



Synthesis and Characterization of 1,2-Dinitroguanidine (DNG) and its Derivatives^{*)}

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Abstract: 1,2-Dinitroguanidine (DNG), (1), is a novel explosive with reported high performance and moderate sensitivity [1, 2]. Synthesis of DNG and its salts has recently been reported [3]. X-ray studies on the crystal structure of DNG and its thermal stability can also be found in the literature [4, 5]. In this paper, complementary studies on the synthesis, reactivity and thermal characteristics of this compound and some of its derivatives are presented.

Keywords: 1,2-dinitroguanidine, DNG, synthesis, characterization

Introduction

Substituted *N,N'*-dinitroguanidines have been known since the 1950s [6]. Despite the extensive studies [7, 8], which resulted in the synthesis of several interesting substances in this series, the un-substituted 1,2-dinitroguanidine itself had never been reported until recently, when different groups of Russian researchers simultaneously presented both the synthetic approach [3] and basic properties of the compound [3, 4].

Judging by the molecular composition of DNG, which is an oxidizer (+5.4%), one can treat the substance and its derivatives as attractive ingredients in both explosive and propellant formulations. Surprisingly, very little information about their properties as energetic materials has so far been published [1, 2].

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For this reason, a preliminary estimate of the most important properties of these compounds was performed.

Results and Discussion

Synthesis

1,2-Dinitroguanidine (DNG) was easily synthesized by the reported method [3] with some minor modifications. In comparison to the published procedure, more nitric acid was used in the nitration mixture to ensure a controllable reaction course. Our observations that the nitration of mononitroguanidine (MNG) to DNG is a slow process taking place in a very reactive nitrating media (Figure 1), concur with those of Astrat'ev *et al.* [3].

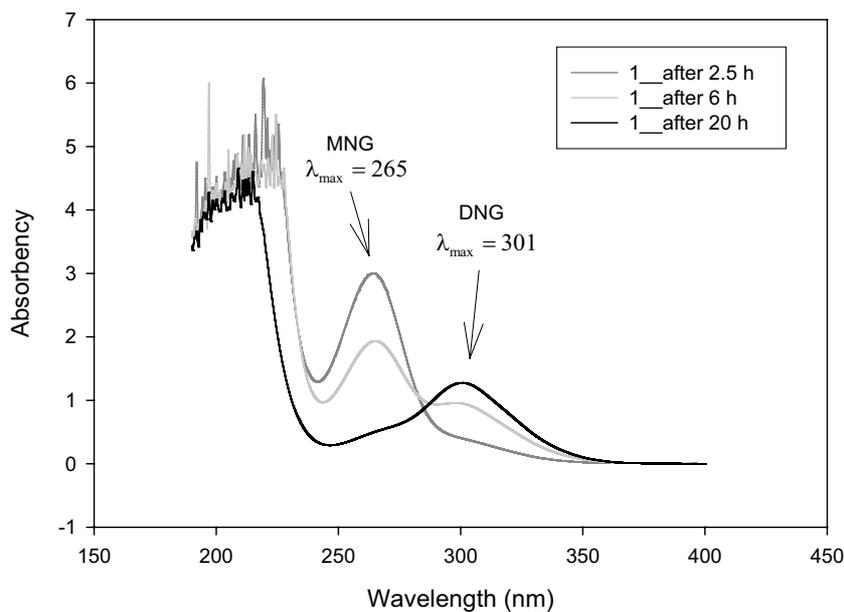


Figure 1. UV spectrum of the reaction mixtures for the nitration of MNG to DNG; nitrating mixture HNO_3 : oleum (65% SO_3) = 0.55: 0.45.

Furthermore, an instability of DNG in such mixtures was noticed. Its concentration is strongly dependent on the reaction time (Figure 2) and the composition of the nitrating media. The yield of DNG never exceeded 80%.

