

## Synthesis, characterization and thermal behavior of hydrazinium nitroformate (HNF) and its new N-alkyl substituted derivatives

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Two new derivatives of hydrazinium nitroformate (HNF) viz., mono methyl hydrazinium nitroformate (MMHNF) and dimethyl hydrazinium nitroformate (DMHNF) have been synthesized and characterized by elemental, spectral and thermal analysis. The nitration of isopropanol using fuming nitric acid and sulphuric acid yielded nitroform which on neutralization with equivalent quantities of hydrazine hydrate yielded HNF, whereas neutralization with methyl hydrazine and dimethyl hydrazine solution in xylene solvent gave title compounds MMHNF and DMHNF respectively. MMHNF and DMHNF were thermally stable up to 128-137°C whereas the decomposition of HNF commenced at 120°C. The impact sensitivity data established relatively less susceptibility of MMHNF and DMHNF than that of the HNF. Performance of MMHNF and DMHNF was also predicted theoretically by applying Linear Output Thermodynamic User friendly Software for Energetic Systems (LOTUSES) code. Out of the three compounds synthesized, HNF finds potential application as a eco-friendly oxidizer and MMHNF may find application as a potential high performance energetic material and DMHNF appears to be potential ingredient for melt castable high explosive formulations.

**Keywords:** Hydrazinium nitroformate, oxidizers, energetic additives, thermolysis.

**IPC Code:** G01K; C01B

The oxidizers play a vital role in deciding the energy potential of rocket propellants due to their exothermic chemical reactions with the fuel moieties. Ideally, the oxidizer should have high oxygen content and a superior positive heat of formation ( $\Delta H_f$ ). The well-known oxidizers used in the military and civil applications are ammonium nitrate (AN) and ammonium perchlorate (AP).

The present day workhorse oxidizer of rocket propellants is AP. However, composite propellants based on it produce a large quantum of hydrogen chloride in exhaust, which results in pollution of the environment. Further, its combustion products leave a trail in humid weather, which is not desirable for specific applications. This called for the need to develop new oxidizers in place of AP, superior to co-existing alternative ammonium nitrate (AN) which is less energetic due to lower oxygen balance (+17%) as well as negative heat of formation (-87 kcal/mol) than that of AP ( $\Delta H_f = -70$  kcal/mol, OB = +35%). Moreover, AN is highly hygroscopic and undergoes

crystal phase transition at around 32 °C resulting in undesirable dimensional changes at operation temperature leading to crack formation in monolithic grains. In the present global scenerio ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are emerging as likely substitutes to ammonium perchlorate<sup>1,2</sup>. Although, both ADN and HNF have lower oxygen balance (+25 and +13% respectively), their  $\Delta H_f$  (-40 and -17 kcal/mol respectively) is superior to that of AP. Hexanitrohexaazaisowurtzitane (HNIW; CL-20) having  $\Delta H_f$  of 94 kcal/mol is also being investigated<sup>3</sup> as a rocket propellant ingredient. HNF has certain advantages over ADN such as ease of synthesis, nonhygroscopic nature, higher density and melting point. It is more economical than CL-20.

Nitroform (NF) is the key synthon in the synthesis of HNF. Various researchers<sup>4,7</sup> reported the nitration of acetylene gas/acetic anhydride/acetone to obtain nitroform. However, these methods were found hazardous due to high degree of exothermicity in the process. The synthesis of NF<sup>8</sup> (25% yield) by the nitration of isopropanol is considered safe method. These researchers developed the extraction method of

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NF from nitric acid by using methylene chloride<sup>9,10</sup>. In view of the problems associated with earlier attempts to use HNF in solid propellants, a research project was initiated by The Netherlands Agency<sup>11,12</sup> for Aerospace Programs (NAAP) to develop HNF/Al/glycidyl azide polymer (GAP) solid propellants. Its production commenced in 1990 after a pilot plant of 30-100 kg per annum production capacity became operational at NAAP in mid 1993. Researchers from USA reported<sup>13,14</sup> the production of HNF on commercial scale. Recently, HNF was also synthesised in HEMRL, India<sup>15-17</sup>. However, the finer details of the actual process for the synthesis of HNF are reported in the form of patents and classified reports due to its importance as a eco-friendly oxidizer.

