

Dedicated to Full Member of the Russian Academy of Sciences
V.A. Tartakovskii on the 70th Anniversary of His Birth

Chemistry of Urea Nitro Derivatives: III.* Reactions of *N,N'*-Dinitrourea with Bases

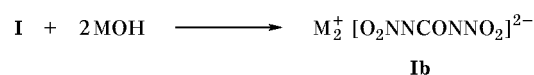
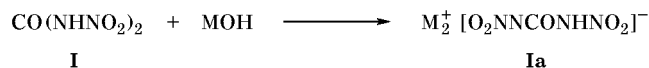
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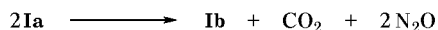
Abstract—*N,N'*-Dinitrourea reacts with bases to form the corresponding acid or neutral salts. Its reaction with hydrazine yields 4-nitrosemicarbazide, and the reaction with hydroxylamine leads to *N*-hydroxy-*N'*-nitrourea.

The development of a simple procedure for preparation of *N,N'*-dinitrourea has opened a new way to *N*-nitroamines starting from urea [1, 2]. The availability of *N,N'*-dinitrourea salts makes it possible to synthesize new compounds on their basis. Symmetric *N,N'*-dinitrourea is a fairly strong dibasic acid which is capable of undergoing stepwise ionization with formation of acid and neutral salts [2]:

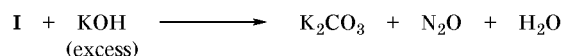


M = Na, K, Cs.

The existence of acid salts **Ia** was proved by physical methods, as well as by the transformations **Ia** → **I** and **Ia** → **Ib**. Neutral salts **Ib** are formed on prolonged heating of aqueous solutions of salts **Ia**:



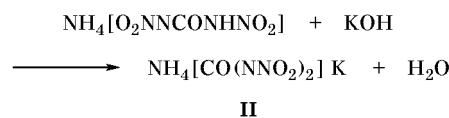
In the presence of excess alkali, these salts undergo complete decomposition:



All dinitrourea salts, especially acid, are very sensitive to impact and are capable of decomposing with

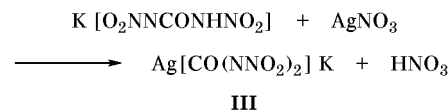
explosion; therefore, they should be handled with special precautions.

While studying reactions of acid dinitrourea salts with alkalis, salts containing various cations were obtained. Treatment of an aqueous solution of dinitrourea monoammonium salt with aqueous KOH and subsequent precipitation with ethyl alcohol gave a salt whose melting point (194°C) clearly differed from that of the initial monoammonium salt (105–107°C):

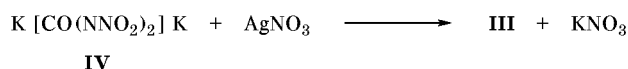


This reaction could give rise to both dipotassium (mp 182–186°C) (Table 1) and diammonium dinitrourea salt (mp 135°C). The concentrations of K⁺ and NH₄⁺ cations in the salt, determined by potentiometric titration, are consistent with the binary salt structure. However, this does not mean that it is not a mixture of two or three substances. On the other hand, a mixture of substances usually has a lower melting point than those of the pure components.

A distinct proof for the existence of binary dinitrourea salts was obtained by quantitative preparation of of potassium–silver salt **III**. The same product was synthesized from dinitrourea dipotassium salt **IV** by exchange reaction with silver nitrate:

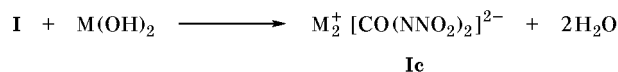


* For communication II, see [1].



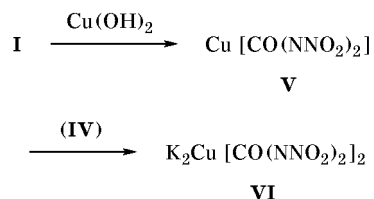
When dinitrourea was taken as initial compound, the reaction followed the standard scheme to give the silver salt.