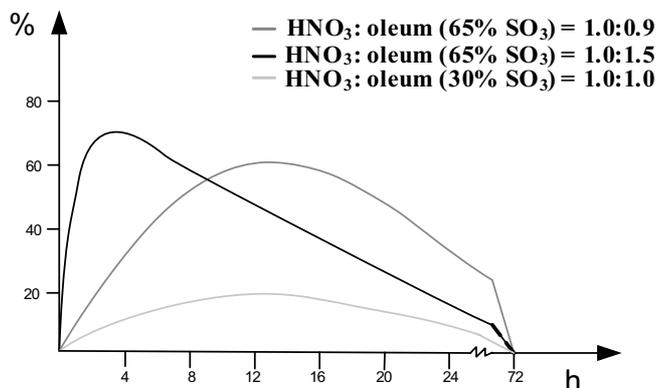
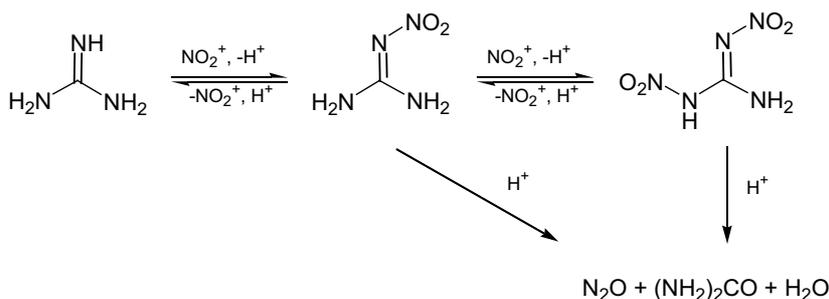


Figure 2. Yield of DNG from MNG in different nitrating mixtures and its dependence on the reaction time.

For this reason, the reaction course was in all cases monitored by UV spectroscopy, to detect the full conversion of MNG to DNG and the maximum concentration of the latter. Despite these efforts, the product contained small amounts (2-5%) of MNG, after extraction from the diluted nitrating mixture.

All these findings can be easily understood in view of the known fact that *N*-nitration is a reversible process and nitramines are prone to irreversible decomposition in strongly acidic media [9] (Scheme 1).



Scheme 1. Reaction sequence in the nitration of MNG to DNG.

Physicochemical properties

Samples of DNG produced by this method needed further purification, which was achieved by dissolution of the crude product in diisopropyl ether, followed by removal of the insoluble MNG by filtration. The purified product was identified by elemental analysis and mass-spectroscopy; its spectral characteristics (UV, NMR) were identical with those found in the literature [3].

DNG is indeed a very acidic product. Our measurements resulted in a pK_a value of 0.95, which agrees reasonably well with the value (1.11) reported by Astrat'ev *et al.* [3]. The density of crystalline DNG (1.895), estimated by pycnometry in the present work, is also rather close to that (1.884) obtained from X-ray measurements [4]. Salts of DNG, such as ammonium (ADNG), lithium (LiDNG), sodium (NaDNG), potassium (KDNG) and hydrazinium (HDNG) were easily obtained by careful neutralization of its solutions in an alcohol with an appropriate base. The properties of DNG and some of its salts, compared to the well-known compounds (RDX, PETN) are summarized in Table 1.

Table 1. Properties of DNG and its salts

	Density g/cm ³	ΔH_f , kcal/mol	Sensitivity Friction, N	Sensitivity Impact, cm/J
DNG	1.895*/1.884**	0.0 ***	90	22 /5.5
ADNG	1.86*	- 36.60 *	250	78/19.1
KDNG	Not measured	Not measured	130	28 /6.9
RDX	1.802	14.7	195	32/7.8
PETN	1.76	-127	60-80	15-20/3.8-5.0

* - present work ** - reference [4] *** - reference [2]

