Synthesis, characterisation, thermal and explosive properties of 4,6-dinitrobenzofuroxan salts

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Abstract

Two new initiatory molecules, e.g. rubidium and cesium salts of 4,6-dinitrobenzofuroxan (DNBF) have been prepared by reacting sodium salt of 4,6-dinitrobenzofuroxan (DNBF) with rubidium nitrate and cesium nitrate, respectively, at $60\,^\circ C$ in aqueous medium. The characterisation of compounds by IR, ^{1}H-NMR, elemental analysis and metal content is described along with some of the evaluated thermal and explosive properties. The results indicate that cesium salt of DNBF (Cs-DNBF) appears promising initiatory and may suitably replace potassium salt of DNBF (K-DNBF), being used currently in initiatory compositions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Primary explosives such as mercury fulminate, lead azide, styphnate and tetrazene are being used world-wide since their synthesis. However, the use of mercury fulminate has become obsolete due to its dead press nature and instability. Similar features were also observed to some extent with tetrazene derivatives. Further, lead-based azides are also hazardous in nature. Therefore, efforts are being continued globally to develop a lead-free initiatory. The molecules which are able to replace lead azides are silver azide, mercury nitrotetrazole, bis-nitrotetrazolato cobalt tetramine perchlorate (BNCP) and salts of 4,6-dinitrobenzofuroxan (DNBF).

DNBF, a well-known and versatile electrophile has been prepared by number of workers as a starting material for synthesis of different explosives [1–3]. Due to electron deficient

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nature of this molecule, it forms stable Π or Meisenheimer complexes with electron rich species [4] and a series of different stable Meisenheimer complexes based on primary, secondary and tertiary aromatic amines have been reported [5]. In order to utilise its importance further, the optical and magnetic resonance of metallo tetraphenyl porphyrins based on DNBF have also been reported [6].

DNBF has also been used for the preparation of 5,7-diamino-DNBF (CL-14) [7], an insensitive energetic material whose explosive properties are better than well-known thermally stable explosives, such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Further, its electron deficiency has been exploited to prepare a number of salts based on alkali metals, alkaline earth metals and some transition metals. The most important member of this series is the potassium salts of DNBF (K-DNBF) [8] which has been used in initiatory composition for both military and commercial applications. In continuation of this work, sodium, barium and silver salts of DNBF have also been prepared and studied in detail [9].

In view of the versatile importance of DNBF salts, our efforts have been concentrated to synthesise a few new initiatory molecules of this class which have not been studied so far. We report here the synthesis and characterisation of rubidium and cesium salts of DNBF as well as their thermal and explosive properties.

2. Experimental

The melting points were determined on open capillary tubes and are uncorrected. The IR spectra were recorded on Perkin-Elmer infrared spectroscopy using a KBr matrix. ^{1}H-NMR spectra were recorded on a Brucker 90 MHz apparatus and the chemical shifts were recorded in δ units of parts per million with reference to tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on a Carlo-Ebra elemental analyser EA 1108 and the metal contents were determined by using atomic absorption spectrometry (model Chemito 201).

Deflagration temperature [10] was determined by heating 0.02 g of sample in a glass tube in Wood's metal bath at a heating rate of 5 °C/min and the temperature at which the sample was ignited/decomposed was recorded as the deflagration temperature. Differential thermal analysis (DTA) was recorded by heating 10 mg of sample at a rate of 10 °C/min in the presence of static air. The impact sensitivity was determined by the Fall Hammer method using a 2.0 kg drop weight. Friction sensitivity was determined using a Julius Peter apparatus by following standard methods [11]. The spark sensitivity was also determined by following the standard method [12] where explosive sample under test is kept in the cavity and the gap between the copper electrodes is adjusted to 2 mm. The energy stored in the charged capacitor is discharged through spark gap by activating the relays.

2.1. Materials

2,4,6-Trinitrochlorobenzene or picrylchloride [13] (as prepared from picric acid on treatment with pyridine followed by phosphorusoxychloride), with a melting point of 82–83 °C, was used as the starting material. Sodium azide was commercially obtained from Ubichem

Ltd., Middlesex, UK, while rubidium nitrate and cesium nitrate were procured from the Aldrich Chemical Company. Sodium hydrogen carbonate, acetic acid and methanol (SQ Grade, Qualigens) were used without further purification.

