Russian Chemical Reviews **79** (9) 819 – 833 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n09ABEH004067

Nitramide

A A Lobanova, S G Il'yasov, G V Sakovich

Contents

I.	Introduction	819
II.	Structure and physical properties of nitramide	819
III.	Methods for the synthesis of nitramide	822
IV.	Chemical properties of nitramide	826
V.	Conclusion	831

Abstract. The review is devoted to nitramide, the first member of the nitramine homologous series. The methods of its synthesis, structure as well as physical and chemical properties are considered. The bibliography includes 194 references.

I. Introduction

Nitramide was synthesized for the first time by Thiele and Lachmann [1] in 1894. This compound has always attracted attention of chemists as the first member of the nitramine homologous series, as an elementary reactive building block for the design of more complex structures and as a model for the investigation into properties of substances at the boundary between organic and inorganic ones. It is already more than 100 years that scientists have been involved in studies on the properties of nitramide and development of methods of its synthesis. Nitramide can be considered as nitric acid amide and simultaneously as the ammonia nitration product (nitramine). Nitramide has obviously been given insufficient attention in the well-known review articles devoted to the chemistry of nitramines.[2, 3]

Nitramide plays very important role in the chemistry of nitramines. Some properties of nitramide, for example, spectral, are considered to be the reference characteristics for compounds of the nitramine group, which allows monitoring the changes in the properties of nitramines upon introduction of different substituents into nitramide molecule.

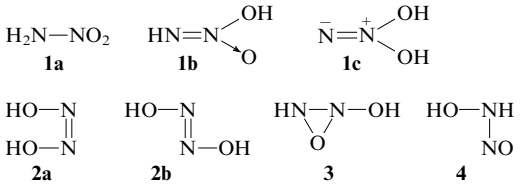
Nitramide is an intermediate in various syntheses. It has particular significance in the preparation of dinitramide [$HN(NO_2)_2$] and its salts and in elaboration of new promising methods for their synthesis.[4] Up to now trinitramine [$N(NO_2)_3$] has not been obtained and synthesis from nitramide is regarded as the most probable pathway among potential approaches.[5]

Nitramide was detected as an intermediate in processes of decomposition of different cyclic and linear nitramines, which allows consideration of new mechanisms of decomposition of nitramines and prediction of the boundary conditions for their stability.

II. Structure and physical properties of nitramide

1. 1. Structure and spectral characteristics

Preparation of nitramide raised intense discussions regarding the structure of the nitramide molecule for which seven versions have been proposed (**1a** – **c**, **2a**,**b**, **3**, **4**).



1a **1b** **1c** **2a** **2b** **3** **4**

Thiele gave preference to nitric acid amide (**1a**) on the basis of the method of its synthesis and certain chemical reactions, while it can also react in the tautomeric form **1b**, that is imidonitric acid.[6, 7]

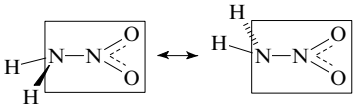
Hantzsch [8] in his earlier studies tried to prove impossibility of the amide structure because nitramide possessed high acidity and its properties differed from those of genuine amides.[9 – 11] Hantzsch believed that the structure of nitramide corresponded better to the formula **2a**. He changed his opinion since hyponitrous acid (**2a**, **2b**) [12] and nitrosohydroxylamine (**4**) have been prepared,[13] but nevertheless could not accept the structure **1a** and insisted on the structure of imidonitric acid (**1b**).[14, 15]

A A Lobanova Federal State Unitary Enterprise 'Federal Research and Production Centre Altai' ul. Sotsialisticheskaya 1, 659322 Biysk, Altai Territory, Russian Federation. Fax (7-3854) 31 13 09, tel. (7-3854) 30 59 53, e-mail: post@frpc.secna.ru
S G Il'yasov, G V Sakovich Institute for Problems of Chemical and Energetic Technologies, Siberian Branch of the Russian Academy of Sciences, ul. Sotsialisticheskaya 1, 659322 Biysk, Altai Territory, Russian Federation. Fax (7-3854) 31 13 09, tel. (7-3854) 30 59 37, e-mail: ilysow@ipcet.ru (S G Il'yasov), tel. (7-3854) 30 59 98, e-mail: admin@ipcet.ru (G V Sakovich)

Received 15 March 2010
Uspekhi Khimii **79** (9) 894 – 909 (2010); translated by P M Chukurov

Later, the structure of nitramide as the nitric acid amide was confirmed from determination of the dipole moment of nitramide in dioxane solution (3.75 D),[16] as well as by the Raman and IR spectra [17] in which no stretching vibrations of the OH and =N groups were found. Additional evidence was derived from the synthesis of the ^{15}N-labelled compound.[18] The dipole moment of nitramide in the gas phase is equal to 3.57 D,[19] *i.e.*, it is close to the value in dioxane solutions. Theoretical calculations gave the value of 3.76 D,[20] which agrees well with the experimental data.

The structure of nitramide in the vapour phase was investigated by microwave spectroscopy.[19] It was found that the nitramide molecules are nonplanar: the nitrogen and oxygen atoms were coplanar, but the plane of the H−N−H group was rotated relative to the plane N−NO_2. The possibility of rotation around the bond N−N determines inversion of the nitramide molecule.[21] The calculated value of the inversion barrier is equal to 6.3 kJ mol^{-1} (Ref. 22).



Nonplanariy of the nitramide molecules was further validated by experimental studies and calculations.[23, 24]

Methods of vibrational and electronic spectroscopy were applied for a comparative study of the interaction between the amino and nitro groups in nitramide where these groups are immediately adjacent to each other and in *p*-nitroaniline where the amino and nitro groups are separated by a system of conjugated π-bonds.[25] No evidence for enhanced electronic interaction between these groups in nitramide was established, this is even less pronounced as compared with *p*-nitroaniline. The relatively low energy of p−π-conjugation in nitramide owing to the nonplanar conformation of its molecule is the reason for the observed effect. Overlapping between the p_y-orbital of the N−H bond and the p_y-orbital of the second lone electron pair of the nitro group oxygen atom additionally stabilizes the nonplanar structure.

From a comparison of the structures of nitramide (Fig. 1) and related amides [cyanamide (H_2NCN) or formamide (H_2NCHO)], it can be noted that the length of the H−N bond (1.005 Å) in nitramide is closer to that in ammonia (1.017 Å)[26] than in the amide group of formamide (1.027 Å).[27] The length of the N−N bond (1.427 Å) in nitramide is smaller than in hydrazine (1.46 Å). The dissociation energy of the N−N bond in nitramide is 230 kJ mol^{-1} (Ref. 28).

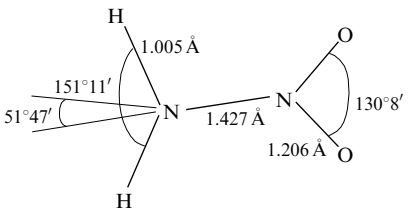


Figure 1. Values of angles and bonds lengths in the molecule of nitramide.[19]

The distances between the oxygen atoms in the nitro group of nitramide and in such molecules as HNO_3, FNO_2 and $ClNO_2$ are very similar. The distances N−O (1.206 Å) in nitramide and nitric acid are virtually the same.[29, 30]

Nonempirical molecular orbital calculations indicate that the length of the N−N bond in nitramide molecule and the angle between the planes of the fragments H−N−H and N−NO_2 are different for an equilibrium structure, a transition state of the inversion of the amino group and an internal rotation state.[31]

X-Ray photoelectron spectroscopic studies of nitramide revealed very high N1s binding energies of the amino group (401.4 eV) and the nitro group (407.4 eV), whereas in other 30 compounds containing amino, amide and nitro groups these values vary in the range 399.8–400.0 eV.[32]

Calculations demonstrate that the values of orbital energies corresponding to lone electron pairs of the nitrogen atom of the nitramide amino group depend on the configuration of the N atom.[33]

The overall configuration of nitramide is described in Ref. 34. Quantum chemical calculations of nitramide can be found in Refs 35–37 and calculations of the structure and energies of bond vibrations are given in Ref. 38. An opinion exists [39] that a dimeric structure of nitramide is quite possible, the calculated geometry of the dimer is shown in Fig. 2.

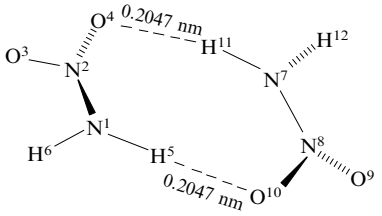


Figure 2. Calculated geometry of the nitramide dimer.[39]

UV spectra of nitramide are characterized by an absorption maximum in the range 204–207 nm. The extinction coefficient is equal to 7200–7800 litre mol^{-1} cm^{-1} and depends on the method of its synthesis and purification.[40–43] The absorption maximum of the anion is shifted to 225 nm.[44]

On the basis of theoretical interpretations of UV spectra [41] an assumption is advanced that the observed spectral characteristics are caused by the existence of two structures with charge transfer:

$$H_2NNO_2 \rightleftharpoons HN{=}NO_2^-H^+.$$
1a

UV spectra of nitramide in the gas phase and the mechanism of nitramide photodissociation were investigated with recourse to theoretical calculations [45] and the most probable photodissociation products (NH_2, NO_2, NH_2NO, NO and O) were proposed.

Excited and ionized states of the nitramide molecule were studied with the use of an approach of configurational interactions for clusters with an adapted symmetry, and obvious similarity of nitramide and dimethylnitramine was found.[46] The calculation of 16 singlet and 13 triplet vertical transitions were used for construction of the wave function

by the SAC-CI method. Thus, 14 ionized states with relative intensities of the absorption maxima were derived by a single field approach. The single broad band of absorption in the UV spectrum of nitramide was assigned to two transitions: $n\,\pi NO_2 \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$.

Vibrational spectra of nitramide and assignements of absorption bands were described.[17,47–52] The IR spectra of nitramide in the aci-form (**1b**) were used in the study of methylenenitramine salts and these spectra made it possible to prove the ionic structure of the salts.[52]

IR spectra of nitramide and its isotopic modifications ($^{15}NH_2NO_2$, ND_2NO_2, $^{15}ND_2NO_2$) at 12 K in argon and nitrogen matrices were investigated.[48] In this work, theoretical calculations of frequencies in the spectra were performed on the basis of a normal coordinate treatment in conjunction with self-consistent field (SCF) approach and valence force field of nitramide was obtained. Theoretical concepts and experimental data were simultaneously applied for interpretation of the obtained spectra. All fundamental frequencies of the nitramide molecule have been assigned. Quantum chemical calculations resulted in somewhat overestimated values of the vibration frequencies but their order and assignments to symmetric and asymmetric types of the vibrations completely correlate with the experimental data. A part of these experimental data and the calculated frequencies are presented in Table 1.

Table 1. Experimental and calculated vibration frequencies in the NH_2NO_2 molecule (cm^{-1}).[48,51]

Experimental IR spectrum		Calculations	Assignment [a]
Ar-matrix	N_2-matrix		
Symmetric vibrations			
3359	3361	3734	$\nu(NH_2)$ (97)
1558	1581	1815	$\delta(NH_2)$ (86)
1350	1368	1747	$\nu(NO_2)$ (51) + ν(NN) (25) + $\delta(NO_2)$ (17)
951		1196	ν(NN) (36) + $\nu(NO_2)$ (28) + $\delta(NO_2)$ (15)
798	776	975	$\delta(NO_2)$ (50) + ν(NN) (37)
693	713.5	813	$\delta(NO_2)$ (50) + $\delta(NH_2)$ (25)
628	587	600	$\delta(NH_2)$ (51) + $\nu(NH_2)$ (25) + ν(NN) (17)
Asymmetric vibrations			
3478	3474	3868	$\nu(NH_2)$ (100)
1613	1611	2070	$\nu(NO_2)$ (78)
1227	1239	1374	$\delta(NH_2)$ (74) + $\nu(NO_2)$ (24)
485		581	$\delta(NO_2)$ (79)
402	404	417	τ(NN) (37)

[a] Distributions of potential energy of vibrations in percents are given in parentheses.