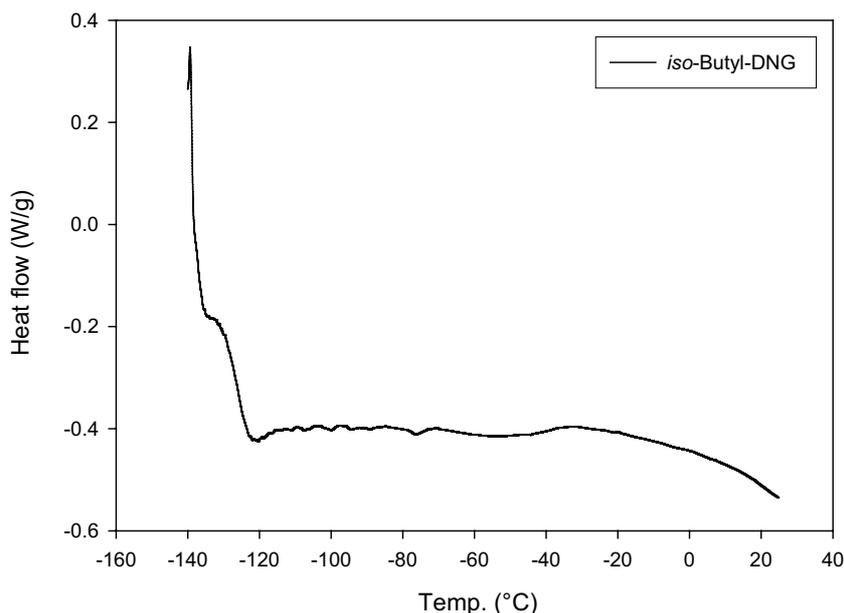
These data show that, contrary to the earlier claims [1], DNG is a rather sensitive compound. Both impact and friction sensitivity of this compound is very close to that of PETN; the same conclusion was drawn in the recent studies [5] on the thermal stability and related properties of DNG.

Unlike in alkylation and substitution reactions [3], the reactivity of DNG or strictly speaking its anion in reactions of Michael type is quite low (Table 2). Denitration of DNG into MNG is the most frequently occurring reaction. This is in line with the behavior of some anions of primary nitramines, which undergo such reactions only with difficulty [10, 11].

Table 2. Attempted Michael reactions of DNG

Michael donor	Michael acceptor	Temperature	Result
DNG, NaDNG	Methyl acrylate	RT, reflux	Denitration into MNG
DNG, NaDNG	Acrylic acid	RT, Reflux	Denitration into MNG
DNG	Methyl vinyl ketone	RT	Denitration into MNG
NaDNG	Methyl vinyl ketone	RT	Addition
DNG	Acrylonitrile	RT	Denitration into MNG
NaDNG	Acrylonitrile	RT	Product mixture

Our attempts to obtain *N*-alkyl-*N,N'*-dinitroguanidines using the same technique as for nitration of MNG to DNG were unsuccessful. Nitration of *N*-alkyl-*N'*-nitroguanidines, which in turn were obtained by the known methods [12] in mixtures of concentrated nitric acid and oleum (65% SO₃) resulted mainly in the decomposition of the starting materials. Since *N*-alkyl-*N,N'*-dinitroguanidines are interesting as low melting energetic materials [7, 8], they were synthesized in this work by the old method [8], of which the previously unknown *iso*-butyl-DNG showed interesting properties as a potential plasticizer, (Figure 3).

**Figure 3.** DSC thermogram showing the low temperature properties of *iso*-butyl-DNG.

Thermal stability

While this work was in progress, the results on the thermal behavior of DNG at elevated temperatures (115-155 °C) in solid state and in solutions were published by Russian researchers [5]. It was found [5] that DNG is less stable in comparison with other energetic nitramines, such as MNG and RDX. The diminished thermal stability of DNG was attributed to prototropic equilibria in this highly acidic compound [5]. No predictions about the long-term stability of DNG or any of its derivatives were made.

Our DSC measurements on DNG and its salts have shown that DNG itself is indeed less stable than either MNG or RDX, melting with vigorous decomposition at 174-175 °C (Figure 4).

