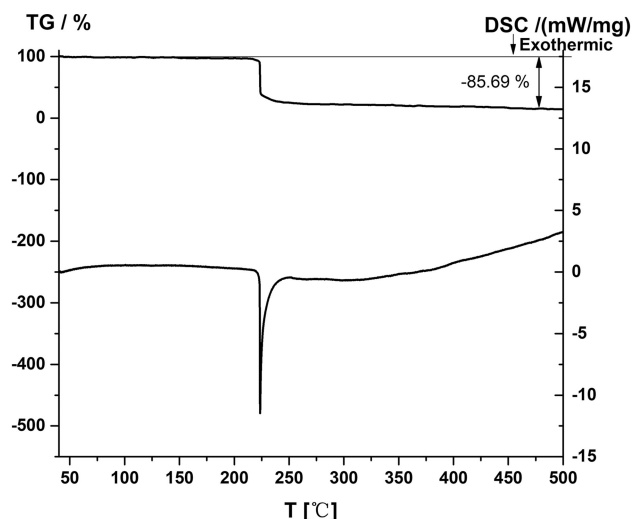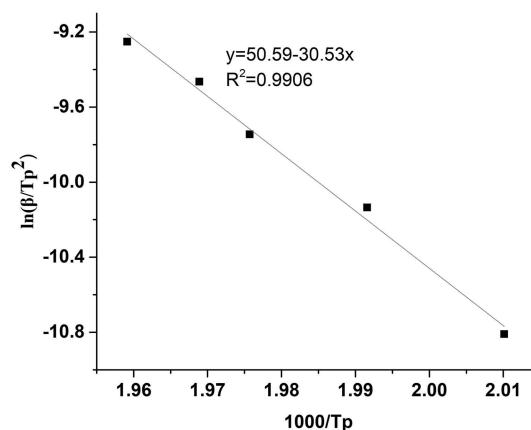**Figure 3.** The linear fitting of TNAE-guanidine's $\ln(\beta/T_p^2)$ for $1000/T_p$ relationships.

Table 1. Dynamic parameters of TNAE-guanidine.

B (K·min^{-1}) [a]	Tp/K [b]	Ek/ (kJ·mol^{-1})[c]	ln (A/s^{-1}) [d]	r2 [e]
5	497.48			
10	502.11			
15	506.15	253.74	60.92	0.9906
20	507.90			
25	510.43			

[a] DSC heating rates. [b] Decomposition temperature. [c] Calculated activation energies. [d] Calculated preexponential factor. [e] Linear correlation.

3.3 Sensitivities and Energetic Performance

To evaluate the TNAE-guanidine more thoroughly, the sensitivities toward impact and friction were determined by using the BAM standard methods (Table 3). The results

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Table 2. Thermodynamic parameters of TNAE-guanidine.

Tp0/K	$\Delta S\neq/$ $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta H\neq/$ $kJ\cdot mol^{-1}$	$\Delta G\neq/$ $kJ\cdot mol^{-1}$
495.78	249.04	249.62	126.15

Table 3. Energetic properties of TNAE-guanidine compared with TNAE and RDX.

	TNAE-guanidine	TNAE[j]	RDX[k]
$T_d{}^{[a]}/°C$	223.71	158.7	229.7
$\rho^{[b]}/g\cdot cm^{-3}$	1.531	1.836	1.806
$\Omega^{[c]}/\%$	−52.26	5.92	−21.6
$N^{[d]}/\%$	55.43	41.48	37.84
$\Delta_fH^{[e]}/kJ\cdot mol^{-1}$	380	43	83.8
$D^{[f]}/m\cdot s^{-1}$	10057	9750	8748
$P^{[g]}/GPa$	42.9	41	34.9
IS[h]/J	>40	1	7.5
FS[i]/N	>360	160	120

[a] Decomposition temperature (DSC/5 K·min). [b] Measured density. [c] Oxygen balance. [d] Nitrogen content. [e] Calculated (CBS-4 M method) enthalpy of formation. [f] Detonation velocity. [g] Detonation pressure. [h] Measured Impact sensitivity. [i] Measured Friction sensitivity. [j] Ref. [2b, 4]. [k] Ref. [15].

showed that TNAE-guanidine was very insensitive toward impact and friction. Compared with RDX and TNAE, TNAE-guanidine has a similar thermal stability and much lower sensitivity toward impact and friction, which can be classified as insensitive toward impact and friction. In addition, due to the introduction of guanidine ion, the oxygen bal-

ance of TNAE-guanidine falls to −52.26%, while the nitrogen content reaches to 55.43%. It suggests that large amounts of non-toxic N_2 release during TNAE-guanidine decomposition.

The detonation parameters were predicted by Empirical Kamlet-Jacobs equations, and listed in Table 3 [14]. The theoretically computed detonation velocity and detonation pressure were 10057 m·s⁻¹ and 42.9 GPa, respectively, which were closed to those of Na salt of TNAE, and were much better than those of RDX. These properties demonstrated that the TNAE-guanidine may be used as an insensitive and nitrogen-rich energetic material.

3.4 Solubility

The solubility of TNAE-guanidine in water, propanone, ethyl ethanoate, and dichloromethane in the range of 293.15 K to 313.15 K are listed in Table 4. Figure 4 shows that TNAE-guanidine solubilities in all solvents increased as exponential rate in all the experiments, and ln*x* shows the usual linear relationship with inverse absolute temperature. Therefore, the solubility of TNAE-guanidine are correlated as Eq. (1).

$$\ln(x) = A + B/T[K] + C\ln(T[K]) \tag{1}$$

where *x* is the mole fraction of solute, T is absolute temperature, and A, B and C are parameters of the exponential expression. The relative deviation (δ) is defined in Eq. (2).