Treatment of dinitrourea or its salts with bases or the corresponding bivalent metal salts gives dinitrourea salts containing either similar or different cations, depending on the conditions:



M = Mg; Ca; Ba.

In the reaction with copper(II) hydroxide, the exchange process can be accompanied by complex formation where dinitrourea anion acts as ligand:



The reaction of dinitrourea dipotassium salt **IV** with copper(II) sulfate in solution was studied by spectrophotometry using the molar ratios technique which makes it possible to determine the composition of the resulting complexes. The smooth trend of curve 2 in Fig. 1 indicates dissociation in water of the complexes formed. Curve 1 in Fig. 1 has four plateaux

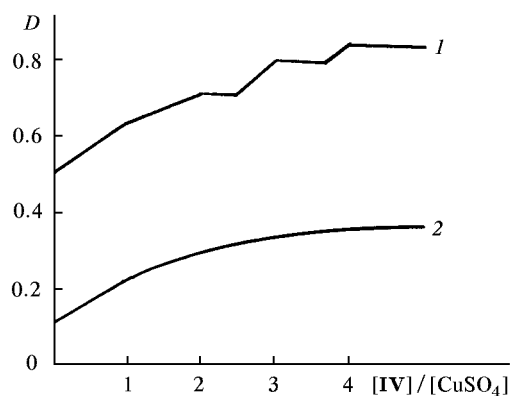
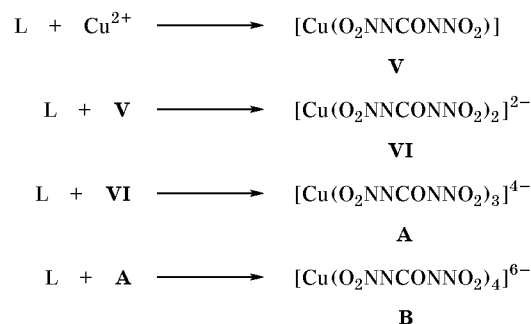


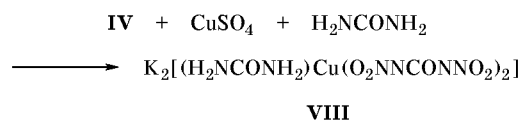
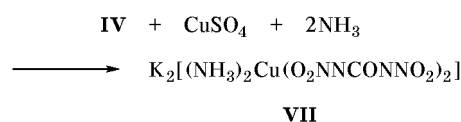
Fig. 1. Plots of optical density at $\lambda = 800$ nm of solutions versus molar ratio of *N,N'*-dinitrourea dipotassium salt (**IV**) and CuSO_4 : (1) water, $l = 2$ cm, $[\text{CuSO}_4] = 5 \times 10^{-3}$ M; (2) 0.05 N potassium hydrogen phthalate, $l = 5$ cm, $[\text{CuSO}_4] = 0.01$ M.

corresponding to the CuSO_4 :**IV** ratios 1:1, 1:2, 1:3, and 1:4; these data suggest formation of four kinds of complexes according to the following equations (which are typical of stepwise complex formation [3]):

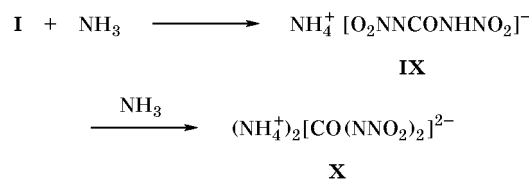


Among the assumed products, we isolated and identified compounds **V** and **VI**. Insofar as complexes **A** and **B** were not isolated, we believe that they exist in solution at spectrophotometric concentrations of 10^{-3} to 10^{-4} M.