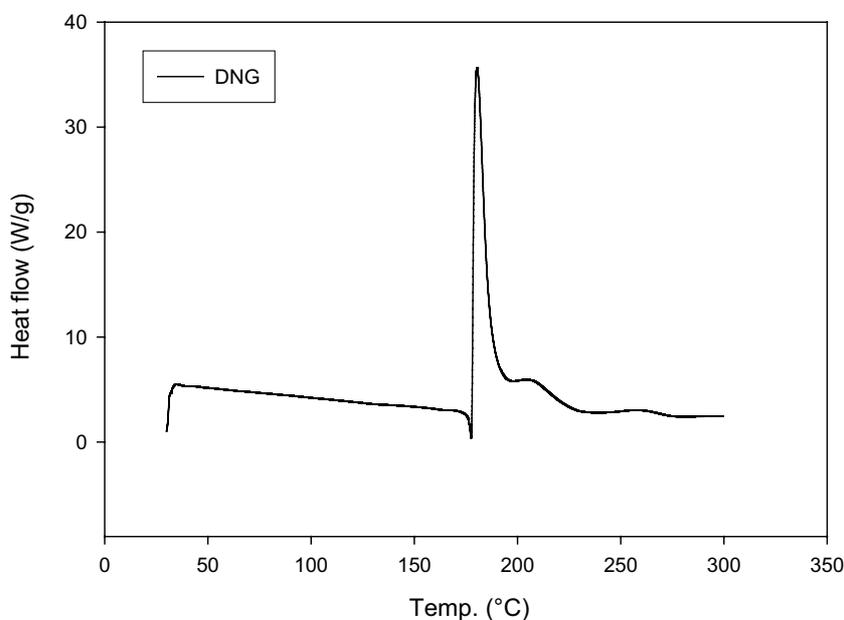


Figure 4. DSC thermogram of DNG.

Salts of DNG are characterized by varying thermal stability (Figure 5-7). Of these, the ammonium and potassium salts seem to be most interesting (Figure 5 and 6, respectively).

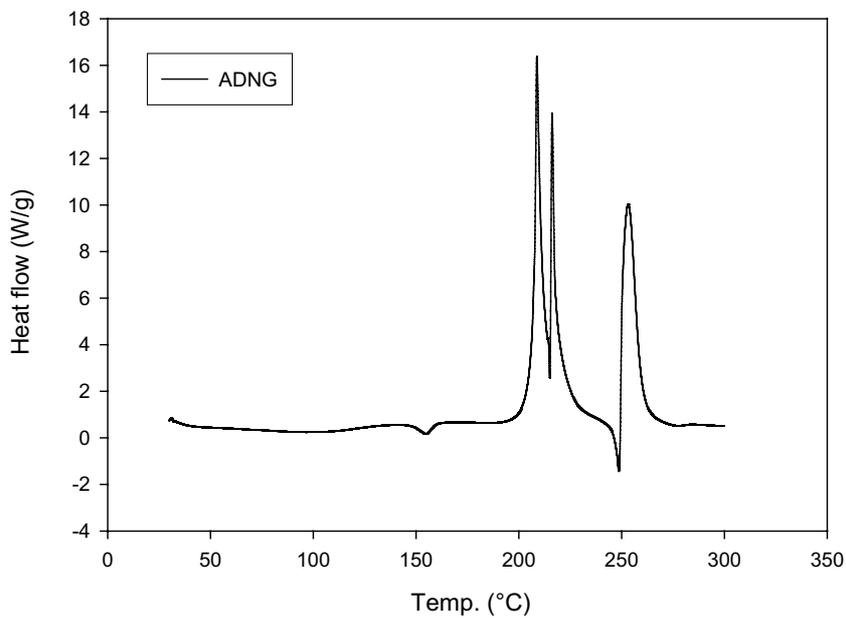


Figure 5. DSC thermogram of ADNG.

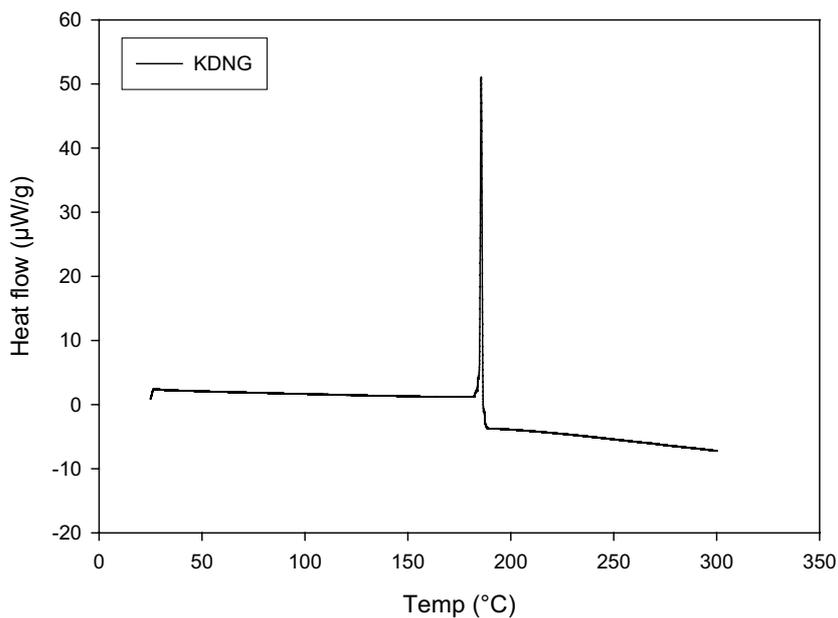


Figure 6. DSC thermogram of KDNG.