The ^1H and ^{14}N NMR spectra of nitramide NH_2NO_2 and nitrourethane $RNHNO_2$ were investigated.[53] It was established that all protons in nitramide belong to the amine type protons, so this study additionally confirmed the structure **1a**.

The NMR spectra of nitramide in acetonitrile, ethyl acetate and diethyl ether were obtained in a wide range of concentrations and temperatures.[54] Changes in the proton chemical shifts of the amino group suggest association of the nitramide molecules with the solvent molecules at low temperatures. The electron-withdrawing NO_2 group in nitramide causes a downfield shift of the proton resonance signal, which corroborates the acidic properties of the amide protons. The chemical shift of the nitrogen nuclei (^{14}N) of the NH_2 group is δ +132 relative to NH_4^+, which suggests the high degree of ionic character of the H–N bonds and correlates with the data from the ^1H NMR spectrum.

The chemical shifts in ^1H, ^{14}N and ^{15}N NMR spectra of nitramide are given in Table 2.

Table 2. Characteristics of ^1H, ^{14}N and ^{15}N NMR spectra of nitramide.

Solvent	Chemical shifts δ (see [a])			Ref.
	$\mathbf{H}_2NNO_2$	$H_2\mathbf{N}NO_2$	$H_2N\mathbf{N}O_2$	
DMSO-d_6	11.5	–	–	55
MeCN	9.2	–	–	54
Et_2O	9.5	–	–	54
AcOEt	9.5	–	–	54
THF-d_8	10.1	−221/−220.3	−26/−25.5	47

[a] For the nitrogen nuclei, the values of δ for $^{14}N/^{15}N$ are given by slash relative to $MeNO_2$.

2. Physical properties of nitramide

Nitramide forms colourless plate-like crystals with a specific luster. It is readily soluble in water, ethanol, ether, acetone and ethyl acetate, moderately soluble in *m*-cresol, isopentyl alcohol and dioxane, slightly soluble in chloroform, hexane and petrol and insoluble in naphtha.[1,11,16,43,56,57]

Nitramide crystallizes in the monoclinic system and the unit cell contains four molecules. The density of crystals is 1.783 g cm^{-3} at 20 °C (Ref. 58) and 1.8692 g cm^{-3} at −173.16 °C (Ref. 47).

The melting point of nitramide depends on the presence of trace amounts of water in a sample, according to different studies it varies in the range from 68 to 81 °C (with decomposition).[6,29,38,43,59] Dry nitramide melts at 81–82 °C. Derivatographic investigation shows that thoroughly dried nitramide melts without decomposition and flares up at 120 °C.[59]

Heat of decomposition of nitramide to gaseous dinitrogen oxide and liquid water was measured as 118.07 ± 3.56 kJ mol^{-1} and the standard enthalpy of formation of nitramide from the elements was calculated as 86.37 ± 3.56 kJ mol^{-1} (Ref. 60).

Thermal decomposition of nitramide samples purified by ordinary reprecipitation with subsequent sublimation in vacuum was investigated.[61] The enthalpy of formation of nitramide was calculated from the experimental data and this value is equal to −76.48 kJ mol^{-1} for the sublimed samples of nitramide and −86.32 kJ mol^{-1} for the non-purified ones. Thermodynamic properties (specific heat capacity, entropy and the Gibbs energy changes) were calculated for nitramide in the ideal gas state in the temperature range from 0 to 1500 K.[62] The enthalpy of formation of nitramide in the ideal gas state at 298.15 K ($\Delta_f H^\circ$) is −3.000 kJ mol^{-1} (Ref. 63).

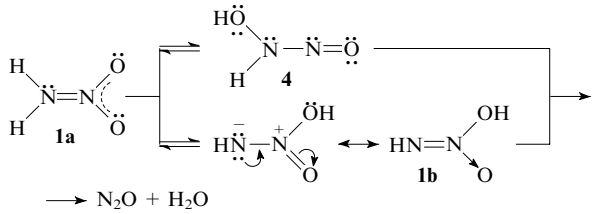
A theoretical analysis of thermal decomposition of nitramide makes it possible to choose two pathways from a variety of possible routes.[64] The preference is given to the

Table 3. Comparison of characteristics for nitramide, methylnitramine, dimethylnitramine and dinitramide.

Parameter	H_2NNO_2 (**1a**)	$MeNHNO_2$ (**8**)	Me_2NNO_2 (**9**)	$HN(NO_2)_2$ (**7**)
$T_{m.p.}$ /°C	79 – 81 (see [43,47])	38 (see [68])	57 – 58 (see [69])	liquid, unstable in the NH form
Density /g cm^{-3}	1.783 (see [58])	1.2433 (see [70])	–	–
pK_a (25 °C)	6.59 (see [66])	6.15 (see [71])		−5.62 (see [72])
Stability of the anion	unstable	little stable		stable
IR spectrum /cm^{-1} (see [49,73])				
ν_{as} NO_2	1546 vs	1580 – 1599 vs	1546 sh	1645 s
	1534 vs	1558 – 1578 vs	1515 s	1625 s
ν_s NO_2	1379 vs	1342 – 1350 vs	1315 m	1255 m
		1334 vs	1291 m	
UV spectrum (λ_{max}) /nm				
NH form	205 – 207 (see [43])	232.5 [a]		210 (see [73]) [b]
				223 [c]
anion	225 (see [44])	228 (see [74])		225, 285

Note. Description of band intensities in the IR spectra: vs is very strong, s is strong, m is medium, sh is shoulder. [a] In 10^{-4} M HCl; [b] in H_2SO_4; [c] in ether.

pathway *via* **4** as an intermediate, that is, isomerization of nitramide into nitrosohydroxylamine is presumed:



$\longrightarrow N_2O + H_2O$

However, it is not excluded that in the thermal decomposition of nitramide the nitro – nitrite rearrangement occurs.[65]

$$\underset{\textbf{1a}}{H_2N-NO_2} \longrightarrow \underset{\textbf{5}}{H_2N-ONO}.$$

Nitramide is a weak monobasic acid with the dissociation constant of 3.0×10^{-7} at 25 °C (pK_a = 6.52).[59,66]

The singly-charged anion of nitramide ($HN_2O_2^-$, **6**) is unstable. Ammonium salt of nitramide can be prepared by the reaction of nitramide with ammonia in ether,[11] but this salt decomposes on attempted isolation by filtration. Sodium and potassium salts exist at 0 °C for not more than 1 min, but at −80 °C these salts are stable for several minutes in the absence of water.[59] Dry nitramide decomposes with flashing on exposure to ammonia vapour.

Nitramide mercury salt is more stable; however, it also decomposes during storage with formation of mercury oxide and dinitrogen oxide.[6,59]

$$HgNNO_2 \longrightarrow HgO + N_2O.$$

This salt is extremely sensitive to mechanical impact, but is thermally stable up to 95 °C. Attempts to prepare other salts from the mercury salt by exchange reactions were unsuccessful; the reaction with hydrogen sulfide affords mercury sulfide and results in regeneration of nitramide:

$$HgNNO_2 + H_2S \longrightarrow HgS + H_2NNO_2.$$

Relative stability of mercury salt can be explained by higher contribution of covalent constituent to the Hg=N bond, which is typical of mercury salts of organic nitro compounds.[67]

Some properties of nitramide, dinitramide (**7**), methyl- (**8**) and dimethylnitramines (**9**) are compared in Table 3.

The introduction of the nitro group, *i.e.*, the electron-withdrawing substituent, in the molecule of nitramide exerts pronounced effect on the properties. The dinitramide thus formed is a strong acid. Spectral characteristics of dinitramide are closer to those of methyldinitramine [$MeN(NO_2)_2$, **10**] than to nitramide.[73] Dinitramide is stable only in the anionic form.

Substitution of fluorine or the nitrile group for one proton in the molecule of nitramide causes similar changes in properties. Fluoronitramide ($FNHNO_2$, **11**) is stable only in the anionic form, like dinitramide. Fluoronitramide salts with bulky cations (for example, with tetraphenylphosphonium) are the most stable ones, but ammonium salt is unstable as well as the free acid **11**.[75] Nitrocyanamide ($NCNHNO_2$, **12**) is also stable as a salt or in hydrated state;[76] like dinitramide, it is also a strong acid. In the UV spectrum of the nitrocyanamide anion, the position of the absorption maximum (λ_{max} = 265 nm, ε = 8900 litre mol^{-1} cm^{-1}) does not change in a wide range of the medium acidity.[77]

III. Methods for the synthesis of nitramide

The described methods for the synthesis of nitramide can be divided into the following groups:

— synthesis from carbamic acid derivatives;
— nitration of ammonia;
— nitration of ammonia sulfo derivatives;
— preparations from urea and guanidine nitro derivatives;
— decomposition of nitramines;
— miscellaneous methods.

1. Synthesis from carbamic acid derivatives

For the first time, nitramide was synthesized from urethane **13**.[1,6]

$$EtOC(O)NH_2 \xrightarrow[H_2SO_4]{EtONO_2} EtOC(O)NHNO_2 \xrightarrow[ether]{NH_3}$$
13

$$\longrightarrow EtOC(O)NNO_2NH_4 \xrightarrow[MeOH]{KOH}$$

$$\longrightarrow KOC(O)NNO_2K \xrightarrow[water,\ ice]{H_2SO_4} [HO_2CNHNO_2] \xrightarrow{-CO_2}$$
14

$$\longrightarrow NH_2NO_2$$
1a

The yields of products in each step are 75%–80%. The practical implementation of this method is associated with certain experimental difficulties, especially in the last steps where dipotassium nitrocarbamate (**14**) forms. If the reaction mixture is not completely protected against moisture, an explosive inflammation is possible. Extraction of nitramide from the solution is a very laborious operation. Three or four extractions with ether only at low temperature (0–2 °C) enable isolation of 75% of nitramide. This technique was modified [78] and was used for decades for the preparation of nitramide in spite of its complexity.

Nitration of ammonium carbamate (**15**) affords nitramide in the yields less than 5%.[79] Two parallel reactions proceed upon the action of nitric acid on ammonium carbamate:

$$H_2NC(O)ONH_4 \xrightarrow{2\ HNO_3}$$
15

$$\xrightarrow[\text{pathway } a]{} NH_2NO_2 + NH_4NO_3 + CO_2 + H_2O$$

$$\xrightarrow[\text{pathway } b]{} 2\ NH_4NO_3 + CO_2$$

The ratio between the pathways *a* and *b* was established to be 0.35 : 0.65. The starting compound, ammonium carbamate, has low stability and easily transforms into ammonium carbonate, which creates additional difficulties.

2. Nitration of ammonia

In the synthesis of nitramide by nitration of ammonia, it is necessary to strictly observe conditions for the isolation and storage of nitramide. First attempts to carry out nitration of ammonia by nitryl chloride were unsuccessful:[80,81] among the reaction products (NH_2Cl, $NH_2NH_2 \cdot HCl$, NH_4NO_2, NH_4Cl), no nitramide was found.

