

Synthesis and Properties of Dinitrourea (DNU) and its Salts

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Synthese und Eigenschaften von Dinitroharnstoff (DNU) und seinen Salzen

Die Synthese und Eigenschaften von Dinitroharnstoff und seinen Salzen (NH₄, Hexamethylenamin, K), über die bisher noch nicht in der Literatur berichtet wurde, werden beschrieben. DNU kann hergestellt werden durch Nitrierung von Harnstoff mit hoher Ausbeute, >90%. Eine spontane Zersetzung des DNU und seiner Salze unterhalb ihres Schmelzpunkts wurde beobachtet während der thermischen Analyse (DTA-TG). Die geringe Stabilität des DNU schließt die Möglichkeit seiner Verwendung als energiereiches Material aus. Vorläufige Untersuchungen haben gezeigt, daß DNU verwendet werden kann als Vorstufe für die Synthese stabiler Nitroamine

Synthèse et propriétés de la dinitro-urée (DNU) et de ses sels

On décrit la synthèse et les propriétés de la dinitro-urée et de ses sels (NH₄, hexaméthylamine, K), sur lesquelles la bibliographie était muette jusqu'à présent. DNU peut être fabriqué par nitration d'urée avec un haut rendement, >90%. Une décomposition spontanée de DNU et de ses sels en-dessous de son point de fusion a été observée pendant l'analyse thermique (DTA-TG). La faible stabilité de DNU en interdit l'emploi comme matériau énergétique. Des études provisoires ont montré que DNU pouvait être utilisé comme phase préalable à la synthèse de nitroamines stables.

Summary

Synthesis and properties of dinitrourea and its salts (NH₄, hexamethyleneamine, K) which have not been yet reported in literature, are described. DNU can be synthesized by nitration of urea with a high yield (>90%). Spontaneous decomposition of DNU and its salts below their melting points was noted during thermal analysis (DTA-TG). Low stability of DNU excludes the possibility of using it as an energetic material. Preliminary studies have shown that DNU can be used as a precursor in the synthesis of stable nitroamines.

1. Introduction

Uses of cyclic dinitrourea compounds as energetic materials have been reported recently⁽¹⁾. Many of them show good or satisfactory stability and interesting useful properties, e.g. 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6)⁽³⁾. The presence of dinitrourea moiety in cyclic structure of nitroamine ensures high density of material and as a consequence good energetic performance.

The materials mentioned above are useful intermediates in the synthesis of stable energetic materials of the type bis-nitroamino compounds. The susceptibility of dinitrourea moiety to hydrolysis is utilized in these processes^(1,2).

The goal of the present work was to synthesize dinitrourea (DNU) or its simple salts in pure form and use them as the starting materials in the synthesis of stable nitroamino compounds. We expected that so far not reported DNU would be a much more powerful explosive than mononitrourea (MNU) and that the susceptibility to hydrolysis of mononitro derivative will be sustained in dinitrourea. The description of synthesis and purification of DNU and its salts, and also the results of elementary, thermogravimetric and thermal analysis is discussed in this paper.

2. Synthesis

DNU was obtained via a direct nitration of urea with a mixture of equal parts of 98% HNO₃ and 20% oleum. The stirred mixture of acids was cooled at -15°C to -10°C and urea was dosed at such rate to keep the reaction temperature below 0°C. The stirring was continued for 30 min at temperature 0°C to +5°C. The resulted precipitate of the crude DNU was filtered, cold and used as the starting material in further transformations. The yield of the crude product was ca. 95%. At room temperature, particularly in the presence of water and traces of acids, DNU undergoes decomposition which may lead to spontaneous ignition. The pure DNU has an ignition temperature 147–9°C. The identification of the DNU structure was performed after its transformation into diammonium salt.

Diammonium salt of dinitrourea was obtained in direct synthesis from crude DNU and water solution of ammonia (~13%) at 20°C. The product precipitates as a colorless solid. The ammonium salts originated from acidic impurities of DNU were left in the solution. The product was separated by filtration, washed few times with ice-cold water and dried in vacuum desiccator over silica gel. The results of elementary analysis of the salt are given below:

	H%	C%	N%
Experimental:	4.16 4.35	6.64 6.81	44.98 46.69
Theoretical:	4.35	6.52	45.65

The yield was ca. 55% based on the amount of DNU. Partial hydrolysis of substrate occurred during formation of DNU salts. Beside CO₂, nitramine was the main hydrolysis by-product. It decomposed into N₂O and H₂O.