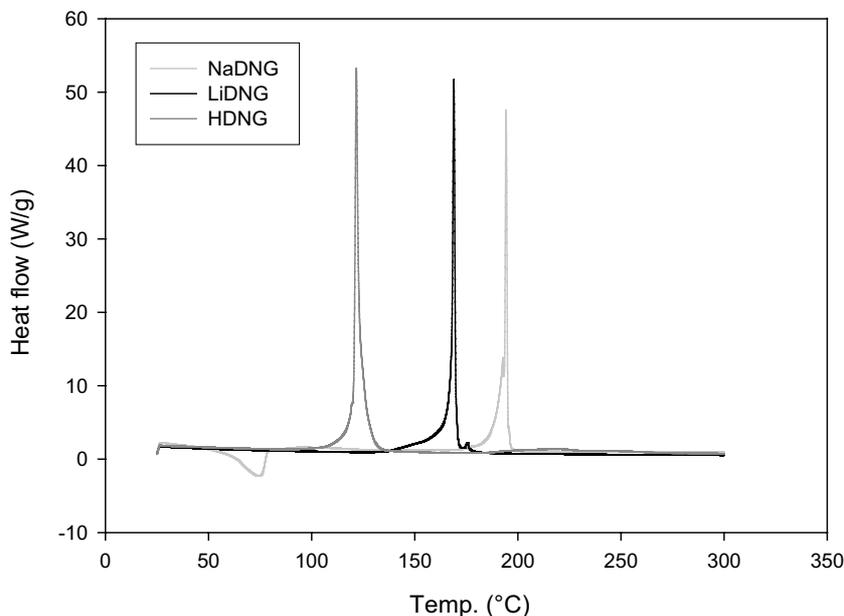


Figure 7. DSC thermogram of NaDNG, LiDNG and HDNG.

It can be seen (Figure 4-6) that the temperature range, 170-200 °C, in which vigorous decomposition of DNG (ADNG /KDNG) takes place does not differ dramatically from that of RDX (200-220 °C) [13]. This prompted us to investigate further the long-term stability of these products, using the standard method (STANAG 4582). Figure 8 demonstrates that DNG itself has an acceptable thermal stability.

By contrast, salts of DNG (Figure 9) and *iso*-butyl-DNG (Figure 10) did not pass the test. In all cases, violent decomposition of the samples was observed after several days.

