

A Study on the Condensation of Nitramide (NH_2NO_2) with Formaldehyde and the Characteristics of the Products Formed

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Eine Studie über die Kondensation von Nitramid (NH_2NO_2) mit Formaldehyd und Charakterisierung der entstehenden Produkte

Versuche zur Synthese von aliphatischen Polymethylenitroaminen durch die Reaktion zwischen NH_2NO_2 und Formaldehyd wurden unternommen. Der Syntheseprozess wurde ausgeführt in einem Zweikomponentensystem Wasser/Ethylacetat. Die Löslichkeit des erhaltenen Produkts und seine Zersetzungsempfindlichkeit in verschiedenen Lösungsmitteln wurde untersucht. Die Wärmefestigkeit und die Temperatur der Selbstzersetzung wurde bestimmt mittels DTA-TG. Trotz ihrer Eigenschaft als energetisches Material zeigt die Verbindung geringe Empfindlichkeit gegen mechanische Einflüsse (Reibung).

Étude de la condensation du nitramide (NH_2NO_2) avec le formaldéhyde et caractérisation des produits formés

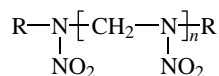
On a entrepris des essais de synthèse de polyméthylènenitroamines aliphatiques par réaction entre NH_2NO_2 et du formaldéhyde. Le processus de synthèse s'est déroulé dans un système à deux composants eau/ester acétique. On a étudié la solubilité du produit obtenu et sa sensibilité de décomposition dans différents solvants. La résistance à la chaleur et la température de décomposition spontanée ont été déterminées par DTA-TG. Malgré ses propriétés de matériau énergétique, le composé n'est que très peu sensible aux influences mécaniques (frottement).

Summary

Attempts have been made to synthesize aliphatic polymethylene nitroamines through reactions between NH_2NO_2 and CH_2O . The process of synthesis has been achieved in a two-component system: water/ethyl acetate. The solubility of the obtained product, as well as, its susceptibility to chemical decomposition in different solvents have been studied. The product's heat resistance and its temperature of self-decomposition have been determined through the DTA-TG method. Despite being an energetic material, it shows little sensitiveness to mechanical stimuli (friction).

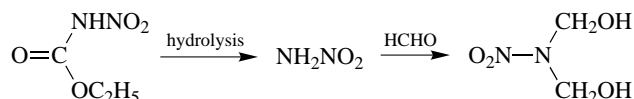
1. Introduction

The goal of this scientific work was to obtain aliphatic nitramines and study their characteristics:

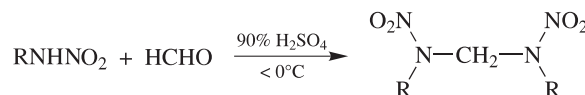


It is well known⁽¹⁾, that such compounds are formed as by-products of RDX and HMX synthesis. Under such conditions, more aliphatic products are formed when there exists an excess of amine groups in the system.

Chapman and his co-authors⁽²⁾, by conducting a series of reactions between organic nitramines and formaldehyde, have ascertained that under certain conditions aliphatic nitramines will form. No attempts have been made with NH_2NO_2 due to the fact that it differs in its reactivity and other characteristics from organic amines. In Ref. 4 dimethylol nitramine was obtained, through a reaction between nitrourethane and formaldehyde, with the assumption that the nitrourethane would hydrolyse and NH_2NO_2 would form:



In an acid and dehydrating medium apart, from attachment, we can observe the condensation of primary nitramines with formaldehyde⁽³⁾:



In accordance with this mechanism, further polycondensation of NH_2NO_2 into a product with a longer chain (polymethylenenitramine) seemed possible.

In a water solution, NH_2NO_2 shows acid properties⁽⁹⁾. It decomposes in reactions with bases⁽⁹⁾. Due to this fact the process could only be run under a specific low pH-value (maximum value 1.6).