Hexamethyleneamine salt of dinitrourea was obtained in action of crude DNU on water solution of $(\text{CH}_2)_6\text{N}_4$ (15 wt%) at 20°C. The results of elementary analysis are given below:

	H%	C%	N%
Experimental:	4.74	28.22	39.13
	4.73	28.53	39.00
Theoretical:	4.85	28.97	38.53

Dipotassium dinitrourea salt was obtained by neutralization of the crude DNU with 5% KOH solution at 20°C. The salt was purified by crystallization from organic solvents. The obtained product possessed insufficient purity due to contamination with solvent. It seems that potassium salt of DNU forms complexes with organic solvents but this needs further investigation.

DTA-TG analysis was carried out for the product which was crystallized from diethyl ether and dried in vacuum desiccator over silica gel.

Thermogravimetric (TG) and differential thermal analysis (DTA) were conducted using a MOM Budapest Derivatograph-PC thermoanalytic network system.

3. Properties of DNU and its Salts

The stability of DNU strongly depends on its purity. The crude, separated DNU still containing nitrating acids, kept

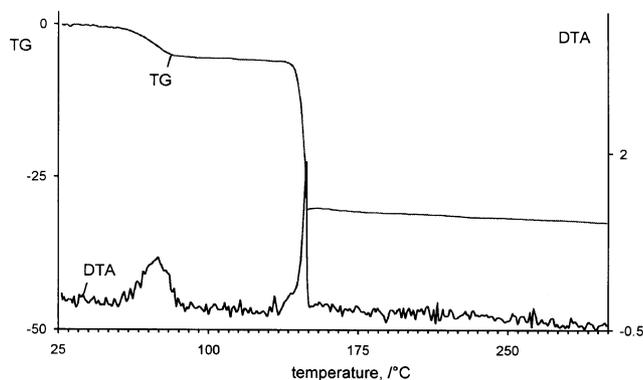


Figure 1. Thermogram of DNU.

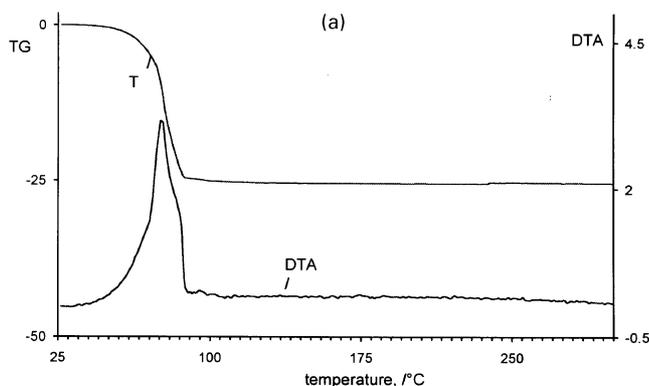
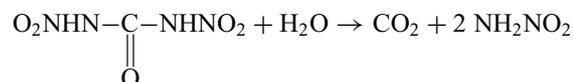


Figure 2 (a). Thermogram of crude NH_2NO_2 .

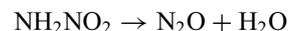
at 25°C for 20 minutes undergoes self-ignition. The attempts of DNU purification by recrystallization from diethyl ether and careful drying in a vacuum were unsuccessful. The results of elementary and thermal analysis show ca. 80% purity of dinitrourea. The loss of weight (~16%) with exothermic effect at 74°C observed during thermal analysis of DNU shows, in our opinion, the contamination of DNU with nitroamide (ND) NH_2NO_2 .

For comparison differential thermal analysis of crude nitroamide was performed. The peak of exothermal decomposition of NH_2NO_2 appears at approximate temperature as the first exothermal peak on DTA curve of dinitrourea (Fig. 2a). The presence of an endothermal peak of melting was observed at temperature just below the exothermal decomposition peak only for samples of NH_2NO_2 which had been purified by recrystallization from ethyl acetate (Fig. 2b).

The absence of mentioned peak was noted on the thermograms of NH_2NO_2 after its first crystallization and of DNU. After decomposition of NH_2NO_2 the remaining substance decomposes spontaneously at 138–148°C (Fig. 1). Nitroamide originates in DNU samples probably during handling, according to the equation:



The thermal decomposition of NH_2NO_2 at ~74°C undergoes according to the following equation:



The resulted water evaporates quickly with N_2O gas to the stream of carrier gas and cannot cause the further hydrolysis of DNU. This hypothesis was confirmed by independent thermal analysis of DNU, the sample was heated to 80°C in the stream of dry argon in DTA-TG apparatus (decomposition of NH_2NO_2 and removing of its decomposition products) and after cooling to room temperature repeated heating of the sample to ignition temperature (Fig. 3)

The volatile component (NH_2NO_2) was removed at 74°C and the remaining substance was stable until 130°C (loss of weight ca. 2%) in dry, oxygen free atmosphere. Above

