

Original article

Synthesis and properties of energetic salts based on 3-nitro-5-nitroimino-1,2,4-oxadiazole



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ABSTRACT

A series of 3-nitro-5-nitroimino-1,2,4-oxadiazole-based energetic salts were synthesized from 3-nitro-5-nitroimino-1,2,4-oxadiazole anion and nitrogen-rich cations. They were fully characterized by IR, elemental analysis and NMR spectroscopy. The structure of triaminoguanidinium salt (**1-e**) was confirmed by single crystal X-ray diffraction. All salts showed good thermal stability with decomposed temperature ranging from 155 °C to 258 °C, and positive heats of formation from 226.0 kJ/mol to 554.1 kJ/mol. Thus, the theoretic detonation pressure was predicted from 28.70 GPa to 37.60 GPa and velocities from 8526 m/s to 9354 m/s. Among them, guanidinium salt (**1-c**) exhibited both high decomposition temperature (258 °C) and detonation velocity (9319 m/s).

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1. Introduction

Energetic materials are used for various military and civilian purposes [1,2]. Particularly, high-energy density materials (HEDMs) have attracted considerable attention [3–5]. The preferred characteristics for HEDMs include high density, positive heat of formation, positive oxygen balance, low sensitivity, and etc. Some substituents, such as nitro group (NO₂) and nitroamine group (NHNO₂), play an important role in increasing the oxygen balance and density [6]. Therefore, the introduction of the nitro or nitroamine group into the energetic molecules is an efficient approach to improving the detonation performance of energetic materials. However, most of them are sensitive [7]. In order to solve the conflict of sensitivity and high energy, salification is an effective way. And thus prepared energetic salts usually possess some advantages such as low vapor pressure and low sensitivity [8].

Stability and sensitivity of energetic salts are influenced by cations and anions. We can take advantage of nitrogen-rich compounds bridge between anions and cations [9]. Among these anions, our group has recently focused on the 1,2,4-oxadiazole

parent ring and synthesized its energetic derivatives with high energy, high thermal stability and low sensitivity [10,11]. Herein, we reported a series of energetic salts derived from 3-nitro-5-nitroimino-1,2,4-oxadiazole (**NON**).

2. Experimental

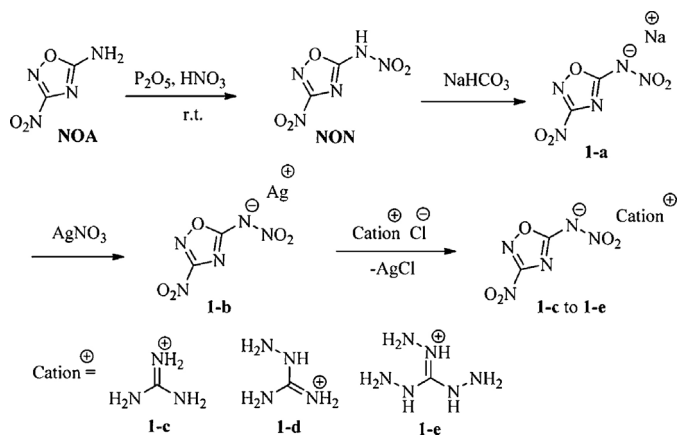
¹H NMR and ¹³C NMR spectra were recorded on a BRUKER Advance 400 spectrometer at 400 and 100 MHz, respectively. IR spectra were carried out on an IR-408 or BRUKER Alpha using KBr pellets. Elemental analyses were measured using an Elemental Vario MICRO CUBE elemental analyzer. Melting and decomposition points were obtained by differential scanning calorimetry (DSC) on a METTLER Toledn apparatus at a scan rate of 10 °C/min.

2.1. Preparation of 3-nitro-5-nitroimino-1,2,4-oxadiazole (**NON**) and its sodium salt **1-a**

P₂O₅ (5 g, 35 mmol) was solved in fuming HNO₃ (6 mL) at –15 °C, followed by the addition of 3-nitro-5-amino-1,2,4-oxadiazole (**NOA**) [10a] (260 mg, 2 mmol). The reaction mixture was stirred at room temperature for 12 h. Then the mixture was poured into ice water and the product **NON** was neutralized with solid NaHCO₃ till pH 8.0. The sodium salt was extracted with ethyl

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Scheme 1. Synthesis of 3-nitro-5-nitroimino-1,2,4-oxadiazole (**NON**) and salts of **1-c**, **1-b**, **1-e**.

acetate (50 mL \times 4). The combined organic layers were dried over anhydrous Na_2SO_4 . And the solvent was removed under reduced pressure to afford sodium salt (**1-a**) (296 mg, 75%) for the next step (Scheme 1).

2.2. Preparation of silver salt **1-b**

A solution of AgNO_3 (340 mg, 2 mmol) in H_2O (25 mL) was added dropwise to a solution of the sodium salt **1-a** (394 mg, 2 mmol) in H_2O (15 mL) upon stirring at room temperature. After 2 h stirring the precipitate was collected, washed with water and dried giving a yellow solid of silver salt **1-b** (451 mg, 80%).

2.3. General procedure for synthesis of energetic salts **1-c**, **1-d**, and **1-e**

A solution of guanidinium chloride (1 mmol), aminoguanidinium chloride (1 mmol), or triaminoguanidinium chloride (1 mmol) in water (2 mL) was added dropwise to the suspension of precursor salt **1-b** (0.5 mmol) in water (10 mL). The mixture was stirred at room temperature for 12 h. The precipitate was filtered off, and the filtrate was dried under vacuum yielding crude product. Pure samples suitable for elemental analysis were prepared by recrystallization from water.