In the first stage, the process may have a typically ionic character with the participation of carbonium ion $^+\text{CH}_2\text{OH}$ and $^-\text{NHNO}_2$. The methylolnitramine obtained during this step can further participate in the polycondensation process. With these assumptions in mind, the condensation process was run under varied conditions and using different substrates with nitramino units.

2. Experimental Research

2.1 Polycondensation of CH_2O with NH_2NO_2

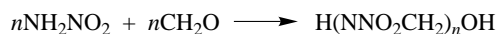
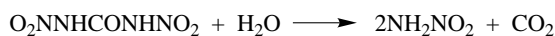
The attempts of running polycondensation in a water solution, through mixing a water solution of nitramide with formaldehyde, did not give positive results. A stable product of condensation did not form.

In further experiments formaldehyde (1.5 g) in the form of a 36% water solution (formalin) and nitramide (3.4 g) in crystalline form were used. The nitramide was solubilized in the formalin solution and then the pH-value of the solution was lowered to approximately 1.6 through adding a KOH solution, 30 cm³ of ethyl acetate were added to this solution and mixed. After 120 min, the product began to form on the phase boundary.

The first portion of the product (2.1 g, with a breakdown temperature of about 160°C) separated from the two-component solution after 24 h. The second portion of the product (1.4 g, with a breakdown temperature of approximately 155°C) was obtained after the next 24 h. The total yield of the product (assuming condensation to an aliphatic product) equals approximately 96% of the theoretical yield.

2.2 Synthesis of the Polycondensate Using Dinitrourea (DNU)

Keeping in mind the fact, that nitramide (NH₂NO₂) forms during the hydrolysis of dinitrourea (DNU)⁽⁸⁾, it was decided that this substance would be used in the synthesis of the polycondensate. DNU was obtained in accordance with Ref. 8 from 30 g of urea. After separating the post-reaction acids, DNU was added to 50 cm³ of the solution of formaldehyde with a concentration of 19%. The dissolution of the DNU was conducted in such a way that the temperature of the solution did not exceed 30°C. The pH-value of the solution was raised (pH ≈ 1.7) by dropping a KOH solution, and approximately 120 cm³ of ethyl acetate were added with stirring. During this process partial separation of the precipitate of K₂SO₄ from the solution was observed. K₂SO₄ had formed from the sulphuric acid which remained in the crude sludge of DNU. After filtering off the K₂SO₄, the solution was left to settle for 48 h. After this time, a deposit of the polycondensate separated from the solution. The deposit was filtered off and it was thoroughly rinsed with water until the sulphate ions in the filtrate were removed. 7 g of the product were obtained with a breakdown temperature of 158°C–162°C. The yield of the reaction is based on the following course of the process:



and equals approximately 50%.

2.3 Synthesis of the Polycondensate from Methylene Nitramine

1.46 g of methylene dinitramine (obtained according to Ref. 9) in 10 cm³ of water was mixed with 0.06 g of formaldehyde (in the form of a 36% solution). 20 cm³ of ethyl acetate and five drops of a 10% solution of KOH were added. After approximately 2 h the product started to separate from the solution. After 24 h the product's yield based on an

aliphatic polymer equals approximately 90%. The breakdown temperature of the product was approximately 158°C.

2.4 Identification and Study of the Product of Polycondensation

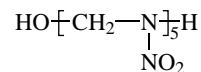
2.4.1 Identification

An initial study showed that all the products obtained through the three different methods possess similar characteristics. They do not easily dissolve in the main solvents. They partly (the lower homologues of the polymer) dissolve in acetone and acetonitrile. The products do not dissolve in diethyl ether, ethyl acetate and acetic acid. They decompose, especially when hot, in DMSO, formamide, a water solution of KOH and even in hot water. The decomposition takes place gradually with the emission of gaseous products, until the entire polymer has disappeared. It was found (through the chromatographic method) that the main gaseous product was N₂O.