This paper reports the synthesis of nitroform (1) by the nitration of isopropanol using fuming nitric acid and sulphuric acid, which on neutralization with equivalent quantities of hydrazine hydrate yielded hydrazinium nitroformate, (HNF, 2) based on the lines of reported methods<sup>8-10</sup>. Two new compounds monomethyl hydrazinium nitroformate (MMHNF, 3) and dimethyl hydrazinium nitroformate (DMHNF, 4) are obtained on neutralization of NF with methyl hydrazine and dimethyl hydrazine respectively. The compounds 2, 3 and 4 were characterized and subjected to sensitivity test as well as thermal studies to assess the effect of substitution. Relative performance potential of the compounds as energetic additive is also theoretically determined.

## Experimental Procedure

### Methods

The melting points of the recrystallised products were measured using Thomas Hoover capillary melting point apparatus. The elemental analysis was carried out on Perkin-Elmer instrument. The IR spectra were determined as nujol mull on a Perkin Elmer-1600 Fourier Transformer (FT) IR spectrophotometer. Proton magnetic resonance (PMR) spectra were recorded on Varian 300 MHz spectrometer with tetramethyl silane as an internal standard. The thermal analysis (2 mg samples) was performed on Mettler Toledo Star Thermo Gravimetry-Differential Thermal Analyser (TG-DTA) system at a heating rate of 10°C/min in nitrogen atmosphere at a flow rate of 80 cm<sup>3</sup>/min. Energy of activation was obtained from TG data by applying the equation proposed by Madhusudnan *et al.*<sup>18</sup>.

The impact test was conducted using a set-up similar to that used in Naval Ordnance Laboratory

(NOL), USA. The test specimens (30-35 mg of powder) were kept between two hardened stainless steel base plates and anvil and a 2 kg drop weight was allowed to fall freely from different heights. Both open end aluminum foil encapsulated specimens were used for evaluation. Ten tests were conducted for each compound. The results are reported in terms of height for 50% probability of explosion ( $h_{50\%}$ ) of the sample. The impact sensitivity studies on benchmark explosives such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 2,4,6-trinitrotoluene (TNT) were also carried out under identical conditions to validate the experimental set-up. The performance parameters of the synthesized compounds were predicted using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES)<sup>19-22</sup>.

### Synthesis of compounds

The starting materials of AR grade were used directly as purchased from the trade. All the chemicals were of Merck/Aldrich make, while methyl hydrazine and dimethyl hydrazine were obtained from indigenous sources as a 20% solution in xylene solvent.

#### *Trinitromethane (Nitroform, NF 1)*

A three-necked flask was assembled with a mechanical stirrer, a thermometer and a dropping funnel. Fuming nitric acid (25.19 g, 0.399 mol) and concentrated sulphuric acid (3.5 g, 0.033 mol) along with dichloroethane were transferred to the flask. Subsequently, isopropanol (2 g, 0.033 mol) was added cautiously with stirring, as the reaction was highly exothermic. The stirring was continued for 4-5 h at ~50°C. A substantial quantity of the brown gases evolved during this step. The reaction mixture was allowed to cool down to room temperature and poured in 100 mL of distilled water. The steam distillation gave trinitromethane (yield 25%), which was washed first with dilute alkali, and then with water. The product was dried over anhydrous sodium sulphate. It recorded boiling point of 50°C (reported 48°C). IR (nujol, cm<sup>-1</sup>): 1567, 1357 (C-NO<sub>2</sub>), 3345 (C-H stretching vibration), 1250 (C-H bending vibration). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 9.8 (1H,s). Anal. Calcd for CHN<sub>3</sub>O<sub>6</sub> (151): C, 7.94; H, 0.66; N, 27.81; Found: C, 7.56; H, 0.75; N, 28.12%.

#### *Hydrazinium nitroformate (HNF, 2)*

Hydrazine hydrate (0.211 g, 0.662 mol) was added dropwise to a solution of trinitromethane (1 g, 0.662

mol) in dichloroethane (15 mL) kept stirring under nitrogen atmosphere at 15-20°C. The stirring was continued for 2 h at 15-20°C. The yellow precipitate (**2**) formed was filtered, dried and recrystallised from methanol (yield 0.302 g, 25%) [mp, 120 -122°C (reported 119-124°C)]. IR (KBr,  $\text{cm}^{-1}$ ), 3244, 2868 (N-H), 1615, 1180( $\text{NH}_3^+$ ), 1515, 1271, 790 ( $\text{NO}_2$ ), 1100 (NCN), 980 (N-N).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{DMSO}-d_6$ ),  $\delta$  4.675 (br,s, 2 H). Anal. Calcd for  $\text{CH}_3\text{N}_5\text{O}_6$  (183): C, 6.52; H, 2.74; N, 38.20; Found: C, 6.55; H, 2.73; N, 38.25%.

