Syntheses and Analyses of N,N′-Dinitrourea

Patrick Goede*, **Niklas Wingborg**, **Helena Bergman**, and **Nikolaj V. Latypov**

Swedish Defence Research Agency Grindsjön, SE-147 25 Tumba (Sweden)

Summary

N,N′-Dinitrourea was prepared through nitration of urea at low temperature in mixed acids in 67 % yield. The prepared material was pure and found to be stable at room temperature. The properties of N,N′-dinitrourea were analysed by: TG, DSC, ignition test in Wood's metal bath, NMR, MS, FT-IR, gaspycnometry and BAM impact and friction sensitivity tests. N,N′-Dinitrourea was found to have a very high density and positive oxygene balance. It was, however, found to be sensitive both to impact and friction.

1. Introduction

There has been a recent interest in N,N′-dinitrourea as a component in Mannich reactions[1] and in the synthesis of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (keto-RDX)[2]. In the keto-RDX synthesis N,N′-dinitrourea is prepared *in situ* without isolation of the compound, to optimize the reaction conditions a request for N,N′-dinitrourea was phrased[3]. Another synthesis of keto-RDX involving N,N′-dinitrourea was recently published[4]. N,N′-Dinitrourea is also a precursor to nitramide a useful starting material for the synthesis of aliphatic nitramines[5]. In an earlier article dealing with the preparation of N,N′-dinitrourea, it was claimed to be unstable and not possible to isolate[6]. Due to the large interest in N,N′-dinitrourea as a starting material in the synthesis of more complex energetic materials we have prepared pure and stable N,N′-dinitrourea and studied its properties.

2. Experimental

The NMR-spectra were recorded on a Varian XL-200 spectrometer. The IR-spectra were recorded on a Bruker IFS 55. Urea (Lancaster), sulphuric acid 95 % (KEBO), nitric acid 100 % (Merck) and trifluoroacetic acid (Baker) were used as supplied.

2.1 Synthesis of N,N′-Dinitrourea

N,N′-Dinitrourea was obtained by nitration of urea in a 50:50 mixture of sulphuric acid and nitric acid at low

temperature (Scheme 1). While our work was in progress an almost identical approach to N,N′-dinitrourea was published[6]. In that article the authors reported that N,N′-dinitrourea undergoes decomposition, which may lead to spontaneous ignition at room temperature. We believe this behaviour is due to trace amounts of acids in their final product. The N,N′-dinitrourea we obtained was washed several times with trifluoroacetic acid to remove all acidic impurities and we found it to be stable for several weeks in a desiccator over silica gel at room temperature.

Caution: N,N′-dinitrourea is a powerful and sensitive explosive and should be handled with appropriate precautions. Employ all standard energetic materials safety procedures in experimental operations involving such a substance.

95 % Sulphuric acid (10.9 ml, 20.0 g, 0.19 mol) was added to 100 % nitric acid (13.2 ml, 20.0 g, 0.32 mol) and then cooled to 0 °C. Urea (3 g, 0.05 mol) was then added to the reaction mixture for about 30 min. Care was taken that the temperature of the reaction mixture wasn't allowed to rise above 5 °C. After the addition the reaction mixture was allowed to stand for another 30 min at 0 °C, during this time a white precipitate formed. The white crystal mass was filtered off on a glass funnel and then washed with trifluoroacetic acid (5×5 ml). The product was dried over vacuum giving 5.0 g (0.033 mol, 67 mol-%) of N,N′-dinitrourea.

^{1}H-NMR (DMSO-D6): δ 8.05 (s, 2H); ^{13}C-NMR (DMSO-D6): δ 149.2; IR (KBr): 1684, 1544, 1419, 1224 cm^{-1};

Anal. Calcd. for $CH_2N_4O_5$: C, 8.00; H, 1.34; N, 37.34 wt-%. Found: C, 7.94; H, 1.39; N, 37.26 wt-%.