3. Synthesis

Synthesis of the rubidium salt of DNBF (Rb-DNBF) and cesium salt of DNBF (Cs-DNBF) involves the following steps:

1. Synthesis of 1-azido-2,4,6-trinitrobenzene.
2. Synthesis of DNBF.
3. Synthesis of sodium salt of DNBF (Na-DNBF).
4. Synthesis of rubidium and cesium salts of DNBF with rubidium nitrate and cesium nitrate, respectively.

3.1. 1-Azido-2,4,6-trinitrobenzene (**1**)

2,4,6-Trinitrochlorobenzene (10 g, 0.04 mol) was transferred into a three-necked round-bottomed flask fitted with a mechanical stirrer and a dropping funnel and 15 ml of methanol was added to it. After this, sodium azide (6.5 g, 0.01 mol) dissolved in 10 ml of distilled water was added dropwise to the reaction flask under vigorous stirring at ambient temperature for about half an hour. After complete addition of sodium azide, it was further stirred for 2 h. The reaction mixture was poured into ice-cooled water. The yellow precipitate, thus obtained, was filtered and washed thoroughly with distilled water to remove excess sodium azide. It was dried at room temperature which afforded a yield of 9.5 g (92%) with a melting point of 87–88 °C, DTA 88 °C (endotherm).

IR (KBr) cm^{-1}: 3051 (Ar–H str), 2165 (–N$_3$ str), 1610 (C=C str), 1545 and 1352 (NO$_2$ asym and sym str). ^{1}H-NMR (DMSO-d$_6$/TMS) δ ppm: 8.1 (s, 2H, aromatic proton). Anal. calcd. for C$_6$H$_2$N$_6$O$_6$ (mol. wt. 254): C, 28.34; H, 0.78; N, 33.07. Found: C, 28.16; H, 0.58; N, 32.89.

3.2. DNBF (**2**)

The compound **1** (10 g, 0.03 mol) was carefully transferred into a two-necked flask fitted with reflux condenser and acetic acid (40 ml) was added to it. The reaction mixture was refluxed for 2 h over an oil bath, cooled to ambient temperature and poured into crushed ice. The yellow precipitate, thus obtained, was filtered and washed with distilled water until it became acid-free. The product was crystallised from methanol, afforded a yield of 7.5 g (84%) with a melting point of 173 °C, DTA 174 °C (endotherm) and 273 °C (exotherm).

IR (KBr) cm^{-1}: 3450 (hydrogen bonded –OH str), 3106 (Ar–H str), 1610 (C=C str), 1590 and 1558 (furoxan ring str), 1534 and 1354 (NO$_2$ asym and sym str). ^{1}H-NMR (DMSO-d$_6$/TMS) δ ppm: 8.8 (s, 1H, C-5 aromatic proton), 8.94 (s, 1H, C-7 aromatic proton). Anal. calcd. for C$_6$H$_2$N$_4$O$_6$ (mol. wt. 226): C, 31.85; H, 0.88; N, 24.77. Found: C, 31.59; H, 0.60; N, 24.46.

3.3. Na-DNBF (**3**)

To a 500 ml three-necked round-bottomed flask, compound **2** (10.0 g, 0.44 mol) was transferred carefully and 100 ml of distilled water was also added to it. After this, sodium hydrogen carbonate (3.65 g, 0.42 mol) was added gradually at 60 °C with continuous swirling till evolution of carbon dioxide ceased. The reaction mixture was allowed to attain ambient temperature and then kept in the refrigerator overnight. The red-brown precipitate obtained was directly filtered and washed three times with cold water and finally with diethyl ether. It was dried to yield, 10 g (92%), m.p. 161–162 °C (explodes), DTA 163 °C (exotherm).

IR (KBr) cm^{-1}: 3440 (hydrogen bonded OH str), 3086 (Ar–H str), 1634 (C=C str), 1590 and 1560 (furoxan ring str), 1532 and 1340 (NO_2 asym and sym str). ^{1}H-NMR (DMSO-d$_6$/TMS) δ ppm: 8.94 (s, 1H, C-5 aromatic proton), 5.83 (s, 1H, C-7 aromatic proton). Anal. calcd. for $C_6H_2N_4O_6Na$ (mol. wt. 249): C, 28.91; H, 0.80; N, 22.48. Found: C, 28.63; H, 0.77; N, 22.26. Sodium content for $C_6H_2N_4O_6Na$ (mol. wt. 249): 9.15% against 9.2% (calcd.).