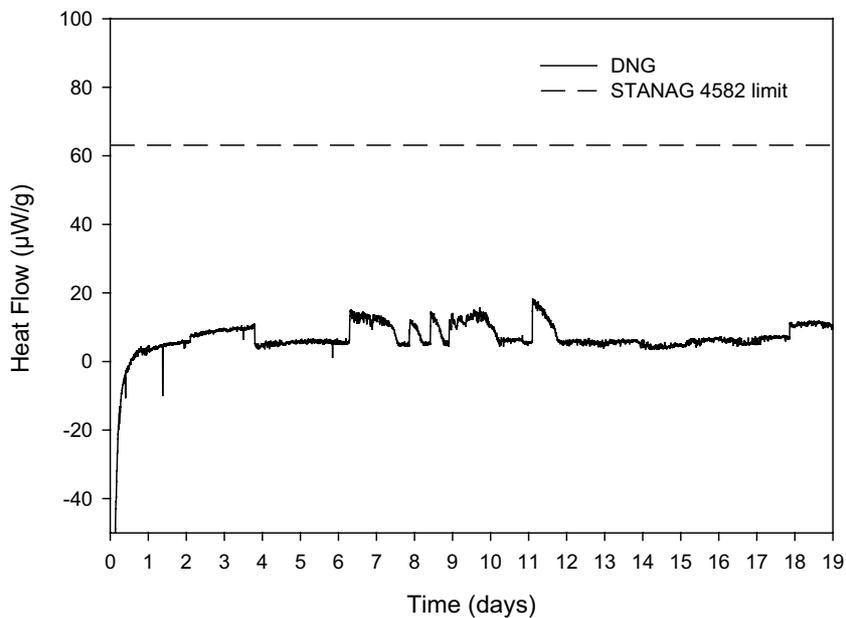


Figure 8. Heat flow calorimetric (HFC) measurements of DNG at 75 °C for 19 days. The signal is jagged due to large amplification.

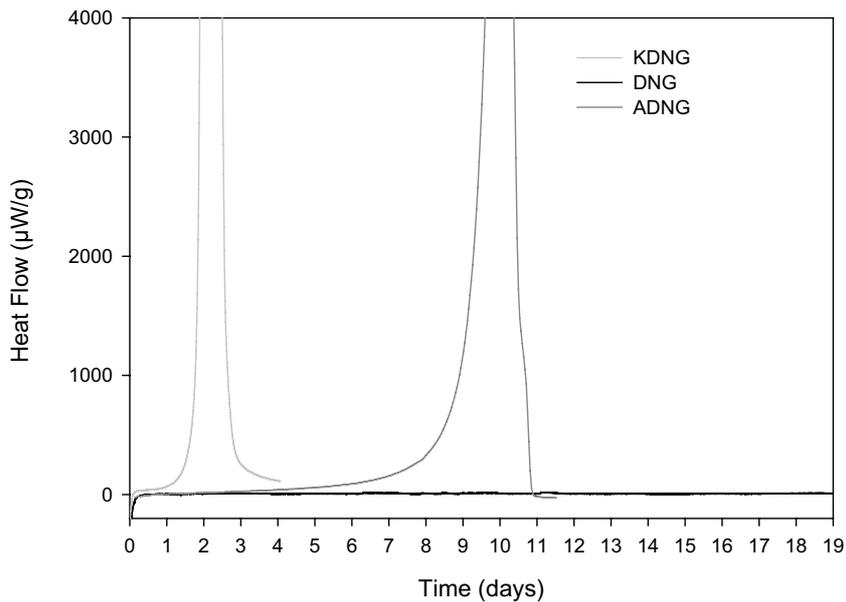


Figure 9. Heat flow calorimetric (HFC) measurements on DNG and salts at 75 °C for 19 days.

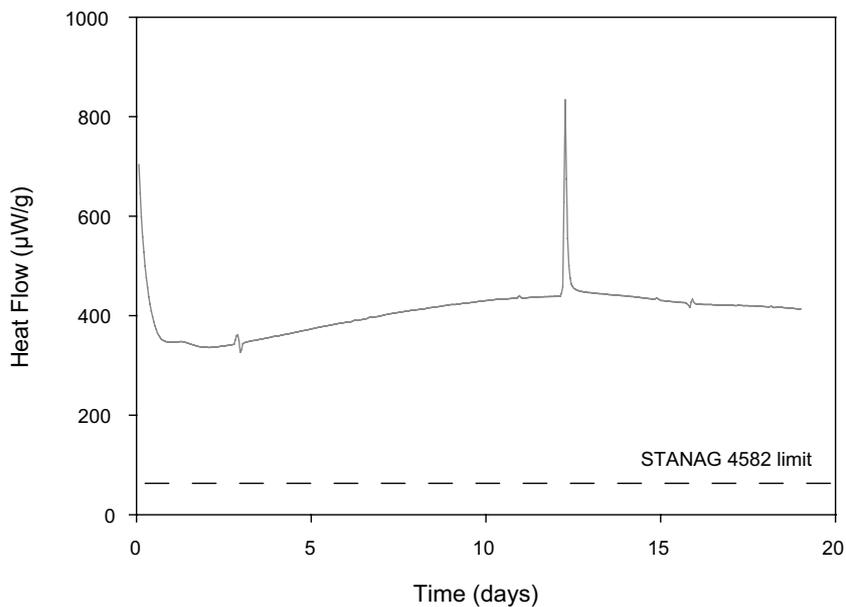


Figure 10. Heat flow calorimetric (HFC) measurements on *iso*-butyl-DNG at 75 °C for 19 days.