3. Analyses

3.1 Differential Scanning Calorimetry, DSC

The DSC used was a Mettler DSC 30 with a ceramic sensor. Every experiment as well as the calibration was performed in a nitrogen atmosphere. The flow of nitrogen was approximately 50 ml/min. The DSC was calibrated with indium (Mettler Calibration Standard) and evaluated according to Mettler's recommendations[7]. The samples were put into aluminium cups with pierced lids.

* Corresponding author; e-mail: patrick.goede@foi.se
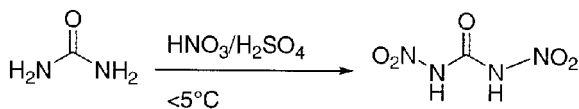
Scheme 1. Synthesis of N,N′-dinitrourea.

At a heating rate of $10\,^\circ$C/min an exotherm reaction starts smoothly at approximately $100\,^\circ$C and becomes very steep at $120\,^\circ$C (Fig. 1). By measuring the exotherm reaction at different heating rates, the activation energy could be calculated, according to ASTM E 698−79, by plotting $-\ln(\beta/T^2)$ vs. $1000/T$ where β is the heating rate in $^\circ$C/min and T is the peak temperature in K (Fig. 2).

The activation energy was then calculated by fitting a straight line to the data and by using Eq. (1):

$$E_a = R\frac{d(-\ln(\beta/T^2))}{d(1/T)} \tag{1}$$

By this method the activation energy was found to be $104\,$kJ/mol.

3.2 Ignition Test in Wood's Metal Bath

In the ignition test the time to ignition was measured as a function of the temperature. This was done by immersing a test tube with the sample in a bath of Wood's metal at a certain temperature. The time to ignition was then measured with a chronometer. In all cases the mass of the sample in the test tube was $24-28\,$mg. The temperature of the bath was increased in steps of approximately $5\,^\circ$C. 34 samples were tested, usually four at each temperature. The ignition temperature is defined to be in the interval between the maximum temperature at which no reaction occurs within $300\,$s and the lowest temperature where a reaction does occur, in at least one of the four samples, within $300\,$s. The method is not very accurate since the time is measured manually. The measurements were started just below the temperature at which
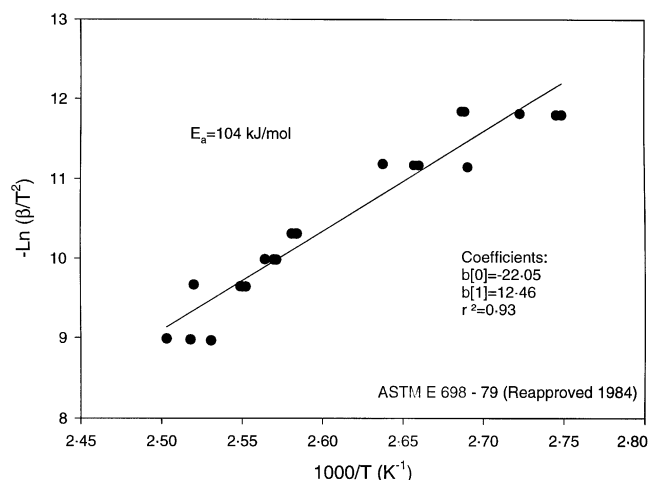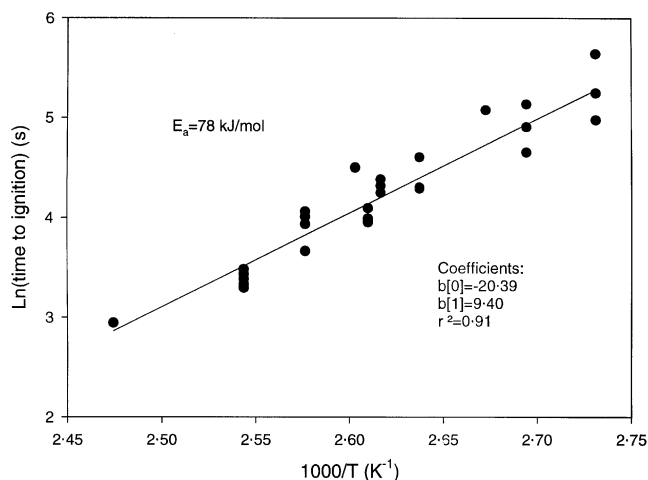

Figure 2. DSC-determination of activation energy: Natural logarithm of β/T^2 vs. $1000/T$.

ignition was suspected from DSC data at a heating rate of $10\,^\circ$C/min.