For the first time, ammonia was successfully converted to nitramide when underwent nitration with nitrogen(V) oxide.[82]

$$NH_3 \xrightarrow{N_2O_5} \underset{\textbf{1a}}{NH_2NO_2} + NH_4NO_3.$$

Nitrogen(V) oxide was cooled to −196 °C and was added to partially crystallized ammonia at −78 °C. Flow of nitrogen was introduced in order to remove other nitrogen oxides from N_2O_5. The addition of nitrogen(V) oxide (0.2 to 0.3 g) was carried out over a period of 15–20 min, and the excess of ammonia was removed under reduced pressure. The temperature of the reaction mixture was gradually raised to −40 °C. Then the reaction mixture was granulated by pouring into liquid nitrogen and the resulting granules (a mixture of nitramide, ammonia and ammonium salts) were fed into solution of nitric acid at ~0 °C and pH 2. Carrying out this reaction at such low temperatures and fast neutralization of excess ammonia made it possible to recover nitramide.

It was found that nitramide can be prepared by nitration of ammonia with different nitronium salts (the nitroyl cation), *e.g.*, NO_2NO_3, NO_2BF_4, NO_2ClO_4, NO_2SO_2F, $(NO_2)_2S_2O_3$, NO_2Cl, if the conditions described above for the reaction and isolation of the product were maintained. It was found by potentiometric titration that the highest yield of nitramide (62%–65%) was achieved with the use of nitronium nitrate and the lowest (6.5%–8.0%) for nitronium chloride. The desired product (nitramide) can only be isolated in the yields of up to 40%.[83–86]

A procedure of nitramide synthesis was described [87] in which nitration of ammonium salts was carried out by nitryl fluoride in the temperature range from −35 to +35 °C with subsequent extraction of nitramide with liquid ammonia at −33 °C. Considering very low stability of the nitramide anion, one can suggest that nitramide played the role of an intermediate only, since under the described conditions it is nitrated to dinitramide at very high rate and in virtually quantitative yield. Apparently, it was ammonium salt of dinitramide [88–90] (which has not been known at that time) that was synthesized as the product.

High-level molecular orbital calculations of a gas-phase reaction of ammonia with nitric acid revealed two putative non-ionic reaction channels with a similar reaction barrier of 192.5 kJ mol^{-1}. One channel occurs *via* a four-membered-ring transition state and affords NH_2NO_2 and H_2O. The other channel passes *via* a five-membered-ring transition state and produces H_2NONO and H_2O.[91] This study confirms once more the ambiguity of reactions between ammonia and a nitrating agent.

An unstable species $[NH_2]$ was obtained in the course of ammonia photolysis and after reaction of this species with NO_2 (N_2O_4) only water and dinitrogen oxide were identified as the reaction products.[92] Presumably, nitramide forms as the primary product and further decomposes *in statu nascendi*:

$$[NH_2] + NO_2 \longrightarrow \underset{\textbf{1a}}{[NH_2NO_2]} \longrightarrow N_2O + H_2O.$$

Since isolation of nitramide from the ammonia nitration products proved to be very difficult problem, the aforementioned methods did not find wide application.

3. Nitration of ammonia sulfo derivatives

Ammonia sulfo derivatives are more promising starting compounds as compared with ammonia due to reduced basicity of the amide group. Nitramide can be synthesized by nitration of salts of imidosulfuric (**16**) and nitrilotrisulfuric (**17**) acids with mixtures of nitric and sulfuric acids at −15 °C, albeit in low yields.[6]

$$\underset{\textbf{16}}{HN(SO_3K)_2} \xrightarrow[HNO_3-H_2SO_4]{} O_2NN(SO_3H)_2 \xrightarrow{H_2O}$$

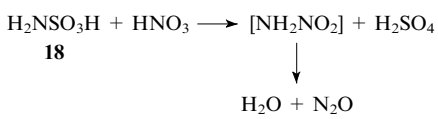
$$\underset{\textbf{17}}{N(SO_3K)_3} \xrightarrow[HNO_3-H_2SO_4]{}$$

$$\longrightarrow NH_2NO_2 + H_2SO_4.$$

Nitration of sulfamic acid (**18**) did not result in nitramide; presumably, the intermediate, nitrosulfamic acid (O_2NNHSO_3H), decomposes *in statu nascendi*.[93,94]

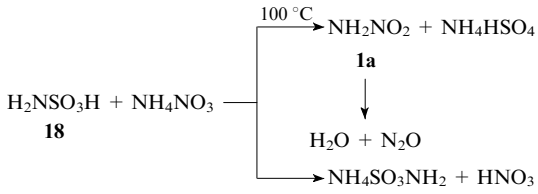
Later, it was established [95] that the reaction of sulfamic acid with nitric acid proceeds quantitatively with formation of dinitrogen oxide. From kinetic studies of this reaction it was inferred [96] that preference should be given to direct

displacement of the sulfo group bound with the nitrogen atom of the amino group by the nitronium cation rather than intermediate formation of nitrosulfamic acid.[97,98]



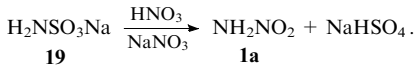
This reaction is the simplest method of synthesis of pure dinitrogen oxide.

The problem of nitration of sulfamic acid aimed at nitramide isolation was also discussed in early studies.[98–101] Sulfamic acid reacts with inorganic nitrates with evolution of dinitrogen oxide at substantially lower temperatures than the decomposition temperatures of the corresponding salts. At temperatures near 100 °C, the reaction of sulfamic acid with ammonium nitrate proceeds very vigorously with flashing at the end.[100] These chemical transformations can be represented by the following scheme:



Nitration of sulfamic acid with nitric acid in the presence of sodium nitrate afforded nitramide in a yield more than 20%.[79]

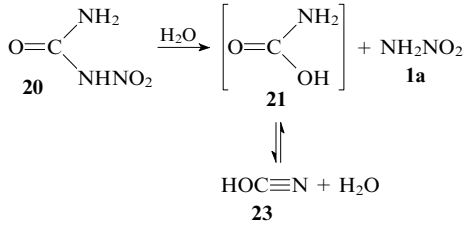
Development of a new method of synthesis of nitramide by nitration of sodium sulfamate (**19**) with 95% HNO_3 free from nitrogen oxides at temperatures from −50 to −20 °C had become a considerable achievement. The yields of nitramide amount to 45%–50%. In the presence of sodium nitrate, the yields increase to 80% (according to the results of potentiometric titration).[101]



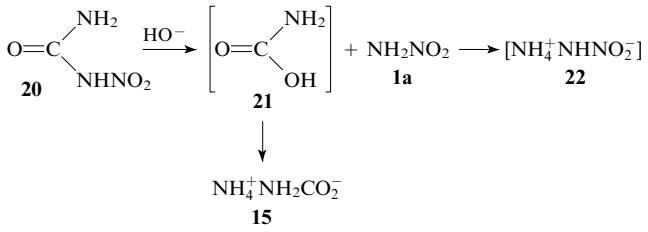
This procedure became the second (after that of Thiele and Lachmann) efficient preparative method, which acquired wide popularity.

4. Synthesis of nitramide from urea, guanidine and biuret nitro derivatives

Nitramide can be prepared by decomposition of nitrourea, nitroguanidine and nitrobiuret,[102–105] but yields of the target product are very low [for example, only 6% in the decomposition of nitrourea (**20**)].

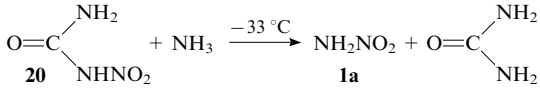


It is believed that unstable carbamic acid (**21**) formed upon decomposition of nitrourea yields is the source of ammonia giving rise to ammonium salt of nitramide (**22**) and ammonium carbamate (**15**).[106] The unstable aci-form decomposes rapidly to dinitrogen oxide and water,[105,107] which precludes isolation of nitramide in higher yields.

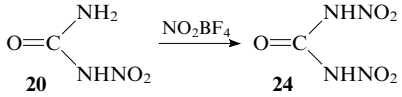


Low yields of nitramide can also be associated with decomposition of nitrourea to dinitrogen oxide and cyanic acid (**23**), avoiding the step of nitramide formation.[108]

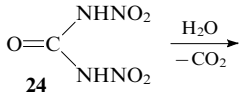
Nitramide is also the reaction product of nitrourea with liquid ammonia at −33 °C.[109] The yield of carbamide was up to 91%. Nitramide formed decomposes at very high rate so that it could be detected only by indirect methods.



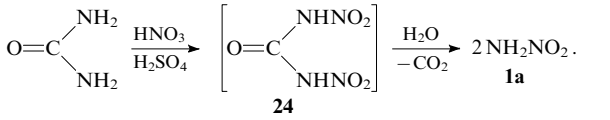
The most suitable method for the synthesis of nitramide is based on the use of *N*,*N*′-dinitrourea (DNU, **24**) [43,110] as the starting compound,which was synthesized for the first time by nitration of nitrourea with nitronium salts.[111]



N,*N*′-Dinitrourea is an extremely reactive compound and decomposes to nitramide upon action of water.



Replacement of the nitrating reagent by more available and technology-friendly mixture of nitric acid and oleum [43,110–112] and refinement of this procedure made it possible to develop a method for the synthesis of nitramide from urea without isolation of fairly unstable DNU.



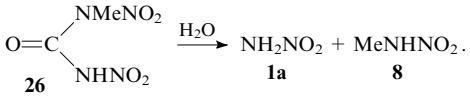
This procedure consists of the following consecutive operations: nitration of urea with an anhydrous mixture of nitric acid and 20% oleum, dilution of the reaction mixture by pouring it onto ice, extraction of DNU with ethyl acetate, washing of the extract with ice-cold water, hydrolysis of DNU to nitramide, removal of the solvent in vacuum and reprecipitation or recrystallization.

In the course of this synthesis, DNU precipitates from the reaction mixture and can be filtered off (with necessary precautions). It is a strong acid with $pK_a = -0.13$, its salts are stable.[110,113,114] An adduct of urea with DNU (**25**) is of interest for the isolation of nitramide because it is rather insensitive to mechanical impact and is well stored. High-purity nitramide can be obtained by mere dissolution of this

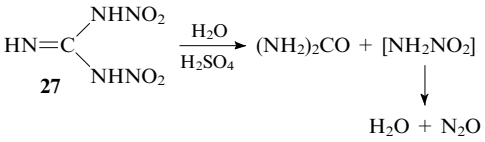
adduct in aqueous sulfuric acid, extraction of the target product with ether and isolation by well-known methods.[115]

$$(NH_2)_2CO\cdot(NHNO_2)_2CO \xrightarrow{H_2SO_4\ (dilute)} \underset{\mathbf{25}}{} \longrightarrow 2\,NH_2NO_2 + CO_2 + (NH_2)_2CO\cdot H_2SO_4.$$
$$\mathbf{1a}$$

Hydrolysis of *N*-methyl-*N*,*N*′-dinitrourea (**26**) produces methylnitramine (**8**) together with nitramide.[116]

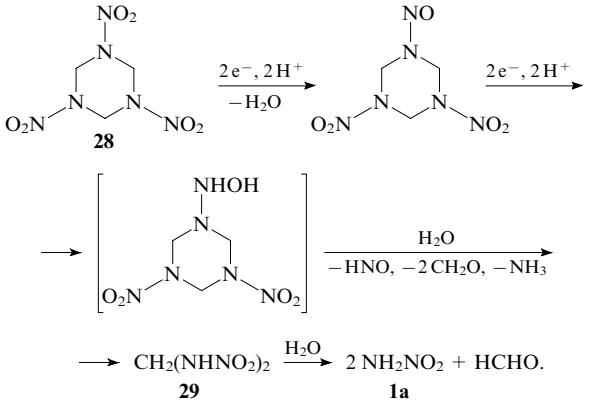


Decomposition of *N*,*N*′-dinitroguanidine (**27**) in aqueous sulfuric acid also gives nitramide, but it decomposes because of high acidity of the solution.[117]

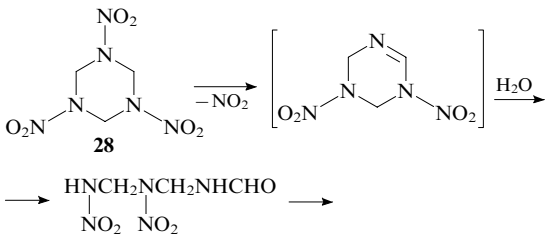


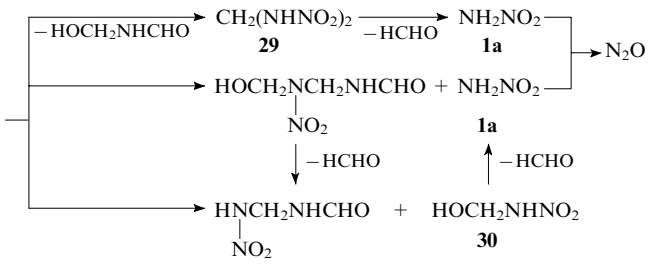
5. Decomposition of nitramines

Electrochemical decomposition of 1,3,5-trinitro-1,3,5-triazacyclohexane (hexogen or RDX, **28**) afforded nitramide identified by HPLC,[118] the following scheme of decomposition was proposed:



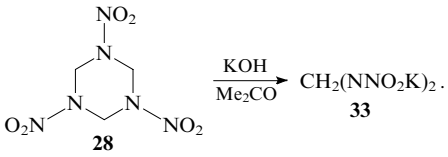
Alkaline hydrolysis of cyclic nitramines in aqueous solutions resulted in a variety of decomposition products including methylenedinitramine (**29**), nitramide (**1a**) and hydroxymethylnitramine (**30**)[119] identified by different techniques.