Moreover, different batches of ADNG revealed an appreciable variation in time for the onset of the decomposition (Figure 11). This might be attributed to variations in purity as well as particle size of the samples.

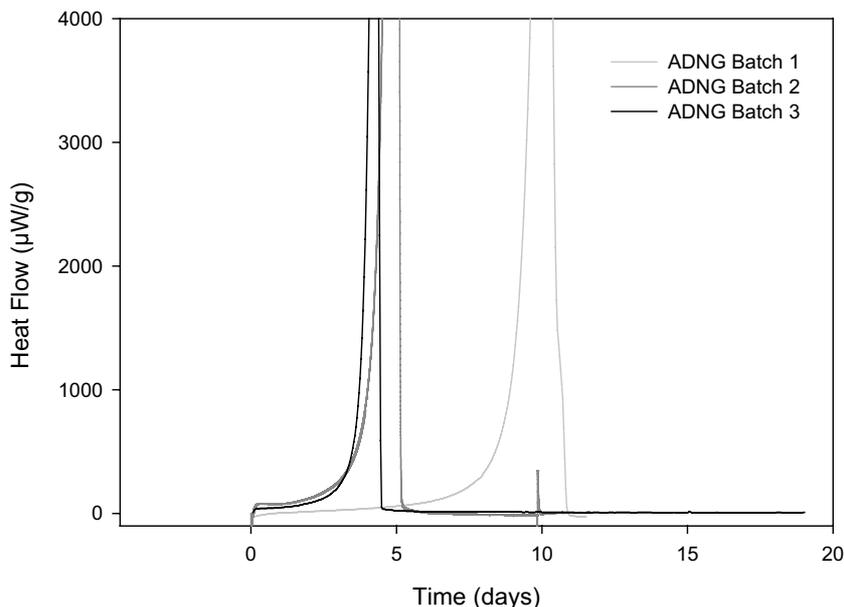


Figure 11. Heat flow calorimetric (HFC) measurements on different batches of ADNG at 75 °C.

These disappointing properties, such as the enormously high acidity of DNG itself and unacceptable thermal stability of its derivatives caused us to suspend further work on this interesting group of compounds.

Experimental

1,2-Dinitroguanidine

12 mL of nitric acid (99%) were placed into a 50 mL round bottom flask equipped with a cooler, magnetic stirrer, thermometer and a dropping funnel. The dropping funnel was equipped with a Teflon pipe, which was located below the surface of the acid. The nitric acid was cooled down to 0 °C by a cooling bath (methylene chloride-dry ice). 3.0 g of dry MNG were added to the nitric acid slowly under vigorous stirring. After all of the MNG has been dissolved 7.5 mL of 65% oleum were added through the dropping funnel also under vigorous stirring.

The reaction mixture was kept below 10 °C with the help of vigorous mixing and external cooling and its course was followed by UV-analysis of quenched

samples (MNG, λ_{\max} 265 nm, $\log \epsilon$ 4.18; DNG, λ_{\max} 301 nm, $\log \epsilon$ 4.32). When the maximum concentration of DNG was achieved (6-8 h) the reaction mixture was poured onto 80-90 g of ice-water mixture keeping the temperature below 10 °C. The crude product was separated by extraction with ethyl acetate (3×50 mL). The combined extract was washed with water (2×30 mL) and thereafter dried with sodium sulfate. The sodium sulphate was filtered off and the filtrate was concentrated under reduced pressure (water pump) until the solid started to crystallize. The solid was filtered off, washed with hexane and dried at room temperature to give 1.28 g (30%) of DNG. The main impurity (MNG) was removed by dissolving the crude product in 60 mL of diisopropyl ether, filtering off the insoluble MNG and removing the solvent under reduced pressure (water pump). Melting point 174-175 °C (dec.), lit.³ T_m 168.5-169 °C.

Salts of DNG

The typical procedure used in this work is as follows: 0.75 g (5 mmol) of DNG were dissolved in 10 mL of ethanol and to this stirred solution an equivalent amount of the respective base, dissolved in 50 mL of ethanol was added at room temperature. The precipitated salt was removed by filtration, washed with minimal amount of pure ethanol and dried in an oven at 40 °C.