The ignition temperature for N,N′-dinitrourea was found to be between $91\,^\circ$C and $93\,^\circ$C (four reactions) which was lower than expected from the DSC data. To calculate the activation energy, E_a, for the ignition of N,N′-dinitrourea, the natural logarithm of the ignition time was plotted versus the reciprocal temperature (Fig. 3).

The activation energy was then calculated by fitting a straight line to the data and by using the Arrhenius equation. By this method the activation energy was found to be $78\,$kJ/mol between $93\,^\circ$C and $131\,^\circ$C. This value was lower than that determined by DSC (Fig. 2). A similar discrepancy between activation energies determined by DSC and ignition test in Wood's metal bath was found for ADN and N-guanylurea-dinitramide[8]. The explanation offered in that case was that the compound had either different decomposition reaction orders or different decomposition mechanisms in the two experiments. It might also be due to the substantially higher heating rate in the ignition test.
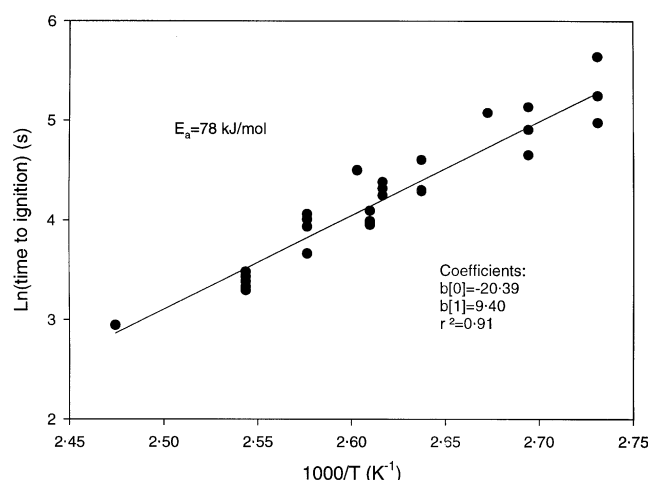

Figure 1. DSC curve for N,N′-dinitrourea at a heating rate of $10\,^\circ$C/min.

Figure 3. Wood's metal bath determination of activation energy: Natural logarithm of time to ignition vs. $1000/T$.

3.3 Thermogravimetry, TG

The TG used was a Mettler TGA 850. The test was performed in a nitrogen atmosphere at a heating rate of $10\,^{\circ}C/min$. The samples were put into alumina cups and the flow of nitrogen was approximately $80\,ml/min$. Prior to the testing, the TG was calibrated according to Mettler's recommendations[7]. The results of the measurements are shown in Figure 4.

As can be seen in Figure 4, the weight started to decrease between 80 and $90\,^{\circ}C$ followed by a steep mass loss between 110 and $120\,^{\circ}C$. The N,N'-dinitrourea decomposition as measured in the TG correlated clearly to the exothermal decomposition found in the DSC (Fig. 1).

3.4 Mass Spectroscopic Data

It has been shown earlier[9] that the thermal fragmentation path of a substance shows similarities to its mass spectral fragmentation. A mass spectroscopic study is thus a natural starting point for acquiring new information about the decomposition mechanism.

The mass spectroscopic study was conducted on a JEOL 300D double-focusing magnetic sector instrument equipped with a PC-based computer system utilizing Technivent Vector/2 software for data analysis. All mass spectra were obtained by using the solid sample inlet and the heating rates were varied. Electron impact spectra at both 70 eV and 20 eV were acquired.