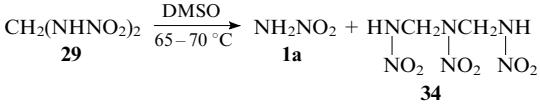


Action of a municipal sludge as a source of microorganisms on 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (octogen or HMX, **31**) at pH 7 resulted in sufficiently fast conversion of this compound to dinitrogen oxide and formaldehyde. Analysis of reaction mixture by HPLC–MS revealed characteristic ions that were identified as molecular ions of methylenedinitramine (**29**) and bis(hydroxymethyl)-nitramine (**32**).[120]

Alkaline hydrolysis of hexogen (**28**) and octogen (**31**) with ethanolic potassium hydroxide in acetone was investigated and one of the decomposition products, *viz*., dipotassium salt of methylenedinitramine **33** was isolated in the yields 30% and 70%.[121]



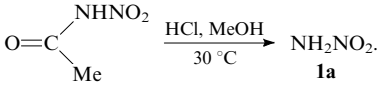
In turn, heating of salt **33** in DMSO produces nitramide and 1,3,5-trinitro-1,3,5-triazapentane (**34**).[122]



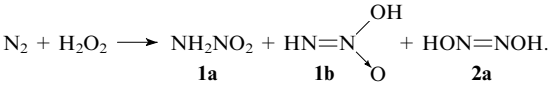
This reaction indirectly completed the decomposition chains of hexogen (**28**) and octogen (**31**) to nitramide *via* methylenedinitramine (**29**).

6. Miscellaneous methods

Nitramide can be prepared by solvolysis of nitroacetamide in methanolic hydrogen chloride[123] for 15 min at 30 °C. The yields of the product depended on the isolation procedure. Sufficiently pure nitramide can be prepared by rapid evaporation of the solvent with subsequent washing of the precipitate with an inert solvent.



Nitramide was detected in products of oxidative fixation of molecular nitrogen by hydrogen peroxide in two different forms, *viz*., as nitric acid amide (**1a**) and imide (**1b**).[124]



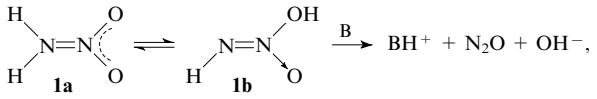
Nitramide synthesized by different methods is purified by reprecipitation,[6] recrystallization[43] and sublimation in vacuum.[47,125]

IV. Chemical properties of nitramide

1. Decomposition of nitramide in aqueous solutions under action of bases

Kinetics and mechanism of base-catalyzed decomposition of nitramide have been the subject of numerous studies, those by Brønsted *et al.*[56, 57, 126, 127] must be considered as fundamental. Brønsted was the first to investigate general base catalysis of decomposition of nitramide, specific ion effects, catalysis in nonaqueous solutions and kinetic isotope effect.

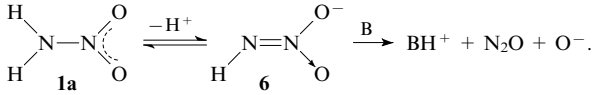
Brønsted and the majority of other authors carried out kinetic measurements by monitoring the evolution of dinitrogen oxide.[126, 128–130] Since nitramide exhibits acidic properties and its decomposition products are neutral, the reaction between the substrate, *i.e.*, nitramide, and a base as a catalyst results in changes in the concentration of the latter in the course of reaction. This permitted the use of only weak bases and restricted experimental pH values by the region with pH lesser than pK_a of nitramide. Brønsted elucidated the mechanism of decomposition in which the isomerization of nitramide was considered to be the first intermediate step.[126]



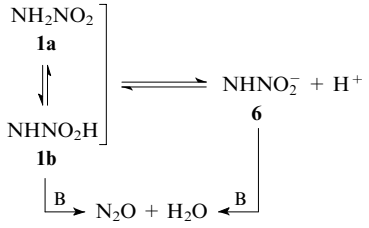
B is base.

Spectrophotometric monitoring of nitramide concentrations made it possible to reduce the concentration of the substrate (to 10^{-4} mol litre^{-1}) and thereby eliminate problems associated with consumption of the catalyst. Thus, it became possible to use rather strong bases and bring the reaction to completion.[44, 131–133]

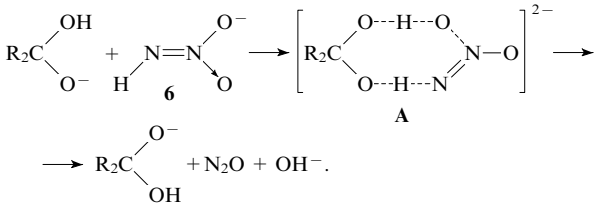
Presumably, preliminary isomerization of nitramide is not obligatory and nitramide is deprotonated immediately under the action of a base.[44, 131]



It was established that the generally accepted pathway of decomposition (with isomerization) takes place in the presence of bases with p$K_{BH^+} \leqslant 8$, and the second pathway (without isomerization) is more characteristic of bases with p$K_{BH^+} > 10$. Both processes can occur with bases possessing pK values in the range between these two limiting cases.

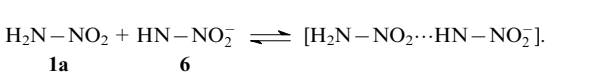


The mechanism of the base-catalysed decomposition of nitramide in aqueous buffered solutions of monofunctional alcohol anions (RO^-) and bifunctional *gem*-diol monoanions [$R_2C(OH)O^-$] was investigated; it was shown that the monofunctional anions give a good Brønsted relation, while the bifunctional anions deviate from this relation. The latter are more reactive than predicted. Apparently, the bifunctional anions act as bifunctional acid-base catalysts, which donate and withdraw protons through a cyclic transition state **A**.

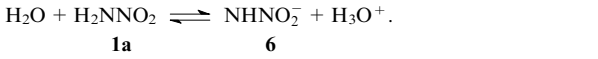


The rate constants for nitramide decomposition at 20.4 °C in aqueous solutions containing mono- ($CF_3CH_2O^-$) and bifunctional anions [$MeC(CF_3)(OH)O^-$] are equal to 0.951 and 1.26 litre mol^{-1} s^{-1}, respectively.[131]

Examination of proton transfer in the base-catalyzed decomposition of nitramide suggests that it is complexes of the anions of nitramide with the starting molecules (not the anions of nitramide themselves) that possess higher chemical reactivity (instability).[134]

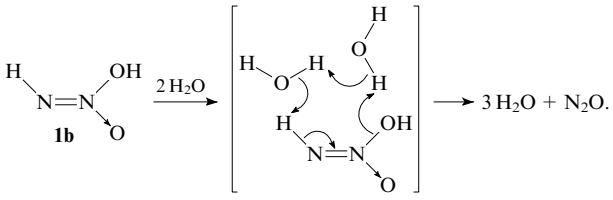


Water reacts with nitramide as a weak base and enables its dissociation.[126]



The rate constant for the decomposition of nitramide in water (as the first-order reaction) is 41.9×10^{-5} min^{-1} at 15 °C, which is higher than that in 0.01 M HCl (3.9×10^{-5} min^{-1}), *i.e.*, the decomposition of nitramide in dilute acidic aqueous solutions proceeds slower than in water. However, this process in water is very slow and is considered to be non-catalytic.

The non-catalytic decomposition of nitramide in water also proceeds *via* the tautomeric form **1b**.The most probable mechanism of this decomposition, as can be suggested, includes a cyclic transition state in which two molecules of water are linked by hydrogen bonds. Here one molecule of water acts as a proton-donor and the other acts as a base.[135, 136]



Thus, the non-catalytic decomposition of nitramide must be defined as a concerted process without involving an intermediate and it qualitatively differs from the acid- or base-catalyzed processes.

The rate of nitramide decomposition in D_2O was found to be lower than in H_2O.[78] Dissolution of nitramide in D_2O results in exchange of both protons and formation of D_2NNO_2 at a rather high rate.[137]

2. Behaviour of nitramide in non-aqueous media

Decomposition of nitramide in a 80 : 20 mixture of dimethyl sulfoxide with water catalyzed by anions of organic acids (Bu^tCO_2H, AcOH, $BnCO_2H$, $ClCH_2CO_2H$, *etc.*) proceeds at lower rates as compared with decomposition in water in the presence of the same catalysts.[138]

The effect of solvents on the decomposition of nitramide catalyzed by aniline derivatives was investigated and the observed rate constant for decomposition (k_{ef}) was shown[139–142] to depend on the dielectric constant of the solvent. The lowest value of k_{ef} was observed in non-polar solvents, *e.g.*, in diethyl ether, and the highest one was observed in solvents containing hydroxyl groups.[142]

This regularity was also confirmed by the results of studies of nitramide stability in different solvents.[125] Higher stability in acetonitrile and ether and lower stability in isopropyl alcohol were explained by association of nitramide molecules with the molecules of these solvents through H-bonds, which was further confirmed by NMR studies.[54] In hydroxyl-containing solvents, the association has more complex character due to an increase in the acidity of the protons of the amino group and formation of the unstable anion $[HNNO_2\cdots HOR]^-$.

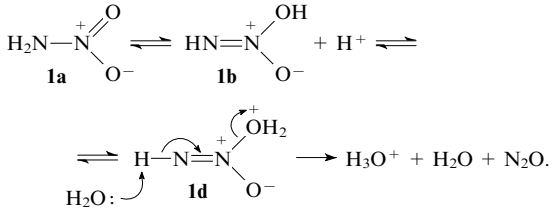
Decomposition of nitramide in mixtures of dioxane with water at 20 °C decreases 42-fold as the concentration of dioxane increases from 0% to 92.5%, and 80-fold at 50 °C.[143]

3. Acid-catalyzed decomposition of nitramide

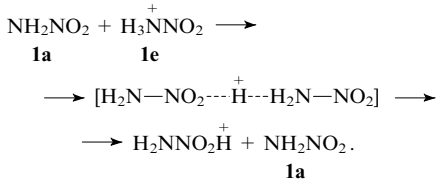
Studies on decomposition of nitramide in acid solutions with acid concentrations in the range 0.01–0.4 mol litre^{-1} and in the narrow interval of temperatures (from 15 to 25 °C) failed to reveal the dependence of the rate constants on acidity of these solutions (or this dependence is very weak).[126, 144–146]

Distinct dependences of the rate constants on the acidity of solutions were established for the acid-catalyzed decomposition of nitramide in a wide range of concentrations up to 20%–80% of hydrochloric, perchloric and sulfuric acids.[78, 135, 147]

A mechanism of the acid-catalyzed decomposition of nitramide was proposed[135] that included the *O*-protonated aci-form of nitramide (**1d**) and its nucleophilic cleavage with water as the rate-limiting step.