**Table 4.** Solubility of TNAE-guanidine as a function of temperature in different solvents under 0.1 MPa.[a]

solvent	T(K)	105x	105x calc	100δ
	293.15	67.3	57.7	14.25
	298.15	77.3	76.0	1.65
Water	303.15	87.6	98.8	−12.79
	308.15	124.5	126.8	−1.82
	313.15	166.2	160.7	3.32
	293.15	0.0335	0.0334	0.23
	298.15	0.0422	0.0437	−3.63
Propanone	303.15	0.0597	0.0579	3.05
	308.15	0.0757	0.0774	−2.27
	313.15	0.0991	0.1046	−5.53
	293.15	0.0888	0.0938	−5.64
	298.15	0.1290	0.1276	1.09
Ethyl ethanoate	303.15	0.1740	0.1684	3.19
	308.15	0.2080	0.2162	−3.94
	313.15	0.2700	0.2703	−0.10
	293.15	0.0469	0.0473	−0.77
	298.15	0.0633	0.0618	2.44
Dichloromethane[b]	303.15	0.0823	0.0845	−2.64
	308.15	0.1220	0.1206	1.16

[a] Standard uncertainties u are $u(T)=0.1$ K, $u_r(p)=0.05$, and related standard uncertainty $u_r(x)=0.05$ (0.95 level of confidence). [b] Since dichloromethane was close to boiling (boiling point: 312.9 K) at the temperature of 313.15 K, no data was measured at 313.15 K.

Table 5. Parameters of Eq. (1) of TNAE-guanidine in different solvents.

solvent	A	B	C	r^2	$\Delta H_{sol}/kJ \cdot mol^{-1}$
water	117.52	−9615.6	16.226	0.9784	38.49
propanone	−491.61	17078.1	73.661	0.9954	46.21
ethyl ethanoate	481.55	−26462.6	−71.323	0.9972	37.67
dichloromethane	−1319.80	53716.7	197.511	0.9966	42.58
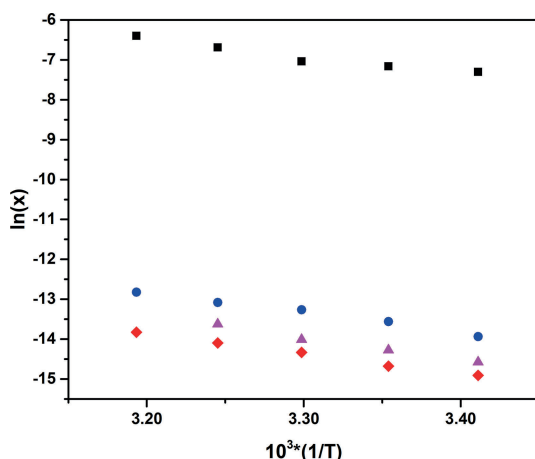
Figure 4. Temperature dependence of ln(x) of TNAE-guanidine in different solvents: ■, water, ●, ethyl ethanoate, ◆, propanone, ▲, dichloromethane.

$$\delta = (x - x\ calc)/x \qquad (2)$$

where x^{calc} represents calculated solubility from Eq. (2).

Table 4 lists the regression parameters of A and B involved in Eq. (1) regarding to all solvents tested.

From Table 4 and Figure 4, it can be seen that TNAE-guanidine has the highest solubility in water, and the solubility of TNAE-guanidine in the tested solvents increased with the increasing of temperature. The solubility in propanone and dichloromethane varies much more obviously with temperature than in other solvents over the selected temperature range. Experimental results show that the order of solubility can be represented as: water > ethyl ethanoate > dichloromethane > propanone.

3.5 Enthalpy of Solution

The solubility could be predicted from van't Hoff equation for an ideal or a non-ideal solution, the enthalpy of solution can be calculated from the slope of the modified van't Hoff equation. The enthalpy of solution ($\Delta_{sol}H$) for TNAE-guanidine was calculated by Eq. (3) based to the reference [16].

$$\ln x = \frac{-\Delta_{sol}H}{R(T)} + \frac{-\Delta_{sol}S}{R} \qquad (3)$$

where $\Delta_{sol}H$ is the enthalpy of solution, $\Delta_{sol}S$ is the entropy of solution, R is the gas constant, and T is the absolute temperature. The enthalpy of solution ($\Delta_{sol}H$) shown in Table 5, is calculated from the slope.

4 Conclusions

Nitrogen-rich TNAE-guanidine was prepared and fully characterized. It showed good thermal stabilities approximately equivalent to RDX but with a much lower sensitivity to mechanical stimuli than RDX. Furthermore, the kinetic parameters including activation energy and pro-exponential factor were calculated by Kissinger equation. Meanwhile, the solubility of TNAE-guanidine in water, propanone, ethyl ethanoate and dichloromethane under temperatures ranging from 293.15 K to 313.15 K were measured by using the gravimetric method (HPLC). The results showed the solubility in water was the highest, and the enthalpy of solution was calculated as well. Based on the above results, TNAE-guanidine could to be a potential energetic material to serve as a promising alternative to to the widely used military explosive RDX.

Acknowledgements

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