All salts decompose on heating without melting: ADNG, dec.205 °C (lit.³ T_m 205 °C); NaDNG, obtained as a solvate (1:1) with ethanol, dec.185 °C (lit.³m.p. 157); KDNG, dec.185 °C (lit.³ T_m 183); LiDNG, dec.165 °C); HDNG, dec.120 °C (lit.³ T_m 135).

1-(*i*-Butyl)-1-nitroguanidine

2-Methyl-1-nitro-2-thiopseudourea (18.55 g, 0.137mol) was added in portions to *i*-butylamine (54.6 mL, 99%, 0.549 mol) at room temperature. After the beginning of addition, the temperature increased up to the boiling point for *i*-butylamine (36 °C) and the addition was accompanied by gas evolution and a strong smell of methyl mercaptan. At the completion of the addition (15 min), all 2-methyl-1-nitro-2-thiopseudourea has dissolved. The resulting solution was stirred for another 1.5 h at 32-36 °C before the solution was concentrated *in vacuo*. The residue was crystallised from ethanol (25 mL) (the crystallization took 24 h at 4 °C). The crystals were filtered off, washed with cold ethanol (5 mL) and dried to get 1-(*i*-butyl)-1-nitroguanidine (14.16 g, 64.6%) as transparent prisms (T_m =120-122 °C, lit. 121 °C [14]). ¹H NMR (DMSO-*d*₆) 8.61 (1H, bs), 7.97 (1H, bs), 7.37 (1H, bs), 3.10 (2H, d, J =7.0, CH₂ (CH₂CH(CH₃)₂)), 1.79 (1H, m, CH (CH₂CH(CH₃)₂)), 0.87 (6H, d, J =6.5, CH₃ (CH₂CH(CH₃)₂)). ¹³C NMR (DMSO-*d*₆) 159.50 (s), 48.02 (t), 19.87 (d), 19.79 (q).

1-(*i*-Butyl)-1,3-dinitroguanidine

To acetic anhydride (21 mL, 0.22 mol), pre-cooled by ice-salt bath to 0 °C, 100% nitric acid (4.57 mL, 0.11 mol) was added drop wise at the same temperature. Then the mixture was cooled to -5 °C. 1-(*i*-Butyl)-1-nitroguanidine (7.07 g, 0.044 mol) was added over 1-2 minutes. When the temperature reached 0 °C, the bath was removed and the temperature was allowed to reach 28 °C over 35 min. The temperature decreased to 21 °C and stirring was continued. After one hour, the acetic anhydride was evaporated *in vacuo*. The residue was poured into water (400 mL), the pH was adjusted to 5-6 with KOH solution and the resulting aqueous solution was extracted with ethyl acetate (4×100 mL). The organic solution was dried with Na₂SO₄, evaporated and purified by column chromatography (2.2:1 *n*-heptane/acetone) to yield pure 1-(*i*-butyl)-1,3-dinitroguanidine (3.07 g) as a light yellow oil. ¹H NMR (DMSO-*d*₆) 10.10 (1H, bs), 9.96 (1H, bs), 3.75 (2H, d, *J*=7.2, CH₂ (CH₂CH(CH₃)₂)), 2.00 (1H, m, CH (CH₂CH(CH₃)₂)), 0.94 (6H, d, *J*=6.7 CH₃ (CH₂CH(CH₃)₂)). ¹³C NMR (DMSO-*d*₆) 156.41 (s), 58.56 (t), 26.89 (d), 19.67 (q). –MS 203.8 (M-1), 158.9 (M-1-NO₂).

Conclusions

1,2-Dinitroguanidine is an interesting energetic material; unfortunately, any formulation work with this highly acidic and sensitive compound seems feasible.

Salts of DNG are readily obtained on neutralisation of DNG with an appropriate base in alcoholic solutions. Neither salts of DNG (ADNG, KDNG), nor *iso*-butyl-DNG – all synthesized and characterized in the present work – have sufficient thermal stability to find application.

Further work on the synthesis of more stable derivatives of DNG and search for stabilizers of DNG salts might be interesting.

Acknowledgements

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