3.4. Salts of DNBF: general procedure

The compound **3** (10 g, 0.04 mol) was carefully transferred into a three-necked round-bottom flask and to this, 150 ml of distilled water was added. The reaction mixture was warmed to 60 °C and at this stage, metal nitrates (∼0.053 mol) dissolved in 60 ml of distilled water, was added slowly. The reaction mixture was swirled three to four times and allowed to cool at ambient temperature. The precipitate, thus obtained, was filtered, washed thoroughly with distilled water and finally with diethyl ether. Following this method, the corresponding rubidium and cesium salts of DNBF were prepared.

3.5. Rb-DNBF (**4**)

The compound **4** was prepared from rubidium nitrate. Yield 10.8 g (86%), m.p. 188–189 °C (explodes), DTA 188 °C (exotherm).

IR (KBr) cm^{-1}: 3444 (hydrogen bonded OH str), 3081 (Ar–H str), 1620 (C=C str), 1590 and 1560 (furoxan ring str), 1540 and 1342 (NO_2 asym and sym str). ^{1}H-NMR (DMSO-d$_6$/TMS) δ ppm: 8.92 (s, 1H, C-5 aromatic proton), 6.10 (s, 1H, C-7 aromatic proton). Anal. calcd. for $C_6H_2N_4O_6Rb$ (mol. wt. 311): C, 23.15; H, 0.64; N, 18.00. Found: C, 22.98; H, 0.49; N, 17.88. Rubidium content for $C_6H_2N_4O_6Rb$ (mol. wt. 311): 27.08% against 27.33% (calcd.).

3.6. Cs-DNBF (**5**)

The compound **5** was prepared from cesium nitrate. Yield, 12.0 g (83%), m.p. 165–166 °C (explodes), DTA 166 °C (exotherm).

IR (KBr) cm^{-1}: 3440 (hydrogen bonded OH str), 3082 (Ar–H str), 1630 (C=C str), 1595 and 1560 (furoxan ring str), 1545 and 1354 (NO_2 asym and sym str). ^{1}H-NMR (DMSO-d$_6$/TMS) δ ppm: 8.91 (s, 1H, C-5 aromatic proton), 6.06 (s, 1H, C-7 aromatic

proton). Anal. calcd. for $C_6H_2N_4O_6Cs$ (mol. wt. 359): C, 20.05; H, 0.55; N, 15.59. Found: C, 19.86; H, 0.39; N, 15.26. Cesium content for $C_6H_2N_4O_6Cs$ (mol. wt. 359): 36.81% against 37.02% (calcd.).

4. Results and discussion

Compound **3**, the parent compound for the synthesis of corresponding rubidium and cesium salts was prepared by following the reaction sequence as depicted in Fig. 1. The compound **3**, thus obtained, was then treated with rubidium nitrate and cesium nitrate to obtain compounds **4** and **5**, respectively, with very good yield and purity. K-DNBF which is used in initiatory compositions for both military and commercial application [8], was also prepared by the reported method [8] in order to compare its properties with newly synthesised Rb-DNBF and Cs-DNBF.

Rb-DNBF is brick-red in colour while Cs-DNBF is buff colour. Rb-DNBF melts/decomposes at 188–189 °C with a crackling sound and Cs-DNBF also decomposes with a crackling sound in the range of 165–166 °C. The salts have been characterised by IR, ^{1}H-NMR, elemental analysis and metal content.
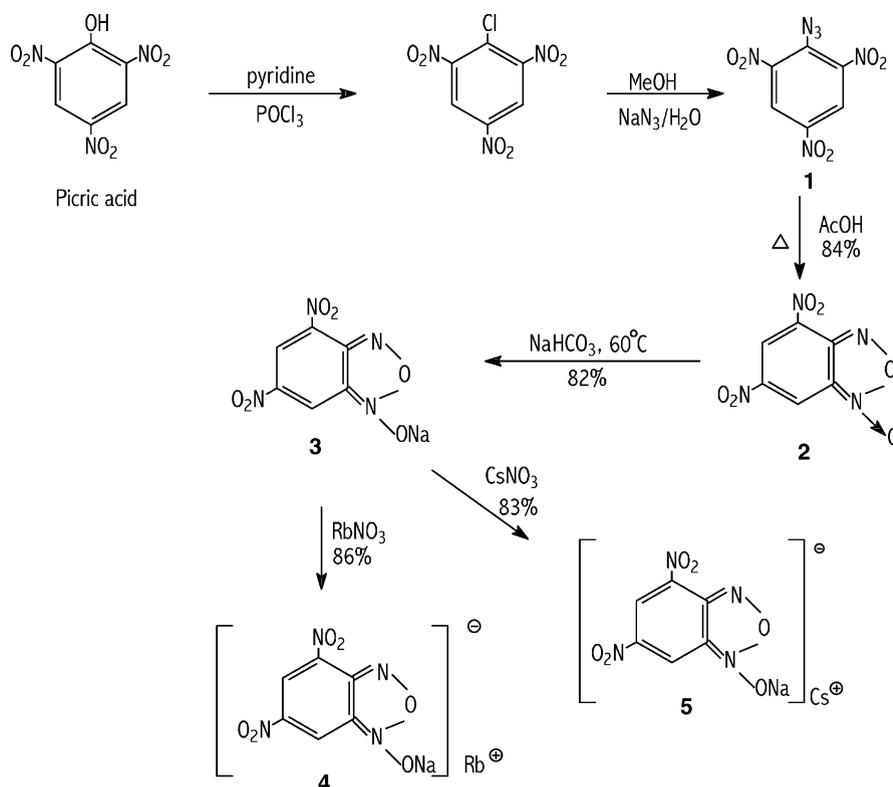