Guanidinium salt 1-c: White solid (94 mg, 80%); mp: 146–148 °C, T_{dec} : 258 °C (peak, 10 °C/min); IR (KBr, cm^{-1}): 3508, 3480, 3407, 3344, 3270, 3190, 1554, 1321; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 6.88 (br s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$):

δ 176.4, 169.9, 158.4; Elemental analysis calcd. (%) for $\text{C}_3\text{H}_6\text{N}_8\text{O}_5$ (234.13): C 15.39, H 2.58, N 47.86, Found: C 15.56, H 2.60, N 47.80.

Aminoguanidinium salt 1-d: White solid (112.1 mg, 90%); mp: 150–152 °C, T_{dec} : 205 °C, 227 °C (peak, 10 °C/min); IR (KBr, cm^{-1}): 3457, 3365, 3174, 1573, 1333; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.55 (br s, 1H), 7.24 (br s, 2H), 6.72 (br s, 2H), 4.68 (br s, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 176.4, 169.9, 159.2; Elemental analysis calcd. (%) for $\text{C}_3\text{H}_7\text{N}_9\text{O}_5$ (249.14): C 14.46, H 2.83, N 50.60, Found: C 14.56, H 2.91, N 50.47.

Triaminoguanidinium salt 1-e: Yellow solid (118.6 mg, 85%); mp: 147–150 °C, T_{dec} : 155 °C (peak, 10 °C/min); IR (KBr, cm^{-1}): 3348, 3318, 3212, 1551, 1389; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.58 (br s, 3H), 4.48 (br s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 176.4, 169.9, 159.5; Elemental analysis calcd. (%) for $\text{C}_3\text{H}_9\text{N}_{11}\text{O}_5$ (279.17): C 12.91, H 3.25, N 55.19, Found: C 13.17, H 3.33, N 55.25.

3. Results and discussion

N-Nitration of **NOA** with P_2O_5 and HNO_3 gave **NON** smoothly. Initially, $\text{Ba}(\text{OH})_2$ was used to deprotonate its acidic hydrogen, but the barium salt failed to be prepared. To our delight, sodium salt **1-a** was formed by addition of solid NaHCO_3 to the reaction mixture. Higher yield of **1-a** (75%) was obtained with extended reaction time, compared with the literature [10a]. Subsequently, the silver salt **1-b** was obtained by treatment of sodium salt **1-a** with AgNO_3 , which is the precursor to prepare **1-c**, **1-d** and **1-e** by metathesis reactions driven by the precipitation of AgCl .

Structures of these energetic salts were identified by ^1H NMR and ^{13}C NMR, IR spectroscopy and elemental analysis. In IR spectra, strong absorption bands at 1562 cm^{-1} and 1335 cm^{-1} confirmed the presence of nitro group, while intense absorption bands in the range of 3174 cm^{-1} to 3457 cm^{-1} could be assigned to the N–H stretch of the nitrogen-rich cations. In ^{13}C NMR spectra, carbon atoms of 1,2,4-oxadiazole ring were found around 176 ppm and 169 ppm.

The single crystal of **1-e** was obtained from dichloromethane-ethanol (5:1, v/v) at room temperature. It crystallizes in the triclinic crystal system (P-1) with two molecules in the unit cell. The single crystal density of **1-e** is 1.773 g/cm^3 , locating between **1-c** and **1-d** (Table 1). In the single crystal structure (Fig. 1), there are three types of hydrogen bonds. The first one occurs between the intramolecular imino group and amino group of cation (N11–H11B...N9 3.5040(16) Å). The second is found between intermolecular amino group of the cation and the oxygen atom of nitro group in the anion (N10–H10...O1 3.0122(13) Å). And the third one takes place between the intermolecular imino group of the cation and the oxygen atom of nitroimino group (N11–H11A...O4 3.0344(12) Å).

Table 1

Physical properties and calculated detonation performance of **1-c**, **1-d** and **1-e**.

Compound	T_m (°C) ^a	T_d (°C) ^b	P (g/cm^3) ^c	OB (%) ^e	ΔH_f (kJ/mol) ^f	IS (J) ^g	P (GPa) ^h	D (m/s) ⁱ
NOA [10]	154	265	1.723	–24.6	177.0	>40	28.16	8013
NON [10]	–	219	1.883	4.6	227.7	15	37.68	9095
1-c	146–148	258	1.888	–27.3	226.0	>40	37.60	9319
1-d	150–152	205, 227	1.660	–28.9	341.4	>40	28.70	8526
1-e	147–150	155	1.773 ^d	–31.5	554.1	6	35.00	9354
TNT [10]	81	295	1.65	–74.0	–67.0	15	19.53	6881
RDX [10]	–	230	1.82	–21.6	92.6	7.4	35.17	8997

^a Melting point.

^b Thermal degradation (peak).

^c Theoretic density [12].

^d Single crystal density.

^e OB = oxygen balance for $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$: $1600[(c - 2a - b/2)/M_w]$. M_w = molecular weight.

^f Heat of formation (Gaussian 09).

^g Impact sensitivity.

^h Detonation pressure.

ⁱ Detonation velocity.

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