The elemental analysis of the product (for the first method of synthesis):

$$\text{C} - 16.45\% \quad \text{H} - 3.36\% \quad \text{N} - 36.04\%$$

If we assume a macromolecule of the polycondensate consisting of 5 mers:



the theoretical values are:

$$\text{C} - 15.46\% \quad \text{H} - 3.09\% \quad \text{N} - 36.08\%$$

2.4.2 Physical and Chemical Characteristics of the Polymer

The thermal behaviour of the polymer was characterized by DTA-TG analysis.

The DTA and TG analysis showed a rapid decomposition of the polymer, distinctive for blasting materials heated to the proper temperature of approximately 140°C (Fig. 1).

The course of the TG shows a gradual mass decrement before the point of spontaneous decomposition, for the raw polymer starting from approximately 120°C. The polymer obtained in the second stage has a lower breakdown temperature (Fig. 2).

The product's sensitivity to friction is smaller than that of HMX. As measured on the Peter's apparatus for HMX – 3.92 kg, for the product being studied – 6.32 kg.

The structure of the polymer HOCH₂–[NNO₂CH₂]_n–OH, according to data available in literature⁽¹⁰⁾, may decompose with the release of formaldehyde and then N₂O. Tests of the obtained product's behaviour in several environments were conducted (Table 1).

The course of decomposition in time (the rate of emission of gaseous products) can be thus characterized as: very fast in the beginning and gradual decomposition towards the end. This can be explained by the lower stability of the low-molecule product being dissolved as opposed to that of a

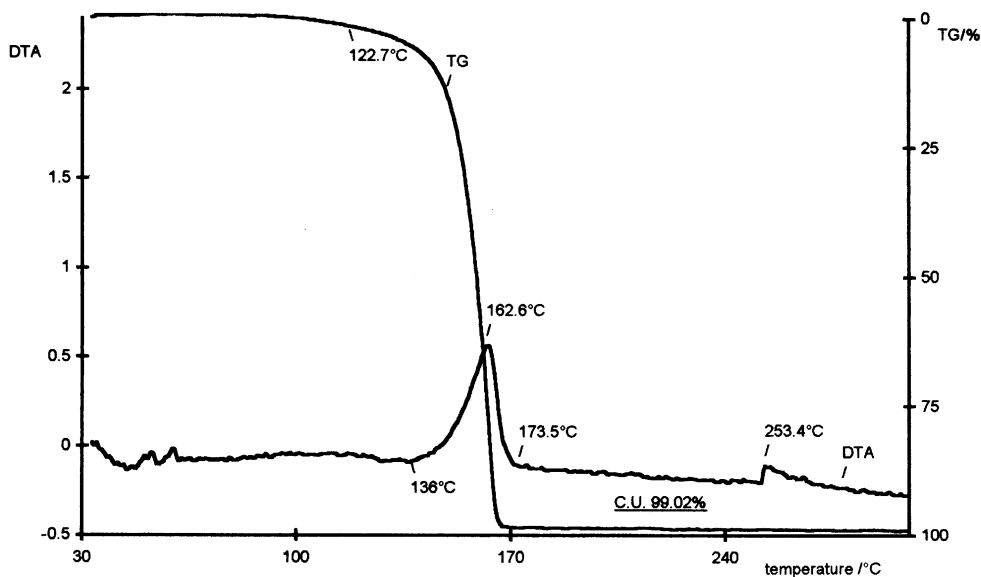


Figure 1. DTA-TG curves of the polymer obtained in the first stage (weight 17.48 mg, heating rate 2°C/min).