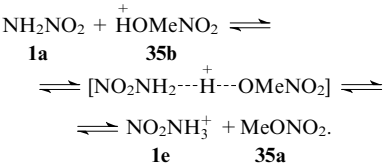
Thermodynamic calculations confirmed[148] that O-protonation of the nitro group is more preferable. The possibility of N-protonation with formation of the species **1e** is not ruled out, but intermolecular rearrangement leads to the proton transfer to the oxygen atom.



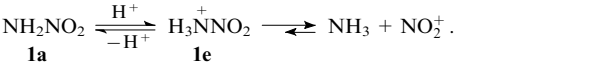
Only dinitrogen oxide and water were found as the decomposition products of nitramide in acidic media. Thus, the mechanism of the acid-catalyzed decomposition of nitramide in aqueous acid solutions is similar to that of a number of primary aliphatic nitramines.[149–151]

4. Nitramide as a nitrating agent in acidic media

As has already been mentioned, nitramide is a weak acid, theoretically it can be N-protonated at the amino group in both strong and rather weak acids. For example, in the protonated methyl nitrate (**35b**)–nitramide system, the proton easily migrates to nitramide possessing more basic properties.[152]



Transformations of nitramide in acidic media can be represented by the following equation:



The negative charge on the N-atom of the amino group of nitramide changes insignificantly upon protonation. It is the charges on the nitrogen and oxygen atoms of the nitro group and hydrogen atoms of the amino group that are mainly affected (Fig. 3). According to calculations,[153] the N-protonation of nitramide results in the increase in the N–N and N–O bond lengths from 1.427 and 1.206 Å to 1.639 and 1.259 Å, respectively.

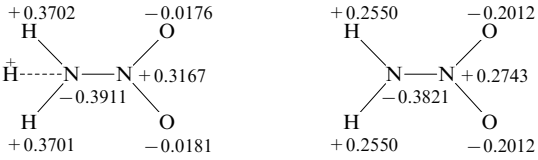
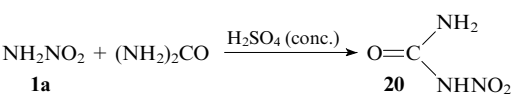


Figure 3. Distribution of charges on atoms in protonated (*a*) and non-protonated (*b*) forms of nitramide.[153]

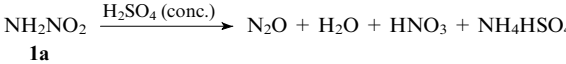
The possibility of N-protonation with subsequent denitration has been discussed repeatedly,[6, 153] but attempts to identify the decomposition products of the nitramide *N*-protonated form failed for a long time. Isolation of some products of nitration by nitramide can be considered as evidence for this reaction.[43] Nitramide decomposes in concentrated sulfuric acid or weak oleum at temperatures from 0 to −30 °C with formation of nitric acid as the reaction product. At −30 °C, dinitramide can be identified by spectrophotometry.

The addition of a nucleophilic reagent, for example, urea, to concentrated sulfuric acid or oleum at 0 ± 5 °C and then nitramide affords nitrourea in yields up to 12%.



Under similar conditions, toluene is converted to mononitrotoluene and urethane forms nitrourethane in the yields 14%–16%.

Thus, under the specified conditions the decompositon of the O-protonated form of nitramide is accompanied by formation and decomposition of the *N*-protonated form; nitric acid and ammonium hydrogensulfate together with dinitrogen oxide and water are the decomposition products of this form in concentrated (>94%) sulfuric acid.

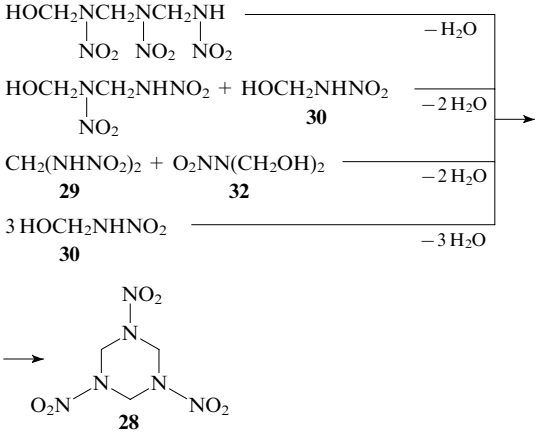


1a

5. Reactions of nitramide with aldehydes

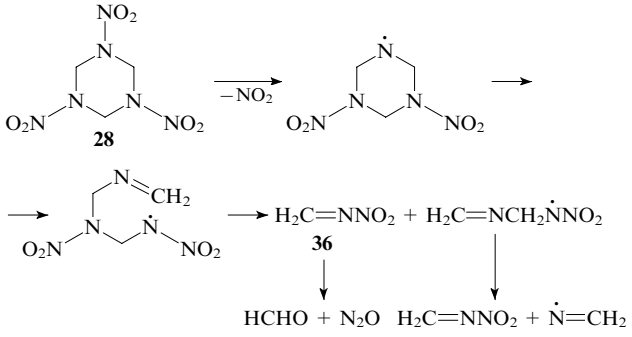
Back in the middle of the 20th century, some investigators [154, 155] considered the reaction products of nitramide with formaldehyde as intermediates in nitrolysis of urotropine or in decomposition of cyclic nitrolysis products. Since polymethylenenitramines were formed as the products,[156–160] it was suggested that hydroxymethylnitramine (**30**) and methylenenitrimine (**36**) served as the intermediates, but attempts to isolate these compounds failed.

The use of modern methods, in particular NMR, in a study of urotropine nitrolysis made it possible to identify various intermediates including bis(hydroxymethyl)nitramine (**32**).[161] The mechanism of formation of hexogen (**28**) was discussed in which nitramide hydroxymethyl derivatives play the key role.



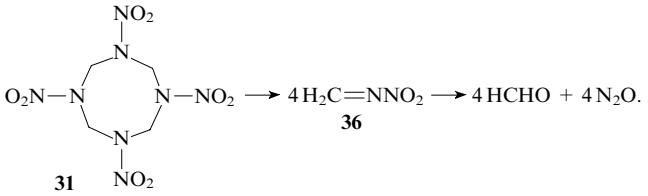
29 **32** **30** **28**

More detailed investigations of decomposition of cyclic nitramines [hexogen (**28**) and octogen (**31**)] [162–165] together with the analysis of their thermodestruction,[166] as well as computer simulation of thermodestruction of these compounds and *N*,*N*′-dinitropiperazine [167–169] allowed suggesting with high probability a scheme of decomposition of cyclic nitramines *via* methylenenitrimine (**36**).[166]



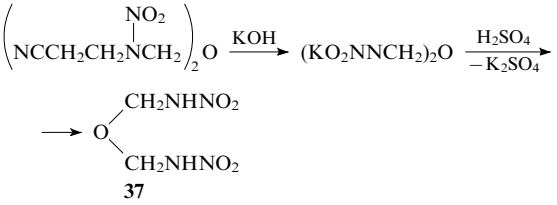
28 **36**

The use of isotopically modified compounds made it possible to obtain results essential for the interpretation of the mechanism of thermodestruction.[170] From the study of thermolysis of octogen (**31**) containing the ^{15}N-labelled NO_2 group and the ^{14}N-labelled amino group it was concluded that it is the C–N bonds rather than the N–N bonds that undergo predominant cleavage. A mechanism of the thermodestruction with simultaneous cleavage of four C–N bonds with formation of methylenenitrimine (**36**) was proposed.



36 **31**

Bis(nitraminomethyl) ether (**37**) was synthesized by an indirect route; this crystalline compound proved to be very reactive.[171]



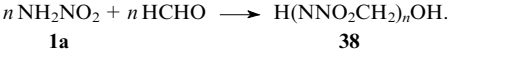
37

Bis(hydroxymethyl)nitramine or (2-nitro-2-azapropane-1,3-diol, **32**) can be obtained by coupling of nitramide with formaldehyde in aqueous solutions.[43, 69, 172]



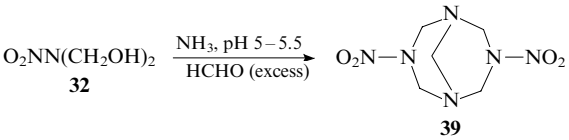
1a **32**

The changes in proportions of the reactants result in polymethylenenitramines **38** in high yields.[173]



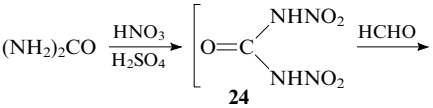
1a **38**

Bis(hydroxymethyl)nitramine (**32**) is used for the synthesis of a number of cyclic nitramines,[174] including 1,5-dinitro-3,7-endomethylene-1,3,5,7-tetrazacyclooctane (DPT, **39**), which is the intermediate in production of octogen.

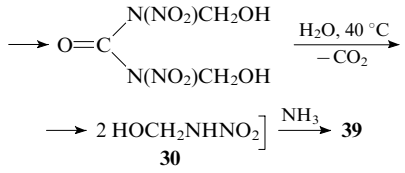


32 **39**

Since urea is the most available starting material for the synthesis of nitramide, the method of the production of DPT from urea has great perspectives.[175, 176]

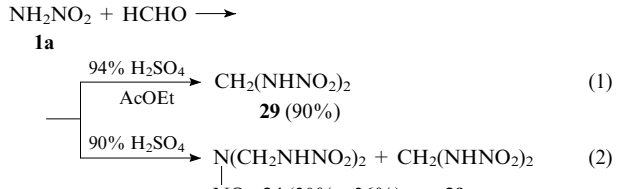


24



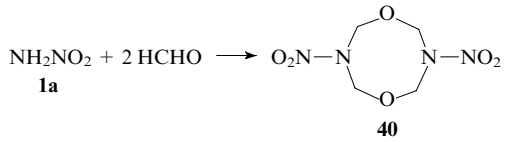
Synthesis of DPT from nitrourea[177] proceeds presumably *via* bis(hydroxymethyl)nitramide (**32**)[178] as well.

The reaction of nitramide with formaldehyde in the presence of sulfuric acid produces a number of products.[43] If this reaction is carried out in ethyl acetate at temperatures from −8 to −5 °C for 20 min, methylenedinitramine(**29**) can be obtained in yields up to 90% [reaction (1)]. Coupling of nitramide with paraformaldehyde in 90% sulfuric acid results in a mixture of methylendinitramine and 1,3,5-trinitro-1,3,5-triazapentane (**34**) [reaction (2)], the yields of the latter is 30% – 36% following separation and additional purification.

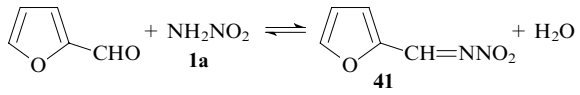


The ratio nitramide : formaldehyde varies in the range 3 : 1. The reaction (1) is a very suitable method for the efficient synthesis of methylenedinitramine.

The reaction with a twofold excess of formaldehyde results in 3,7-dinitro-1,5-dioxa-3,7-diazacyclooctane (**40**) in yields up to 80%.