#### *Mono methyl hydrazinium nitroformate (MMHNF, 3)*

Methyl hydrazine solution in xylene (0.22 g, 0.478 mol) was added dropwise to a solution of trinitromethane (0.750 g, 0.496 mol) in dichloroethane (10 mL) stirred under nitrogen atmosphere at 10-15°C. The stirring was continued at 10-15°C for 2 h. The precipitate (**3**) formed was filtered, dried and recrystallised from methanol (yield 0.195 g, 20%), mp, 128-130°C. IR (KBr,  $\text{cm}^{-1}$ ), 3232, 2854 (NH), 2920 (C-H), 1615, 1180 ( $\text{NH}_3^+$ ), 1512, 1274, 785 ( $\text{NO}_2$ ), 1114 (NCN), 980, 785 (N-N). Anal. Calcd for  $\text{C}_2\text{H}_7\text{N}_5\text{O}_6$  (197): C, 12.45; H, 3.60; N, 35.80; Found: C, 12.18; H, 3.55; N, 35.53%.

#### *Dimethyl hydrazinium nitroformate (DMHNF, 4)*

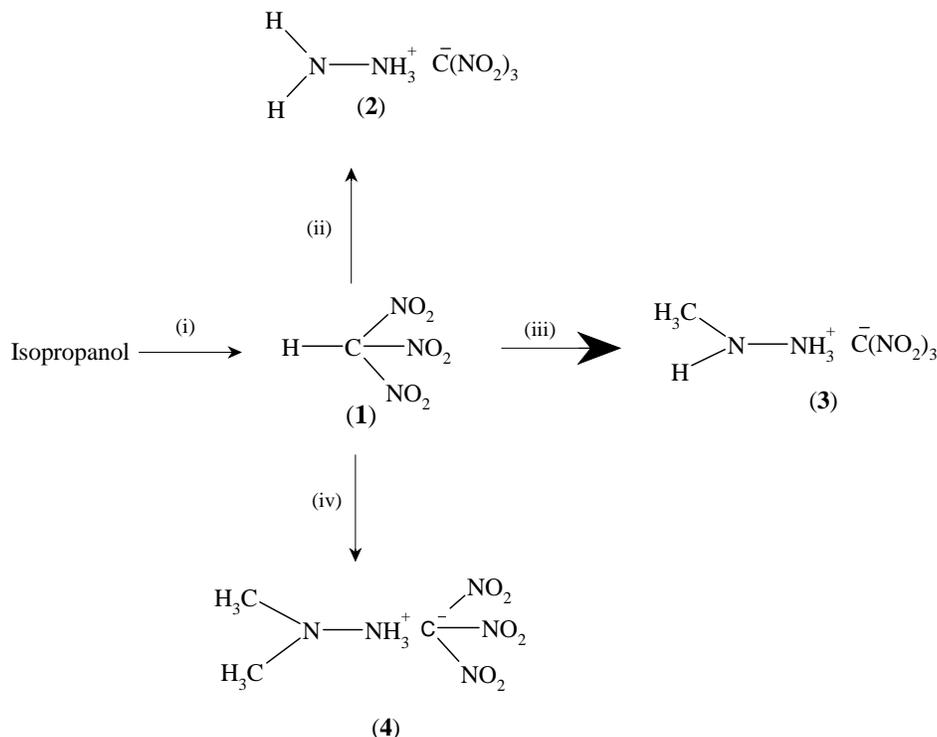
Dimethyl hydrazine solution in xylene (1.04 g, 0.492 mol) was added dropwise to a solution of trinitromethane (0.750 g, 0.496 mol) in dichloroethane (10 mL) stirred under nitrogen atmosphere at 15-20°C. The stirring was continued for 2 h at 10°C. The precipitate (**4**) formed was filtered, dried and recrystallised from methanol (yield 0.239 g, 23%), mp 137-140 °C. IR (KBr,  $\text{cm}^{-1}$ ), 3216, 2750 (NH), 2934 (C-H), 2181, 1615, 1180 ( $\text{NH}_3^+$ ), 1586, 1550, 1512, 1271 ( $\text{NO}_2$ ), 1105 (NCN), 980, 788 (N-N). Anal. Calc. for  $\text{C}_3\text{H}_9\text{N}_5\text{O}_6$  (211): C, 17.06; H, 4.26; N, 33.17; found: C, 17.00; H, 4.29; N, 33.21%.