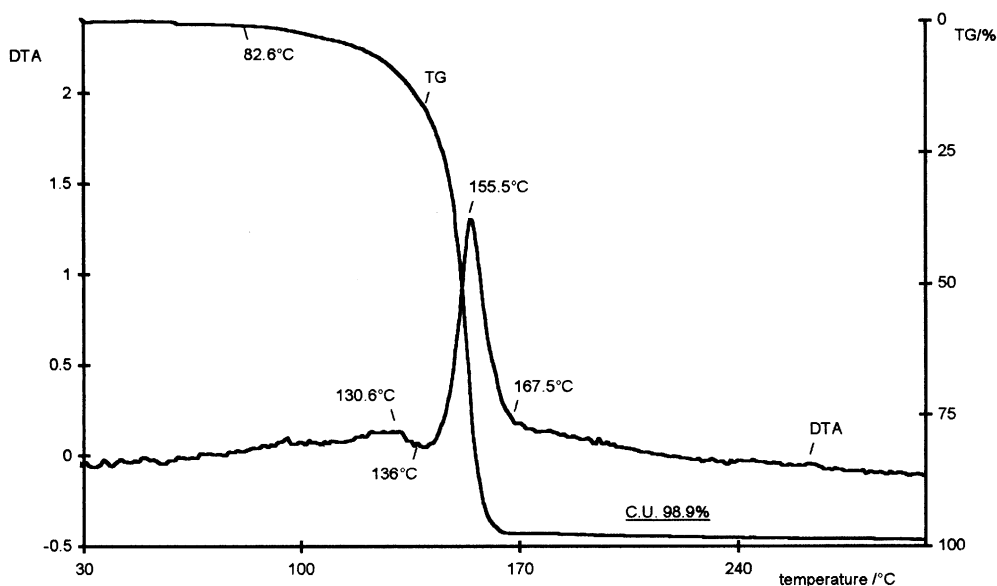


Figure 2. DTA-TG curves of the polymer obtained in the second stage (weight 48.6 g, heating rate 2°C/min).

Table 1. Results of the Measurement of the Product's Decomposition in Different Environments

Solvent	Temp. [°C]	Time of full chemical decomposition [min]	Polymer/solvent [g/cm ³]	Amount of gaseous products (N ₂ O) [g/cm ³]
Water	96	90	0.005	290 theoret.
Formamide	21	137	0.037	246 exp.
Dimethylsulfoxide	96	180	0.043	330 exp.

polymer with larger macromolecules. The main gaseous product of decomposition is N₂O (determined through the chromatographic method). The theoretical amount of gaseous products emitted, based on the earlier mentioned macromolecule ($n=5$), and emitted N₂O equals approximately 290 cm³/g (STP). The amount of gaseous products emitted was different for decomposition in formamide and

DMSO. The differences in the amounts of gaseous products emitted may amongst others result from the difference in solubility of N₂O (and perhaps CH₂O) in various solvents.

Hydroxymethylene nitramines should show better stability against acids than bases^(10,11), which has been confirmed in the process of synthesis, where acid properties of NH₂NO₂, in the reaction in the phase boundary, did not prevent the

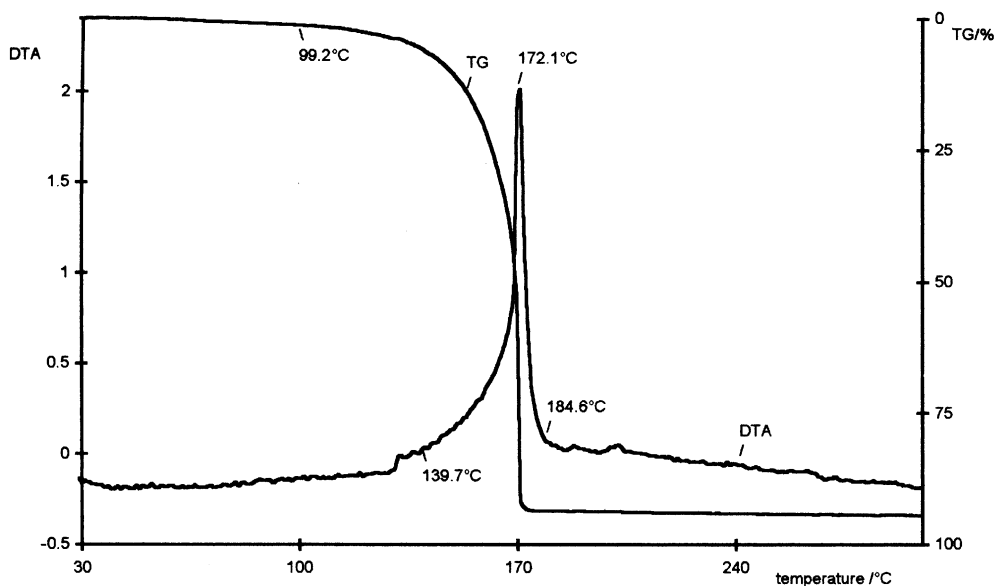


Figure 3. DTA-TG curves of the polymer treated with the concentrated nitric acid (in 10°C) (weight 39.97 mg, heating rate 2°C/min).