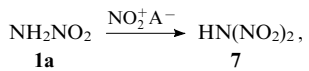
Condensation of nitramide with furfural produces the corresponding *N*-nitroaldimine (**41**).[179]



This is the only example of identification of nitrimine as the coupling product of nitramide with aldehydes.

6. Nitration of nitramide

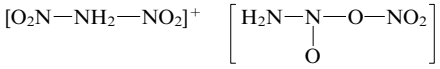
Nitration of nitramide with different nitrating reagents results in dinitramide **7**. The yields of dinitramide upon nitration with nitronium salts in acetonitrile or ethyl acetate[88,180] as well as by mixtures of nitric and sulfuric acids[181] are very high (85% – 95%) and depend on the methods of isolation of the product. This confirms once more high reactivity of nitramide.



A is an anion.

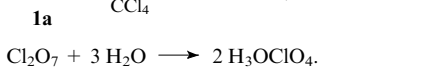
The use of nitronium salts as the nitrating agents permits this reaction to be carried out in various solvents and in a wide range of temperatures. Nitration of nitramide with nitric acid or with mixtures of nitric and sulfuric acids must be performed at temperatures from −30 to −35 °C in order to conserve the resulting dinitramide (**7**). In this case, the maximum yield of the product can be achieved within 5 – 7 min after beginning of the reaction.

Direct nitration of nitramide in the gas phase was studied by spectrometric method and computer calculations; it was assumed that the ions $[H_2N_3O_4]^+$ with different structures can be formed in the course of the reaction,[182] for example:



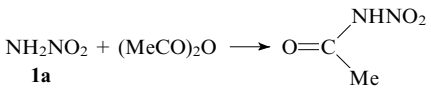
7. Reactions of nitramide with acid anhydrides

The reaction of nitramide with chlorine(VII) oxide in CCl_4 in a wide range of temperatures and concentrations of Cl_2O_7 (from 5% to 50%) was investigated, the evolution of N_2O was observed.[183] In the reaction carried out at 20 °C, fast decomposition of nitramide occurs and solid oxonium perchlorate forms.



At −40°C, the reaction proceeds very slowly and the intact nitramide can be found in the solid phase.

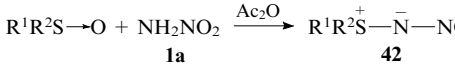
Nitramide dissolved in acetic anhydride affords nitroacetamide in yields up to 40% at room temperature.[43]



Recently, the possibility of nitramide acylation with acid anhydrides has been demonstrated, which opens up new prospects for the use of nitramide in organic synthesis.

8. The use of nitramide in synthesis of organosulfur nitro compounds

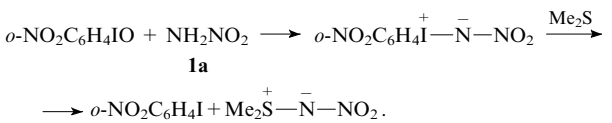
Nitramide reacts with sulfoxides in the presence of acetic anhydride with formation of sulfonium *N*-nitroimides **42**.[184]



R^1, R^2 = Me, Et, Ph.

The yields of the target products **42** (from 15% to 65%) depend on the nature of substituents.

The same compounds can be obtained by exchange reaction between iodonium *N*-nitroimides and dialkyl sulfides, for example:



The results of investigation of spectral properties and calculations of crystal lattice parameters of sulfonium *N*-nitroimides are documented.[185] A comparison of the IR spectra of nitramide (**1a**) and dimethylsulfonium *N*-nitroimide in the range 1600–1200 cm^{-1} reveals that absorption bands of the nitrimine group of the latter are shifted to the long-wave region: 1402 and 1273 cm^{-1} (for nitramide, these are 1546, 1534 and 1379 cm^{-1}).

Pentafluorosulfanylnitramide salts were obtained by reaction of basic reagents with octyl *N*-(pentafluorosulfanyl)-*N*-nitrocarbamate (**43**): in particular, potassium salt **44** was obtained[186] upon action of potassium methoxide in methanol.

$$\underset{\mathbf{43}}{SF_5N(NO_2)CO_2C_8H_{17}\text{-n}} \xrightarrow[MeOH,\ -60\ ^\circ C]{KOMe} \underset{\mathbf{44}}{KSF_5NNO_2^-} + MeCO_2C_8H_{17}\text{-n}.$$

This reaction is carried out in anhydrous media at temperatures from −40 to −60 °C. Structures and melting points of pentafluorosulfanylnitramide salts are close to analogous parameters of dinitramide salts, but exceed them in densities. For example, the melting point and the density of potassium dinitramide are equal to 139 °C and 2.20 g cm^{-3} , and for potassium pentafluorosulfanylnitramide (**44**) they are 137 °C and 2.56 g cm^{-3}, respectively.[186]

9. Miscellaneous reactions

Alkylation of nitramide with diazomethane leads to dimethylnitramine.[187] This is a single known reaction of nitramide alkylation.

$$\underset{\mathbf{1a}}{NH_2NO_2} + CH_2N_2 \longrightarrow \underset{\mathbf{9}}{Me_2NNO_2}.$$

Nitramide reacts with silver cyanate to produce nitrourea.[102]

$$\underset{\mathbf{1a}}{NH_2NO_2} + AgOCN \xrightarrow{HCl} \underset{\mathbf{20}}{O{=}C\begin{matrix}NH_2\\NHNO_2\end{matrix}} + AgCl\downarrow.$$

This is indirect evidence of reversibility of the synthesis of nitramide from nitrourea.

Hydrogenation of nitramide with hydrogen in acid solutions on different catalysts does not produce hydrazine. The total destruction of nitramide molecules occurs with formation of nitrogen and water.[188]

Polarographic reduction of nitramide revealed two cathodic polarographic waves, the half-wave potentials being pH-dependent. The minimum values of these potentials are 1.22 V at pH 4.5 and 1.58 V at pH 8.8. Presumably, nitramide converts first to nitrosoamide (**45**) and then to hydroxyhydrazine (**46**).[189]

$$\underset{\mathbf{1a}}{NH_2NO_2} \xrightarrow{2e^-} \underset{\mathbf{45}}{NH_2NO} \xrightarrow{2e^-} \underset{\mathbf{46}}{H_2NNHOH}.$$

Nitrosoamide (**45**) was found as the nitramide ionization product by electron impact in an ionization chamber of a mass spectrometer.[123] Nitrosoamide was stable for sufficiently long period of time to be detected.

$$NH_2NO_2^{+\bullet} \longrightarrow \underset{\mathbf{45}}{NH_2NO^{+\bullet}} \longrightarrow \underset{\mathbf{45}}{NH_2NO}.$$

Non-empirical calculations of the enthalpy of formation of nitrosoamide from the elements at 0 K showed that this value is 76.6 kJ mol^{-1} higher than that of nitramide. The N–N bond in nitrosoamide is shorter (1.343 Å), than in crystals of nitramide (1.401 Å).[190]

Over the past few years, considerable attention has been concentrated on the possibility of nitro–nitrite rearrangement in nitramide. In spite of the absence of direct experimental investigations of this reaction, the results of calculations suggest the possibility of this process. Different mechanisms of the rearrangement are considered in the literature.

As has already been noted (Section II.2), the nitro–nitrite rearrangement may proceed in the thermal decomposition of nitramide.[65] The MCSCF/4-31G optimized transition state for rearrangement of NH_2NO_2 to NH_2ONO is shown in Fig. 4.

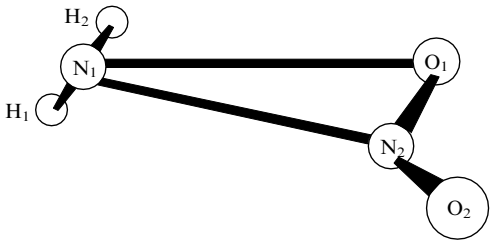


Figure 4. Optimized transition state in nitro–nitrite rearrangement.[65]

A one-step variant of the rearrangement is preferred in the study.[191]

With the use of the second-order multiconfigurational perturbation theory (CASPT2), potential energy surfaces were calculated for the process of nitramide decomposition ($NH_2NO_2 \rightarrow NH_2 + NO_2$) and for the nitro–nitrite isomerization of nitramide. Computations of numerical energy gradients for stationary points give evidence that the isomerization of nitramide proceeds through two-step pathway.[192]

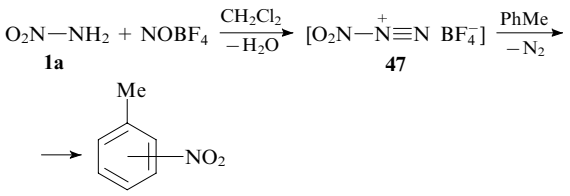
$$\underset{\mathbf{1a}}{NH_2NO_2} \longrightarrow NH_2 + NO_2 \longrightarrow \underset{\mathbf{5}}{NH_2ONO}.$$

The second step requires overcoming of an activation barrier.

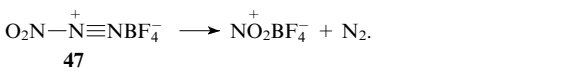
Compound **5** in the form of hydrochloride was assumed to form also in the reaction of nitrosonium tetrafluoroborate with hydroxylamine hydrochloride.[193]

$$HONH_2 \cdot HCl \xrightarrow{NOBF_4} ONONH_2 \cdot HCl.$$

Nitrodiazonium tetrafluoroborate (**47**)[194] is obtained in the reaction of nitrosonium tetrafluoroborate with nitramide in dichloromethane at 0 °C. Nitrodiazonium tetrafluoroborate reacts with toluene added to the reaction mixture with evolution of nitrogen and formation of a mixture of *o*-, *m*- and *p*-nitrotoluenes.



It is believed [194] that toluene is nitrated with nitronium tetrafluoroborate, which originates from nitrodiazonium tetrafluoroborate.



V. Conclusion

Modern investigations devoted to structure and physicochemical properties of nitramide confirm unambiguously the structure of nitramide as nitric acid amide (or nitramine). Calculated parameters of the structure of nitramide and a number of its characteristics are used as the reference values in investigations of structures and properties of primary and secondary nitramines with different substituents at the nitrogen atom.

Nitramide can be obtained upon destruction of nitramines as well as upon nitration of ammonia and its sulfo derivatives. The main condition of the successful preparations of nitramide is to preserve it in reaction mixtures during formation and isolation. From this point of view, the methods for the synthesis of nitramide from *N*,*N*′-dinitrourea and its salts as well as from nitroacetamide are the most promising.

High reactivity of nitramide manifests first of all in reactions involving the NH_2 group. Nevertheless, recent studies show that under more drastic conditions, for example, in gas-phase interconversions of nitramide, reactions involving the nitro group can occur. Such reactions as the nitro–nitrite rearrangement, formation of nitrosoamide in thermal destruction or reduction of nitramide are the examples.

The interest of scientists in investigations of properties of nitramide and methods of its synthesis does not cease for more than 100 years. This fact demonstrates that the chemistry of nitramide is still far from being exhausted. Literature data about alkylation of nitramide and its reactions with acid anhydrides are very scarce. Reactions of nitramide with aromatic aldehydes, especially with heterocyclic ones, and with glyoxal are also investigated scarcely. It is in this field that very promising ways of synthesis of new and well-known chemical compounds are opened.