Fig. 1. Synthetic route for alkali metal salts.

Table 1
Some thermal and explosive properties of Na, K, Rb and Cs salts of DNBF[a]

Properties	Na-DNBF	K-DNBF	Rb-DNBF	Cs-DNBF
Melting point (°C)	161–162 (explodes)	215 (explodes)	188–189 (explodes)	165–166 (explodes)
Deflagration temperature (°C)	160	220	188	166
DTA (°C) (exotherm)	163	222	188	165
Impact sensitivity (height of 50% explosion) (cm)	33.5 (28)	35.0 (29)	35 (29)	30 (24)
Friction sensitivity (insensitive) (kg)	5.4	3.8	1.0	0.2
Spark sensitivity (mJ)				
Does not fire at	22.0	24.0	24.5	20.0
Fires at	24.0	26.5	28.9	24.5

[a] Values in parenthesis indicate the F of I.

IR spectra of Rb-DNBF and Cs-DNBF are very similar, suggesting that both salts possess comparable structural features. The strong absorption bands that are well resolved from the neighbouring C-7 aromatic proton [8] are sharp O–H stretchings at 3440–3444 cm^{-1} and bands at 3081 cm^{-1} are because of C-5 aromatic proton stretchings. In general, the C=C and furoxan rings stretching frequencies appear at 1620–1630, 1590–1595 and 1560 cm^{-1}, while asymmetric and symmetric vibrations of the NO_2 group were absorbed at 1534–1540 and 1342–1354 cm^{-1}, respectively.

In ^{1}H-NMR of the salts, C-5 protons of aromatic ring resonate at δ 8.91–8.92 while chemical shifts of C-7 protons of aromatic ring appear at higher field δ 6.06–6.10 due to formation of hydrogen bonding with the co-ordinate bonded oxygen of furoxan ring [8]. The observed elemental analysis data and metal contents of compounds **4** and **5** are in excellent agreement with the calculated values which confirms the purity of the compounds.

Compounds **4** and **5** were also evaluated for their thermal and explosive properties and the data are presented in Table 1. The compounds **4** and **5** deflagrate with sound at 188 and 166 °C, respectively, which are also supported by DTA thermograms of corresponding exotherms. The decreasing trend in deflagration temperature/melting point is due to [Kr] $5s^1$ and [Xe] $6s^1$ electronic configuration of rubidium and cesium, respectively. This causes a higher melting point of Rb (39 °C) and low melting point of Cs (28 °C). The low melting points are attributed to their larger atomic size, due to which binding energies of their atoms in the crystal lattice are low [14].

The study on explosive properties (Table 1) reveals that compounds **4** and **5** are safe towards impact and the figure of insensitiveness (F of I) is in the order of 24–29, thereby suggesting safe initiators. The friction sensitivity of compound **4** is 1.0 kg while that of compound **5** is only 200 g indicating that compound **5** is quite promising towards friction, which is an important characteristic of an initiator. The spark sensitivity of well-known initiators such as $Pb(N_3)_2$ and AgN_3 functions at 3–5 mJ, whereas, the compounds **4** and **5** are safe up to 24.5 and 20.0 mJ, respectively, indicating they are quite safe for handling than conventional initiators. Even though, during synthesis as well as handling of compounds **4** and **5** static charges of the body were properly discharged by touching copper strips, already connected to the earthing pit.

5. Conclusions

Rubidium and cesium salts of DNBF have been synthesised and fully characterised. The data suggest that Cs-DNBF appears promising in all respects over Rb-DNBF and its properties are better than K-DNBF, a well-known initiatory of this series. Hence, it may find application where K-DNBF is currently being used.

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