formation of the polymer. However dissolving the polymer in the concentrated nitric acid (20 cm³ HNO₃ + 3.7 g of the polymer) led to its substantial decomposition: 0.5 g (~13.5%) did not dissolve, 0.7 g (~19%) after dissolving could be precipitated by the addition of water (the soluble part) and the rest (approximately 67.5%) decomposed.

The part of the product that did not decompose (the part that dissolved as well as the one that didn't) has a higher temperature of spontaneous breakdown (approximately 170°C), but its stability, characterized by the start of decomposition, is lower (~90°C). In the concentrated nitric acid environment only two processes could occur: decomposition of parts of the low molecular weight polymer and the esterification of final hydroxyl groups in polymers with a higher molecular weight.

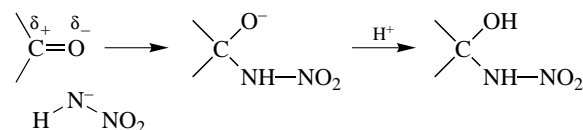
3. Discussion

The fact that no reaction takes place between NH₂NO₂ and CH₂O in a water solution and its gradual course in a two-component system suggests the reaction has an interionic mechanism⁽⁶⁾. When the reaction takes place in a water solution (with the pH-value ≈ 1.6) the ions appear in a highly hydrated form, for example: (NHNO₂)⁻·nH₂O. The hydration coating slows the course of the reaction with CH₂O, whose hydration energy according Ref. 12 is also substantial – it equals approximately 44 kJ/mol.

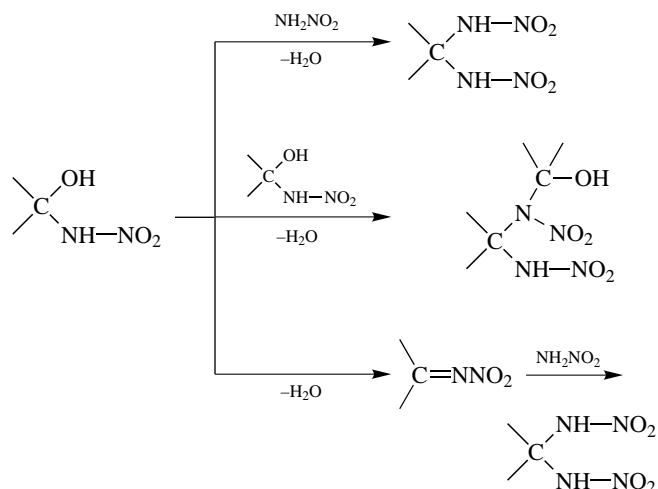
In an organic solvent (ethyl acetate) the polymer formation process does not take place presumably due to the limited concentration of the reacting substances, mainly (NHNO₂)⁻ (lower solubility and lower degree of ionization). For the simple process of nucleophilic addition to the carbonyl group to take place, it is absolutely necessary that the lone electron pair of the nucleophile have the possibility to attack the carbonyl group on the carbon atom that has a positive molecular charge:



In the addition process, the carbon atom from the carbonyl group transforms from hybridization sp² to hybridization sp³:



The polarity of the >C=O group is strengthened when protons can protonate the oxygen atom. An acidic environment does not therefore interfere with the addition process. In the case being examined, when we have two hydrogen atoms next to the nitrogen, the process can further occur according to the polycondensation mechanism. This stage of the process, as a process of dehydration, takes place more slowly and can be catalyzed with acids⁽¹³⁾. It can be described as a multi-direction reaction: using the initial nitramide, another methylol nitramine molecule or as intramolecular dehydration:



In each case the stages of addition (to CH_2O) and condensation, leading to the formation of the product – polymethylene nitramine, can take place in succession. This process is, however, reversible during each of the stages. Under certain conditions, mainly in a base environment, the polymer may fully decompose⁽¹⁴⁾.