A schematic presentation of the synthesis of all the four compounds is given below.

## Results and Discussion

### Spectroscopic studies

The reported melting point of HNF (**2**) varies over a wide range of temperature (119-124°C) mainly due to the difference in purity level of the product<sup>23-26</sup>. The melting point of the product obtained during this work was 120 -122°C. The IR spectra of all the compounds



### Synthesis scheme

**Reagent and conditions:** (i) Fuming  $\text{HNO}_3$ , con.  $\text{H}_2\text{SO}_4$ , 50°C, 4-5 h. (ii) Hydrazine, dichloroethane, 15-20°C, 2 h. (iii) Monomethylhydrazine, dichloroethane, 15-20°C, 2 h. (iv) Dimethylhydrazine, dichloroethane, 15-20°C, 2 h

exhibited absorption bands in the region 1510-1595  $\text{cm}^{-1}$ , which can be attributed to the presence of nitro group. The compounds **2**, **3** and **4** showed IR absorption bands in the range 2750-2868  $\text{cm}^{-1}$  due to  $[\text{NH}_3]^+$  in salt. IR absorption bands due to -CH of compounds **3** and **4** were displayed in the region 2925-2934  $\text{cm}^{-1}$  and can be attributed to alkyl substitution on hydrazine moiety. The C, H, N content obtained experimentally matched with the reported value.

#### Thermal analysis

In TG, HNF (**2**) decomposed in two-stages in the temperature regions of 110-145 and 145-170°C accompanied with the weight loss of the order of 61 and 32% respectively. The compounds **3** and **4** also decomposed in two stages. The compound **3** exhibited decomposition in the temperature range of 115-170 and 170-350°C accompanied with the weight loss of 43 and 40% respectively. The TG results reported by other researchers<sup>3,27</sup> also reveal more or less similar decomposition pattern in DTA-TG except a weak exotherm at 109°C. In case of DMHNF, the first stage of decomposition was observed in the temperature range of 125-210°C accompanied with the weight loss of 30%. The second stage involving weight loss of 18% commenced immediately at 210°C and was completed by 330°C. The residue left after decomposition was 7% in HNF, 17% in **3** and 52% in **4**. This may be correlated with the oxygen balance of the compounds. The relative decomposition temperature as well as correlation factor obtained from energy of activation and frequency factor

(Table 1) indicates that MMHNF and DMHNF are relatively more stable as compared to HNF. The activation energy ( $E_a$ ) obtained from TG experiments for the compounds **2**, **3** and **4** was of the order of 220-265 and 110-150 kJ/mol for first and second stages, respectively. The TG-FTIR of the evolved gases of HNF suggested the evolution of gaseous moieties such as CN and CO (2358  $\text{cm}^{-1}$ ), oxides of nitrogen (3746, 3840 and 1693  $\text{cm}^{-1}$ ) and NH (3200  $\text{cm}^{-1}$ ). These findings are in close agreement with the reported data<sup>15</sup>. Korban *et al.*<sup>26</sup> have reported the formation of ammonium nitroformate (ANF) as an intermediate during slow decomposition of HNF. Williams and Brill<sup>28</sup> have also suggested that AN detected in their experiments during decomposition of HNF originates from decomposition of ANF. The similar decomposition mechanism is envisaged for the compounds **3** and **4**.

#### Sensitivity evaluation

It is reported<sup>27,29,30</sup> that the sensitivity of HNF depends not only on purity but also on the kind of contaminants. The HNF synthesized during this work gave  $h_{50\%}$  of 20 cm, which is close to reported value<sup>1</sup>. The compounds **3** and **4** gave  $h_{50\%}$  of 30 and 35 cm respectively indicating their low vulnerability to impact stimuli (Table 1). The decrease in impact sensitivity of HNF on alkyl substitution can be explained on the basis of increase in the basicity of hydrazine on methyl substitution entailing stronger holding of the nitroformate group leading to greater stability. It can also be correlated with their relative oxygen balance like extent of residue formation during TG experiments.