It was observed that N,N'-dinitrourea did not show a molecular peak (m/z 150) neither at 70 eV nor at 20 eV. This behaviour is typical for thermally unstable compounds. At 20 eV the most significant m/z were 18, 28, 30, 32, 42, 43, 44, 46 and 62. By far the most intense mass peak in the spectra was m/z 44. The spectra at 70 eV were very similar to those at 20 eV, a slight increase in secondary fragments like m/z 26, 27 (CN/HCN) could be detected but the major peaks were still m/z 18, 28, 30, 32, 42, 43, 44, 46 and 62. An example of a recorded spectrum at 70 eV is displayed in Figure 5. Table 1 is a summary of the decomposition peaks
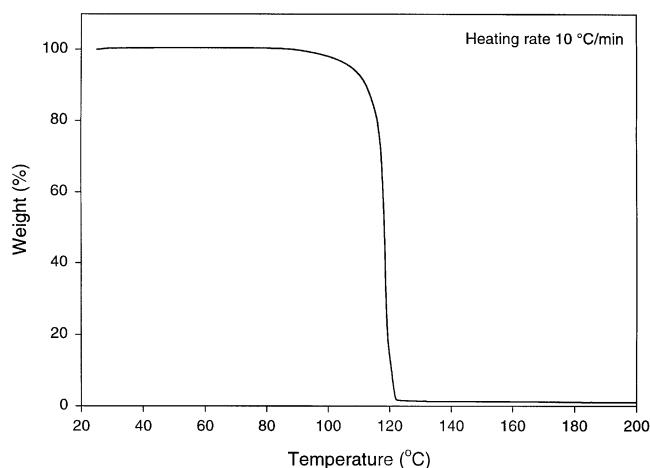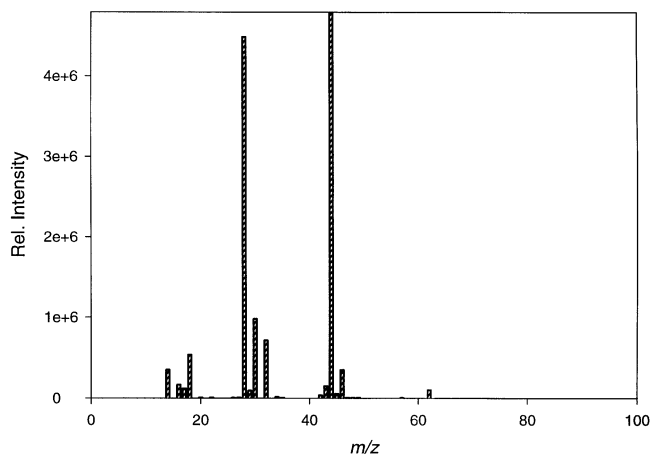

Figure 5. Mass spectra of N,N'-dinitrourea at 70 eV.

found at 70 eV with tentative assignments. To get a full understanding of the thermal decomposition path for N,N'-dinitrourea a more thorough investigation is needed. One of the mechanisms involved seemed to be the breakdown of N,N'-dinitrourea with the concomitant formation of NH_2NO_2 and CO_2. This would require the presence of H_2O, and consequently m/z 18 was observed in the spectra. Since NH_2NO_2 thermally decomposes to N_2O and H_2O only very small amounts of water need to be present to initiate this decomposition chain which thus would be autocatalytic.

3.5 Density

The volume of the sample was measured with a Micromeritics helium pycnometer. Prior to measuring, the apparatus was calibrated with a calibration standard of a known volume. The density was then calculated. The density of N,N'-dinitrourea was found to be $1.98\,g/cm^3$. By the same method the density of NaCl was found to be $2.16\,g/cm^3$ which is very close to the literature value ($2.17\,g/cm^3$)[10].

3.6 Sensitivity

The impact and friction sensitivities were determined according to the BAM standard which conforms to the

Figure 4. TG plot of N,N'-dinitrourea at a heating rate of $10\,^{\circ}C/min$.