In general, the lack of a reaction in a one-component environment and the fact that it takes place only on the phase boundary, may result from:

- a different (than in the respective liquids) positioning of the reacting molecules;
- the mentioned differences in the solvation coating of the reacting substances;
- different conditions of diffusion;
- the different proportion of the local concentration of the reacting substances as compared to the averaging concentration in the respective phases.

The detailed explanation of which of these factors are decisive, requires further research. The fact, that the product does not solubilize (separate) during any of the phases, results in that the polymer product is forming until all the substrates are used up. Under these circumstances, the diffusion process is the factor that limits the rate of the reaction.

4. Conclusion

A study on the synthesis of macromolecular products from NH_2NO_2 and CH_2O has been conducted. The characteristics of the products have been examined. It has been found that the process of synthesis does not take place in a water solution. If a two-component system: water/ethyl acetate, is used, the product forms on the phase boundary. The fact, that the formation of the polycondensate takes place on the phase boundary, may suggest that the reaction occurs with the participation of ions.

The product is not soluble during any of the phases. Furthermore, it solubilizes with difficulty (in small quantities) in acetone and acetonitrile.

The product shows thermal decomposition characteristic of the decomposition of blasting materials in approximately 160°C . However, we can observe gradual decomposition starting from approximately 100°C . The product decomposes when heated in solvents that have a base character.

5. References

- (1) E. J. Orłowa, N. A. Orłowa, W. F. Żilinin, W. Z. Zbarskij, G. M. Szutow, and L. I. Witowskaja, “*Oktogien-tiermostojkoje wzrywczatoje wieszczstwo*”, (Polish trans. – M. Syczewski), MON, Warszawa, 1987.
- (2) F. Chapman, P. G. Oweton, and D. Woodcock, *J. Chem. Soc.* 55, 1631–1657 (1949).
- (3) “*The Synthesis and Reaction of Organic Compounds*”, V2, Pergamon Press, Oxford, NY-Toronto-Sydney-Paris-Frankfurt (Russ. ed. V3 p. 465).
- (4) Lin Xiong *Chem. Abstr.* 255358 h (1991).
- (5) Y. Ogata and M. Okane, *J. Chem. Soc.* 78, 5423 (1956).
- (6) L. A. Janowskaja and S. S. Jufit, “*Organiczeskij syntez w dwuchfaznych sistemach*”, Chimija Moscow, 1982.
- (7) Z. Fang, L. Chen, and F. Li, *Propellants, Explosives, Pyrotechnics*, 22, 78–80 (1997).
- (8) M. Syczewski, H. Boniuk, and I. Cieślowska-Glińska, *Propellants, Explosives, Pyrotechnics* 22, 155–158 (1998).
- (9) T. Urbański, “*Chemistry and Technology of Explosives*,” Pergamon Press, PWN, V. 3, 1961.
- (10) A. Lamberton, C. Lindley, P. Owston, and J. Speekerman, *J. Chem. Soc.* 1641 (1949).
- (11) A. L. Fridman, B. P. Iwszin, and S. S. Nowikow, *Usp. Chim.* 38, 1969 (1448).
- (12) S. S. Jufit, “*Mechanizm mieżfaznowo kataliza*,” Ed. Nauka, Moscow, 1984.
- (13) “*Progress in Physical Organic Chemistry*”, editors G. Cohen, A. Streitwieser, and R. W. Taft, Interscience Publisher, New York, London, 1963, p. 342.
- (14) “*The Chemistry of the Nitro and Nitroso Groups*,” ed. H. Feuer, Interscience Publisher, New York, London, Sydney, Toronto, 1969.

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