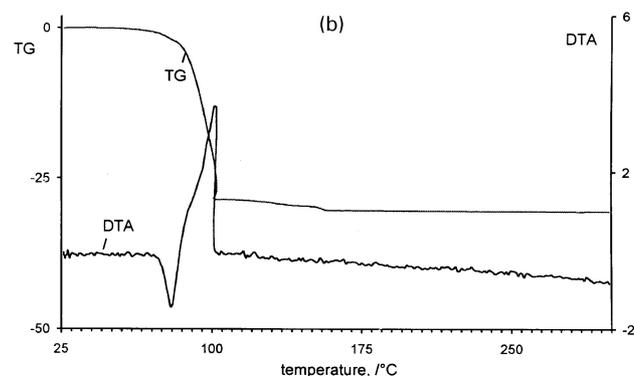


Figure 2 (b). Thermogram of crystallized NH_2NO_2 .

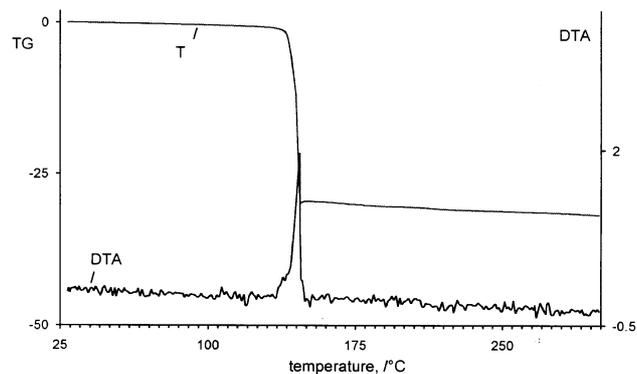


Figure 3. Thermogram of DNU after heating to 80°C.

mentioned temperature decomposition accelerated and finally spontaneous decomposition occurred at ca. 146°C. This temperature (146°C) correlates with the temperature of DNU one-stage heating.

The decomposition of diammonium salt of dinitrourea was the ultimate proof for the assumed scheme of decomposition of DNU. The prepared ammonium derivative of DNU could be purified because of its thermal stability at room temperature. The thermogram of diammonium dinitrourea salt is presented on Fig. 4.

The thermal decomposition of diammonium salt of DNU occurs in a few stages: the first mole of NH_3 group was removed up to 110°C (weight loss 10%, 9.24% calcd.). The second much faster stage of decomposition was connected with releasing the second mole of ammonia until 130°C – total loss of sample weight ~18%. At the end of the second stage the decomposition of DNU itself begins and ends at 140°C with a spontaneous decomposition of the sample. The final temperature (140°C) correlates with those noted on Figs. 1 and 3.

The following reaction scheme describes the thermal decomposition of diammonium DNU salt:

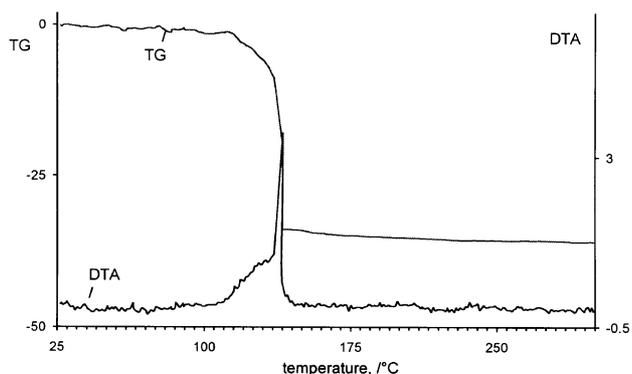
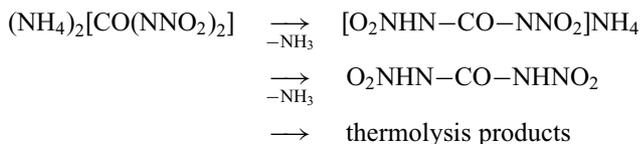
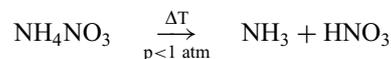
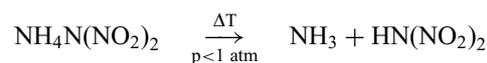


Figure 4. Thermogram of diammonium salt of DNU.

which is similar to the thermal decomposition of ammonium nitrate under certain conditions⁽⁴⁾:



or the ammonium salt of dinitroamide⁽⁵⁾:



The beginning stages of the decomposition of the diammonium salt of DNU, (loss of NH_3) under normal pressure, combine with the decomposition of DNU molecule.

In the case of nonvolatile, polyfunctional base such as hexamethylenamine the multistage decomposition of its salt was not observed. At 120°C the spontaneous ignition of salt was noted (Fig. 5).