References

1. J Thiele, A Lachmann *Ber. Dtsch. Chem. Ges.* **27** 1909 (1894)
2. A Lamberton *Q. Rev. Chem. Soc.* 75 (1951)
3. A L Fridman, V P Ivshin, S S Novikov *Usp. Khim.* **38** 1448 (1969) [*Russ. Chem. Rev.* **38** 640 (1969)]
4. O A Luk'yanov, V A Tartakovskii *Ros. Khim. Zh.* **41** (2) 5 (1997) [a]
5. J A Montgomery, H H Michels *J. Phys. Chem.* **97** 6774 (1993)
6. J Thiele, A Lachmann *Liebigs Ann. Chem.* **288** 267 (1895)
7. J Thiele *Liebigs Ann. Chem.* **296** 110 (1897)
8. A Hantzsch *Liebigs Ann. Chem.* **292** 340 (1896)
9. A Hantzsch *Liebigs Ann. Chem.* **296** 84 (1897)
10. A Hantzsch *Liebigs Ann. Chem.* **296** 111 (1897)
11. A Hantzsch, F E Dollfus *Ber. Dtsch. Chem. Ges.* **35** 226 (1902)
12. P Harteck *Ber. Dtsch. Chem. Ges.* **66** 423 (1933)
13. W Traube *Liebigs Ann. Chem. B* **300** 81 (1898)
14. A Hantzsch, E Strasser *Ber. Dtsch. Chem. Ges.* **64** 655 (1931)
15. A Hantzsch *Ber. Dtsch. Chem. Ges.* **66** 1566 (1933)
16. G Hanter, J Partington *J. Chem. Soc.* 309 (1933)
17. K W Kolerausch, H Wittek *Acta Phys. Austr.* 292 (1948)
18. K Clusius *Helv. Chim. Acta* **44** 1149 (1961)
19. J K Tyler *J. Mol. Spectrosc.* **11** 39 (1963)
20. A V Belik, S K Bakeeva V A Shlyapochnikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2608 (1977) [b]
21. J P Ritchie *J. Am. Chem. Soc.* **111** 2517 (1989)
22. J M Seminario, P Politzer *Int. J. Quantum Chem.* **26** 497 (1992)
23. N I Sadova, G E Slepnev, N A Tarasenko, A A Zenkin, L V Vilkov, I F Shishkov, Yu A Pankrushev *Zh. Strukt. Khim.* **18** 865 (1977) [c]
24. A V Belik, V A Shlyapochnikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2798 (1977) [b]
25. B V Lopatin *Teor. Eksp. Khim.* **13** 530 (1977) [d]
26. V A Rabinovich, Z Ya Khavin *Kratkii Khimicheskii Spravochnik* (Concise Chemical Handbook) (Leningrad: Khimiya, 1978) p. 33
27. *Handbook of Chemistry and Physics* (Boca Raton, FL: CRC Press, 2005) p. 9
28. L M Kostikova, E A Miroshnichenko, Y N Matyushin, in *Proceedings of the 31st Annual Conference of ICT, Karlsrue, 2000* p. 50/1
29. M Davis, N Jonathan *Trans. Faraday Soc.* **54** 469 (1958)
30. G Hofolinger *Chem. Ber.* **103** 3370 (1970)
31. N I Sadova, L S Khaikin, L V Vilkov *Usp. Khim.* **61** 2129 (1992) [*Russ. Chem. Rev.* **61** 1169 (1992)]
32. Ya V Salyn', K V Titova, E N Loginova, V I Nefedov, V Ya Rossolovskii *Zh. Neorg. Khim.* **22** 2998 (1977) [e]
33. V P Ivshin, O A Yashukova, V A Shlyapochnikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1295 (1986) [b]
34. P G Puranik, L Sirdeshmukh *Indian J. Pure Appl. Chem.* **7** 790 (1962)
35. O Gropen, P N Skanske *Acta Chem. Scand.* **25** 1241 (1971)
36. L E Harris *J. Chem. Phys.* **58** 5615 (1973)
37. K Ya Burshtein, I N Fundyler *Izv. Akad. Nauk SSSR, Ser. Khim.* 892 (1974) [b]
38. J Geith, T M Klapötke, R D Harcourt, P P Wolynec *Z. Naturforsch., B* **56** 571 (2001)
39. S Huajie, X Heming, D Haishan *Sci. China, Ser. B* **47** 466 (2004)
40. E C Boly, C M Desch *J. Chem. Soc.* 1747 (1908)
41. K Koji, K Keiji, N Saburo *Bull. Chim. Soc. Jpn.* **37** 1055 (1964)
42. J Stals, C Barradough, A S Buchanan *Trans. Faraday Soc.* **65** 904 (1964)
43. A A Lobanova, S G Il'yasov, N I Popov, R R Sataev *Zh. Org. Khim.* **38** 11 (2002) [f]
44. C H Arrowsmith, A Awwal, B A Euser, A J Kresge, P P T Lau, D P Onwood, Y C Tang, E C Young *J. Am. Chem. Soc.* **113** 172 (1991)
45. J F Arenas, J C Otero, D Pelaez, J Soto *J. Phys. Chem. A* **109** 7172 (2005)
46. I Borges *Theor. Chem. Acc.* **121** 239 (2008)
47. A Häussler, T M Klapltke, H Riotrovski *Z. Naturforsch., B* **57** 151 (2002)
48. M Nonella, R P Mueller, R J Huber *J. Mol. Spectrosc.* **112** 142 (1985)
49. L S Khaikin, O E Grikina, V A Shlyapochnikov, J E Boggs *Izv. Akad. Nauk, Ser. Khim.* 2106 (1994) [b]
50. V A Shlyapochnikov, L S Khaikin, O E Grikina, N O Cherskaya, L E Maksimova, N F Pyatakov *Izv. Akad. Nauk, Ser. Khim.* 2241 (1998) [b]
51. V A Shlyapochnikov *Kolebatel'nye Spektry Alifaticheskikh Nitrosoedinenii* (Vibration Spectra of Aliphatic Nitro Compounds) (Ioshkar-Ola: Mariiskii State University, 2007)
52. N Jonathan *J. Mol. Spectrosc.* **5** 101 (1961)
53. J D Ray, R A Ogg *J. Chem. Phys.* **26** 1452 (1957)
54. G N Boiko, E N Loginova, K V Titova *Zh. Neorg. Khim.* **21** 3254 (1976) [e]

55. A P Cooney, M R Crampton, J K Scranage, P Golding *J. Chem. Soc., Perkin Trans. 2* 77 (1989)
56. J N Brønsted, A L Nicholson, A Delbanco *Z. Phys. Chem. A* **169** 379 (1934)
57. J N Brønsted, J E Vance *Z. Phys. Chem. A* **163** 240 (1933)
58. C A Buvers, A F Trotman-Dickenson *Acta Crystallogr.* **10** 34 (1954)
59. P Vast *Bull. Soc. Chim. Fr.* 2136 (1970)
60. J D Ray, R A Ogg *J. Phys. Chem.* **60** 1460 (1956)
61. A L Vereshchagin, N I Popov, E V Rudnev, in *Nauchno-tekhnicheskoe Tvorchestvo Aspirantov i Professorsko-prepodavatel'skogo Sostava (Materialy 3-i Yubileinoi Nauchno-prakticheskoi Konferentsii)* [Scientific and Technical Work of Post-graduates and the Teaching Staff (Proceedings of the Third Anniversary Scientific and Practical Conference), Biisk, 1995] p. 19; *Ref. Zh. Khim.* 17L79 (1996)
62. O V Dorofeeva, P I Pauline *Thermochim. Acta* **240** (1 – 2) 47 (1994)
63. M Sana, G Leroy, D Peeters, C Wilante *J. Mol. Struct. (THEOCHEM)* **164** 249 (1988)
64. J Stals *Aust. J. Chem.* **22** 2515 (1969)
65. R P Saxon, M Yoshimine *J. Phys. Chem.* **93** 3130 (1989)
66. J N Brønsted, C V King *J. Am. Chem. Soc.* **49** 193 (1927)
67. O A Luk'yanov, O V Anikin, V A Tartakovskii *Izv. Akad. Nauk, Ser. Khim.* 451 (1996) [b]
68. A P N Franchimont, E A Klobbie *Recl. Trav. Chim. Pays-Bas* **7** 354 (1888)
69. R Brian, A H Lamberton *J. Chem. Soc.* 1633 (1949)
70. J Brühl *Z. Phys. Chem. A* **22** 388 (1897)
71. Yu V Serov, A G Bazanov, I V Tselinskii *Zh. Org. Khim.* **16** 472 (1980) [f]
72. B V Gidaspov, I V Tselinskii, V V Mel'nikov, N V Margolis, N V Grigor'eva *Zh. Obshch. Khim.* **65** 995 (1994) [g]
73. V A Shlyapochnikov, N O Cherskaya, O A Luk'yanov, V P Gorelik, V A Tartakovskii *Izv. Akad. Nauk, Ser. Khim.* 1610 (1994) [b]
74. R N Jones, C D Thorn *Can. J. Res. B* **27** 828 (1949)
75. J C Bottaro, R J Schmitt, P E Penwell, M Petrie, R Malhotra *Synthesis* 1151 (2007)
76. S R Harris *J. Am. Chem. Soc.* **80** 2302 (1958)
77. A A Astrat'ev, L L Kuznetsov *Zh. Org. Khim.* **38** 1308 (2002) [f]
78. Ch A Marlies, V K La Mer *J. Am. Chem. Soc.* **57** 1812 (1935)
79. C Canis *Rev. Chim. Miner.* **1** 521 (1964)
80. M Schmeisser *Z. Anorg. Allg. Chem.* **255** 33 (1948)
81. H H Batoy, H H Sisler *J. Am. Chem. Soc.* **74** 3408 (1952)
82. P Vast, J Heubel *C.R. Hebd. Seances Acad. Sci.* **260** 5799 (1965)
83. P Vast, J Heubel *C.R. Seances Acad. Sci., Ser. C* **264** 1697 (1967)
84. P Vast *Rev. Chim. Miner.* **7** 757 (1970)
85. H Barbes, P Vast *Rev. Chim. Miner.* **8** 851 (1971)
86. Yu P Guk, M A Ilyushin, E L Golod, B V Gidaspov *Usp. Khim.* **52** 499 (1983) [*Russ. Chem. Rev.* **52** 284 (1983)]
87. US P. 3071438; *Chem. Abstr.* **59** 447 (1963)
88. O A Luk'yanov, S N Shvedova, E N Shepelev, O N Varfolomeeva, N N Milkina, V A Tartakovskii *Izv. Akad. Nauk, Ser. Khim.* 1569 (1996) [b]
89. WO 91/19669; *Chem. Abstr.* **116** 217513 (1991)
90. US P. 5316749; *Chem. Abstr.* **121** 60802g (1994)
91. R N Musin, M C Lin *J. Phys. Chem. A* **102** 1808 (1998)
92. A R Whyte, L F Phillips *Chem. Phys. Lett.* **102** 451 (1983)
93. E Divers, T Haga *J. Chem. Soc.* 1620 (1896)
94. A Schmidt *J. Prakt. Chem.* **6** 201 (1958)
95. P Baumgarten *Ber. Dtsch. Chem. Ges.* **71** 80 (1938)
96. D Attwood, G Stedman *J. Chem. Soc. Dalton Trans.* 508 (1976)
97. M N Hughes, T R Lusty *Inorg. Nucl. Chem. Lett.* **13** 37 (1977)
98. M N Hughes, T R Lusty, H L Walles *J. Chem. Soc., Dalton Trans.* 530 (1978)
99. M W Hughes, J R Lasty *J. Chem. Soc., Dalton Trans.* 1175 (1976)
100. J Houbel, C Canis *C.R. Hebd. Seances Acad. Sci.* **255** 708 (1962)
101. S Teller-Pollon, J Houbel *Rev. Chim. Miner.* **4** 413 (1967)
102. T Davis *J. Am. Chem. Soc.* **44** 868 (1922)
103. T Davis, A Abrams *J. Am. Chem. Soc.* **47** 1043 (1925)
104. T Davis, K Blanchard *J. Am. Chem. Soc.* **51** 1790 (1929)
105. X Heming, L Yumin, L Yongfu *Propell. Explos. Pyrotech.* **23** 23 (1998)
106. J J Weigand, Ph.D. Thesis, Ludwic-Maximilian-University of München, 2005
107. R A Cox *J. Chem. Soc. Perkin Trans.* 1743 (1997)
108. F Dewhurst, A Lamberton *J. Chem. Soc. B* 788 (1971)
109. G W Watt, R C Makosky *Ind. Eng. Chem.* **46** 2599 (1954)
110. M Syczewski, I Ciéslowska-Glińska, H Boniuk *Propell. Explos. Pyrotech.* **23** 155 (1998)
111. A A Lobanova, R R Sataev, N I Popov, S G Il'yasov *Zh. Org. Khim.* **36** 188 (2000) [f]
112. P Goede, N Wingborg, H Bergman, N V Latypov *Propell. Explos. Pyrotech.* **26** 17 (2001)
113. S G Il'yasov, A A Lobanova, N I Popov, R R Sataev *Zh. Org. Khim.* **38** 1793 (2002) [f]
114. C Ye, H Gao, B Twamley, J M Shreeve *New J. Chem.* **32** 317 (2008)
115. S G Il'yasov, A A Lobanova, E A Litvinova, in *Prikladnye Aspekty Sovershenstvovaniya Khimicheskikh Tekhnologii i Materialov (Materialy Vseros. Nauchno-prakticheskoi Konf.)* [Applied Aspects of Improvement of Chemical Engineering Processes and Materials (Proceedings of All-Russian Scientific and Practical Conference)], Biisk, 1998 p. 119; *Ref. Zh. Khim.* 01.18-19N179 (2001)
116. S G Il'yasov, A A Lobanova *Zh. Org. Khim.* **38** 1866 (2002) [f]
117. A A Astrat'ev, D N Dashko, L L Kuznetsov *Zh. Org. Khim.* **39** 537 (2003) [f]
118. M L Bonin, D Bejan, L Schutt, J Hawari, N J Bunce *Environ. Sci. Technol.* **38** 1595 (2004)
119. V K Balakrishnan, A Halasz, J Hawari *Environ. Sci. Technol.* **37** 1838 (2003)
120. J Hawari, A Halasz, S Beaudet, L Paquet, G Ampleman, S Thiboutot *Environ. Sci. Technol.* **35** 70 (2001)
121. S G Il'yasov, A A Lobanova *Zh. Obshch. Khim.* **75** 130 (2005) [g]
122. L T Eremenko, V V Arakcheeva, G V Lagodzinskaya, B S Fedorov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2407 (1984) [b]
123. H Egsgaart, L Carisen, T Weiske, D Suelzle, H Schwarz *Chem. Phys. Lett.* **199** 643 (1992)
124. T M Nagiev, R D Sadykov, P S Nagi-zade *Zh. Fiz. Khim.* **53** 1621 (1979) [h]
125. K V Titova, E I Kolmakova, V Ya Rossolovskii *Zh. Neorg. Khim.* **23** 1143 (1978) [e]
126. J N Brönstead, K Pedersen *Z. Phys. Chem.* **108** 185 (1924)
127. J N Brönstead, K Volqvartz *Z. Phys. Chem.* **155** 211 (1931)
128. I K J Tong, A R Olson *J. Am. Chem. Soc.* **63** 3406 (1941)
129. C V King *J. Am. Chem. Soc.* **60** 144 (1938)
130. R P Bell, G L Wilson *Trans. Faraday Soc.* **46** 407 (1950)
131. C H Arrowsmith, A J Kresge, Y C Tang *J. Am. Chem. Soc.* **113** 179 (1991)
132. A J Kresge, Y C Tang, A Awwal, D P Onwood *J. Chem. Soc., Chem. Commun.* 310 (1980)
133. C H Arrowsmith, Ph.D. Thesis, University of Toronto, 1986; *Diss. Abstr. Int. B* **47** 4159 (1987)
134. K K Kalnin'sh *Zh. Prikl. Khim.* **80** 956 (2007) [i]
135. R A Cox *Can. J. Chem.* **74** 1779 (1996)
136. M Eckert-Maksic, H Maskill, I Zrinski *J. Chem. Soc., Perkin Trans.* 2147 (2001)
137. V K La Mer *J. Am. Chem. Soc.* **61** 2552 (1939)
138. P De Maria, A Fini *J. Solution Chem.* **6** 727 (1977)
139. G C Fettes, J A Kerr, F McClure, J S Slater, C Steel, A F Trotman-Dickenson *J. Chem. Soc.* 2811 (1957)
140. W W Carnie, P M Duncan, J A Kerr, K Shannon, A F Trotman-Dickenson, J A White *J. Chem. Soc.* 3231 (1959)
141. D D Callander, W D Ferguson, G C Fettis, A F Trotman-Dickenson *J. Chem. Soc.* 3834 (1960)
142. E F Caldin, J Peacock *Trans. Faraday Soc.* **51** 1217 (1955)
143. A Voipio *Suomen Kem. B* **29** 170 (1956)
144. L P Bell, G M Waind *J. Chem. Soc.* 2357 (1951)
145. B Perlmutter-Hauman, M A Woitt *Isr. J. Chem.* **7** 153 (1969)
146. M N Hughes, P E Wimbldon *Inorg. Chim. Acta* **65** 129 (1982)