Table 1—Explosive and thermal properties of HNF, MMHNF and DMHNF

Properties	HNF	MMHNF	DMHNF
Melting point °C	120-122	128-130	137-140
TGA % (weight loss)			
(Temperature range, °C)			
1 <sup>st</sup> step	61 (110-145)	43 (115-170)	30 (125-210)
2 <sup>nd</sup> step	32 (145-170)	40 (170-350)	18 (210-360)
Activation energy (kJ/mol)			
1 <sup>st</sup> step	223	245	265
2 <sup>nd</sup> step	110	134	149
Frequency factor (A)			
1 <sup>st</sup> step	24.93	18.78	14.83
2 <sup>nd</sup> step	10.27	8.89	7.77
Correlation coefficient (r)			
1 <sup>st</sup> step	0.997	0.968	0.869
2 <sup>nd</sup> step	0.994	0.976	0.897
Impact sensitivity ( $h_{50\%}$ ), cm	20	30	35

Sensitivity to impact: RDX, 28-30; HMX, 23-25; Tetryl, 74-78 cm.

Table 2—Performance parameters of HNF, MMHNF and DMHNF and their comparison with the conventional explosives

Sl. No	MW	% Composition (wt.)				OB (%)	VOD (km/s)	C-J P (Gpa)	SI (db)	$\rho$ (g/cm <sup>3</sup> )	RS	PI (%)
		C	H	N	O							
HNF	183	6.52	2.74	38.20	52.43	+13.1	8.902	46.89	356	1.86	154	160
MMHNF	197	12.45	3.60	35.80	48.70	-12.17	9.134	37.15	358	1.78	212	221
DMHNF	211	17.06	4.26	33.17	45.46	-36.16	8.353	31.56	332	1.70	199	208
TNT	227	37.01	2.21	18.50	42.26	-73.96	6.66	19.26	275	1.66	121	125
RDX	222	16.22	2.72	37.84	43.21	-21.61	8.93	36.48	353	1.77	163	169
Tetryl	287	29.2	1.75	24.39	44.57	-47.35	7.77	27.32	317	1.75	125	130

TNT: 2,4,6-Trinitrotoluene; RDX: Hexahydro-1,3,5-trinitro-1,3,5-triazine; Tetryl: N-methyl-N-nitro-2,4,6-trinitroaniline; MW = Molecular weight of HEM; OB = Oxygen balance; VOD = Velocity of detonation; CJ-P = Chapman jouget pressure; SI = Sound intensity;  $\rho$  = Density; RS = Relative strength (as per Bertlot approximation as compared to TNT on a mass basis); PI = Power index (in comparison to picric acid).

### Theoretical performance prediction

The theoretically predicted parameters for **2**, **3** and **4** by LOTUSES code are given in Table 2. The calculated density of HNF (1.86 g/cm<sup>3</sup>) matched with the reported value. The density of compounds **3** and **4** was found less than that of **2**. The theoretically predicted velocity of detonation (VOD) for HNF is on higher side in comparison to reported data<sup>30</sup>. An increase in VOD was observed on methyl substitution **2** on HNF despite decrease in density and oxygen balance. The higher VOD, relative strength and power index of compound **2** may be due to optimization of the oxygen balance due to interplay between the temperature and mean molecular weight of decomposition product. However, this aspect needs further investigations. The disubstituted HNF exhibited decrease in VOD, as anticipated due to negative oxygen balance (-36%) and lower density (1.70 g/cm<sup>2</sup>). Theoretically predicted energetics of **2**, **3** and **4** established their performance potential superior to that of TNT and tetryl (Table 1). Sundarajan and Jain model<sup>31</sup> also gave similar performance trend. However, the VOD obtained by their approach was on the lower side (6.7 to 7.3 km/s).

The performance parameters of the compounds indicated that, HNF finds application as eco-friendly oxidizer and MMHNF may be of interest as a high performance energetic ingredient for explosive and propellant formulations whereas DMHNF could be of interest as an energetic ingredient for melt castable high explosive formulations. However, one has to establish the non-conventional solvent process due to their higher melting points 128 and 137°C respectively.

### Conclusion

The HNF is an upcoming advanced oxidizer for futuristic propellant systems in place of ammonium

perchlorate. Two new derivatives of HNF *viz.*, monomethyl hydrazinium nitroformate (MMHNF, **3**) and dimethyl hydrazinium nitroformate (DMHNF, **4**) were synthesized and characterized. The compounds **3** and **4** decompose in two steps like HNF, suggesting that the basic thermal decomposition mechanism remains same. The hyphenated TG-FTIR studies on HNF also revealed the evolution of gaseous species containing CO, CN, NH and oxides of nitrogen. The substitution of alkyl groups bring down the impact sensitivity, which is a desirable feature from propellant processing point of view. The compounds MMHNF and DMHNF may find application as potential energetic additives for rocket propellants and explosive formulations.

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