A much more thermostable is the potassium salt of DNU. A typical thermogram of the potassium derivative is illustrated on Fig. 6.

The beginning of the decomposition was also observed at 135°C, but ignition temperature was noted at ca. 190°C.

An IR spectrum of the diammonium salt of DNU (Fig. 7) was compared with the spectra of K-RDX and ammonium salt of dinitroamide (Table 1).

The big shifts of the bands assigned to NO_2 and carbonyl groups aside lower frequencies comparing with the appropriate bands existing in IR spectrum of K-RDX and also

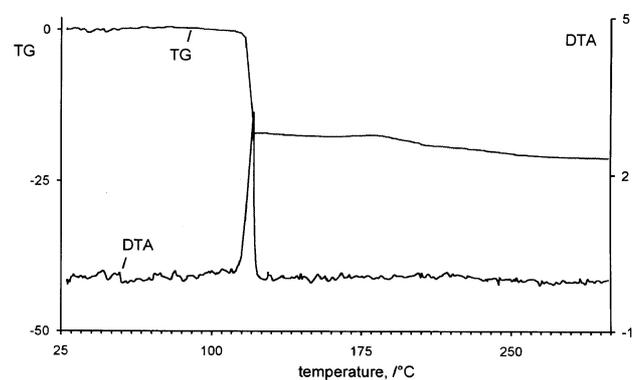


Figure 5. Thermogram of hexamethylenamine salt of DNU.

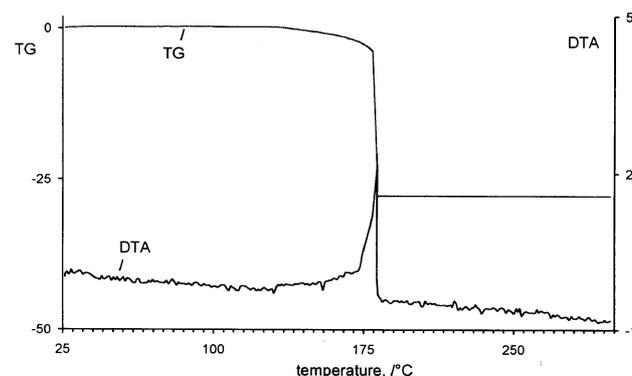


Figure 6. Thermogram of potassium salt of DNU.

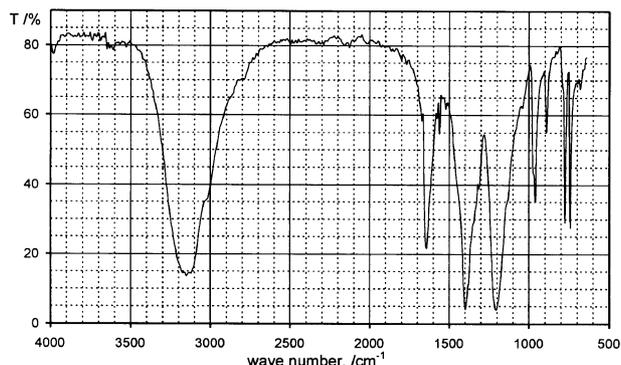
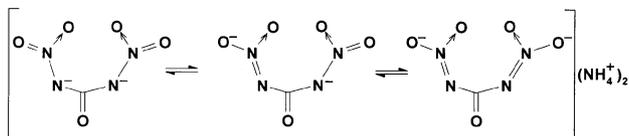


Figure 7. IR spectrum of diammonium salt of DNU.

Table 1. Comparison of the three IR Spectra

Group	(NH ₄ ⁺) ₂ CO(NNO ₂ ⁻) ₂	K-RDX [3]	NH ₄ ⁺ [N(NO ₂) ₂] ⁻ [6]
NH ₄ ⁺	3152	—	3100
NO ₂ asym.	1400	1608	1503
NO ₂ sym.	1208	1280	1200
C=O	1640	1768	—

broadening of NO₂ bands could be interpreted as the existence of a charge delocalization in the ionic structure of diammonium salt of DNU.



Scheme 1. Diammonium Salt of DNU.

4. Conclusion

Dinitrourea is a labile substance and it cannot be used as an energetic material. Simplicity and high yield observed in the synthesis of DNU ensures a convenient route for the preparation of other stable energetic materials. As it was shown by us, simple salts of DNU are so stable (K salt of DNU), that they can be considered to be components of energetic mixtures.

Nitroamide (NH₂NO₂) – product of hydrolysis of DNU can be a cheap half product in the synthesis of stable nitroamines, e.g. nitroamine with a linear structure. This way is temporarily realized and the results will be published soon.

Synthesis of nitrourethane by alcoholysis of DNU is also considered.

5. References

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