147. A A Astrat'ev, L L Kuznetsov, B V Gidaspov *Zh. Org. Khim.* **33** 182 (1997) [f]
148. M Attina, F Cacace, E Ciliberto, G De Petris, F Grandinetti, F Pepi, A Ricci *J. Am. Chem. Soc.* **115** 12398 (1993)
149. J Barrott, I N Denton, A H Lamberton *J. Chem. Soc.* 1998 (1953)
150. P Bruck, A H Lamberton *J. Chem. Soc.* 4198 (1957)
151. R A Cox *Can. J. Chem.* **74** 1774 (1996)
152. G de Petris, F Peri *Chem. Phys. Lett.* **285** 366 (1998)
153. A C Hopkinson, I G Csizmadia *Theor. Chim. Acta* **34** 93 (1974)
154. W J Chute, O C Downing, A F Mc Kay, G S Myers, G F Wright *Can. J. Res. B* **27** 218 (1949)
155. C Castorina, J R Autera *Ind. Eng. Chem. Prod. Res. Dev.* **4** 170 (1965)
156. E Aristoff, J A Graham, R H Meen, G S Myers, G F Wright *Can. J. Res. B* **27** 531 (1949)
157. D Woodcock *J. Chem. Soc.* 1635 (1949)
158. A F Mc Kay, H H Richmond, G F Wright *Can. J. Res. B* **27** 402 (1949)
159. W J Chute, A F Mc Kay, R H Meen, G S Myers, G F Wright *Can. J. Res. B* **27** 503 (1949)
160. A H Lamberton, C Lindley, J C Speakman *J. Chem. Soc.* 1650 (1949)
161. Z Fang, S Wang, F Li *Propell. Explos. Pyrotech.* **23** 317 (1998)
162. X Zhao, E J Hintza, Y T Lee *J. Chem. Phys.* **88** 801 (1988)
163. S A Shackelford, M B Coolidge, B B Goshgarian, B A Loving, R N Rogers, J L Janney, M H Ebinger *J. Phys. Chem.* **89** 3118 (1985)
164. C F Melius *J. Phys. Colloq.* **48** 341 (1987)
165. M Farber, R D Srivastava *Chem. Phys. Lett.* **64** 307 (1979)
166. Yu Shu, B L Korsunskii, G M Nazin *Usp. Khim.* **73** 320 (2004) [*Russ. Chem. Rev.* **73** 293 (2004)]
167. T S Pivina, E V Sokerina, D E Lushnikov, A A Porollo, V P Ivshin *Propell. Explos. Pyrotech.* **24** 99 (1999)
168. T Petukhova, A Porollo, V Korolev, V Ivshin, Y Surikova, T Pivina, in *The 33th Annual Conference of ICT, Karlsrue, 2002* p. 60/1
169. V L Korolev, T S Pivina, A A Porollo, T V Petukhova, A B Sheremetev, V P Ivshin *Usp. Khim.* **78** 1022 (2009) [*Russ. Chem. Rev.* **78** 945 (2009)]
170. B Suryanarayana, R J Graybuch, J R Autera *Chem. Ind.* 2177 (1967)
171. A A Lobanova, N I Lukina, N I Popov, in *Tekhnicheskaya Khimiya. Ot Teorii k Praktike (Dokl. Mezhdunar. Konf.)* [Technical Chemistry. From Theory to Practice (Abstracts of International Conference), Perm', 2008] Vol. 1, p. 283
172. A N Gafarov, G T Shakirova *Izv. Akad. Nauk, Ser. Khim.* 1939 (2009) [b]
173. Z Raszewski, M Syczewski *Propell. Explos. Pyrotech.* **24** 366 (1999)
174. M A Ishchenko, V D Nikolaev, A A Sokolov *Zh. Org. Khim.* **33** 1877 (1997) [f]
175. S G Il'yasov, A A Lobanova, N I Popov, R R Sataev *Zh. Org. Khim.* **38** 1800 (2002) [f]
176. RF P. 2198886; *Ref. Zh. Khim.* 19H141 (2003)
177. US P. 4338442; *Ref. Zh. Khim.* 6H274P (1983)
178. X M Liu, X H Zhang *Kogyo Kayaku* **52** 96 (1991)
179. J W Suggitt, G S Myers, G F Wright *J. Org. Chem.* **12** 373 (1947)
180. J C Bottaro, P E Penwell, R J Schmitt *J. Am. Chem. Soc.* **119** 9405 (1997)
181. US P. 5976483; *Chem. Abstr.* **126** 227269 (1999)
182. F Bernardi, F Cacace, G Petris, F Pepi, I Rossi *J. Phys. Chem. A* **102** 1987 (1998)
183. K V Titova, E N Loginova *Zh. Neorg. Khim.* **40** 1781 (1995) [e]
184. O P Shitov, A P Seleznev, V A Tartakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 1237 (1991) [b]
185. K I Rezchikova, N V Grigor'eva, O P Shitov, V A Shljapochnikov *Mendeleev Commun.* 106 (1991)
186. M E Sitzmann, R Gillardi, R J Butcher, W M Koppes, A G Stern, J S Thrasher, N J Trivedi, Z Yang *Inorg. Chem.* **39** 843 (2000)
187. J Heinke *Ber. Dtsch. Chem. Ges.* **31** 1395 (1898)
188. M N Hughes, M Okolow-Zubkowska, H L Wallis *J. Chem. Soc., Dalton Trans.* 2009 (1981)
189. A Calusaru *Talanta* **20** 1334 (1973)
190. Z Chen, T P Hamilton *J. Phys. Chem. A* **103** 11026 (1999)
191. J Guanzhi, J Quan *Gaodeng Xuexiao Huaxue Xuebao* **12** 1669 (1991); *Chem. Abstr.* **117** 38015 (1991)
192. J Soto, J F Arenas, J C Otero, D Pelaez *J. Phys. Chem. A* **110** 8221 (2006)
193. G A Olah, R Herges, K Laali, G A Segal *J. Am. Chem. Soc.* **108** 2054 (1986)
194. G A Olah, K Laali, M Farmia, J Shih, D P Singh, K O Christe *J. Org. Chem.* **50** 1338 (1985)

[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[c] — *J. Struct. Chem. (Engl. Transl.)*
[d] — *Theor. Exp. Chem. (Engl. Transl.)*
[e] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[f] — *Russ. J. Org. Chem. (Engl. Transl.)*
[g] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[h] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[i] — *Russ. J. Appl. Chem. (Engl. Transl.)*