Table 1. Observed m/z in the 70 eV N,N'-Dinitrourea Mass Spectra and Possible Assignments

m/z	Possible assignment
18	H_2O
26	CN
27	HCN
28	CO, N_2
29	HCO
30	NO
32	H_2NO
42	NCO, H_2N_2C
43	HNCO?
44	H_2NCO?, CO_2, N_2O
45	
46	NO_2
62	NH_2NO_2

Table 2. Sensitivity Data Evaluated at 50% Probability for N,N′-Dinitrourea and RDX

	N,N′-Dinitrourea	RDX
Impact energy (J)	5	7
Friction load (N)	76	120

UN guideline ST/SG/AC.10/11[11], with two exceptions. First: the impact sensitivity was measured with a 2 kg drop weight. Second: the impact and friction testing was done by using an up-and-down method on both sides of the 50% probability level. The results where then calculated at 50% probability. The number of samples tested were 25 in both tests.

According to the results shown in Table 2, N,N′-dinitrourea is very sensitive to friction.

4. Summary and Conclusions

N,N′-Dinitrourea has for the first time been synthesized in pure form and in acceptable yield. It was found to be stable in a desiccator for several weeks without decomposing. It has a high density (1.98 g/cm^3) and a very high positive oxygen balance (+21.33%) which should make it interesting as an energetic material. It is, however, sensitive to friction and impact, has a low thermal stability and is chemically labile. All this taken into consideration we think that N,N′-dinitrourea should preferably be used as a starting material towards more stable energetic materials than as an energetic material in its own right.

5. References

(1) Y. Zhang, M. Yu, and W. Li, "Relationships between Electron Structure of Substitutive Ureas and their Reactivity in Mannich Reaction", *Propellants, Explosives, Pyrotechnics*, *22,* 279−283 (1997).

(2) X. Meihong and Y. Qizheng, "Synthesis of 2,4,6-Trinitro-2,4,6-Triazacyclohexanone", *International Autumn Seminar on Propellants, Explosives and Pyrotechnics*, 1997, Shenzhen, China.

(3) Y. Zhang, H. Yin, P. Li, and W. Li, "Studies on Reaction Forms of Urea or Nitrourea in Keto-RDX Synthesis in Several Nitrating Agents with HPLC, (1) Analysis Method", *24th International Pyrotechnics* Seminar, 27−31 July, 1998, Monterey, California, USA, pp. 637−645 (1998).

(4) H. Boniuk, W. Pilecki, T. Stawinski, and M. Syczewski, "New Method of Synthesizing K-RDX Using Dinitrourea (DNU)", *31st Int. Annual Conference of ICT*, June 27−30, 2000, Karlsruhe, Germany, pp. 46.1−8 (2000).

(5) Z. Raszewski and M. Syczewski, "A Study on the Condensation of Nitramide with Formaldehyde and the Characteristics of the Products Formed", *Propellants, Explosives, Pyrotechnics*, *24,* 366−370 (1999).

(6) M. Syczewski, I. Cielowska-Glinska, and H. Boniuk, "Synthesis and Properties of Dinitrourea (DNU) and its Salts", *Propellants, Explosives, Pyrotechnics*, 23, 155−158 (1998).

(7) *Mettler Toledo Operating Instructions STAR^e Software, Version 5.0*, 1997, pp. 10-1−10-24.

(8) U. Bemm, H. Östmark, H. Bergman, and A. Langlet, "FOX-12, A New Energetic Material with Low Sensitivity for Propellants and Explosives Applications", *Insensitive Munitions & Energetic Materials Conference*, San Diego, CA, USA, November 16−19, 1998.

(9) J. Stals, *Transactions of the Faraday Society*, *6*, 67 (1971).

(10) *The Merck Index*, Merck & Co., Inc., Rahway, NJ, USA, 1989, pp. 1359.

(11) United Nations, "*Recommendations on the Transport of Dangerous Goods. Manual of Tests and Criteria*", ST/SG/AC.10/11/Rev.2, 2nd revised edition; United Nations, New York and Geneva, 1995, pp. 67−123.