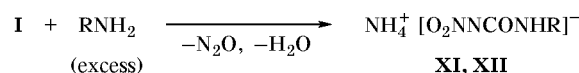
Wide prospects of the application of dinitrourea anion in the chemistry of coordination compounds are demonstrated by the synthesis of salts **VII** and **VIII** (Table 1).



Acid and neutral dinitrourea salts are also obtained with the use of ammonia and amines as bases.



Diammonium salts of dinitrourea undergo decomposition to give nitrourea monoammonium salts by the action of excess ammonia or amine.



XI, R = H; **XII**, R = Me.

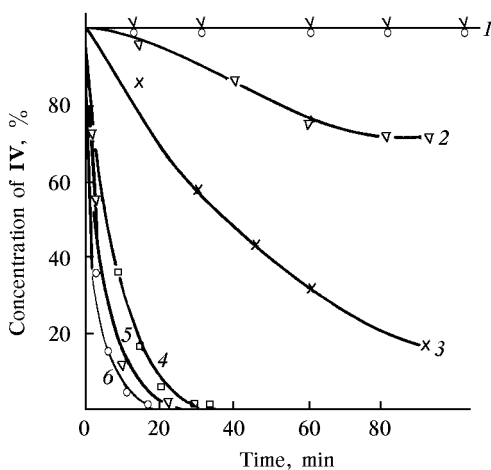
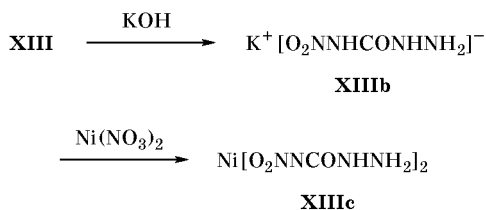


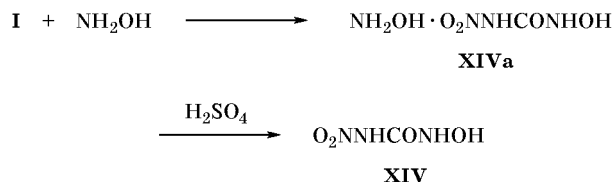
Fig. 2. Kinetic curves for decomposition of *N,N'*-dinitrourea dipotassium salt (**IV**) by the action of amines; **IV**-to-amine molar ratio 1:1, 30°C: (1) Et_2NH ($\text{p}K_a$ 11.09), (2) NH_3 ($\text{p}K_a$ 9.25), (3) BuNH_2 ($\text{p}K_a$ 10.78), (4) MeNH_2 ($\text{p}K_a$ 10.66), (5) NH_2OH ($\text{p}K_a$ 5.95), (6) H_2NNH_2 ($\text{p}K_a$ 6.5).

1585, and 1500 cm^{-1}). In the region of 3400 cm^{-1} we observed a weak diffuse band, and a strong band at 3180 cm^{-1} was present; however, we failed to assign these bands. By contrast, neutral form **XIII'** clearly shows in the IR spectrum absorption bands due to stretching vibrations of free NH_2 group (strong bands at 3460 and 3400 cm^{-1}).

4-Nitrosemicarbazide melts in the temperature range from 227 to 235°C (Boetius device). On repeated heating (after solidification), the sample melts at a higher temperature, 260 – 263°C . Derivatographic study of neutral form **XIII'** revealed an endo effect at 60 – 100°C , which indicates the presence of crystallization water. The structure of 4-nitrosemicarbazide (**XIII**) was also confirmed by its conversion into potassium and nickel salts **XIIIb** and **XIIIc**:



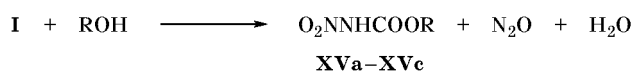
The reaction of dinitrourea with hydroxylamine leads to formation of hitherto unknown *N*-hydroxy-*N'*-nitrourea (**XIV**) which attracts interest from the viewpoint of synthesis of new high-energy compounds. While studying reactions of dinitrourea with bases, we have found that dinitrourea salts can also be used as substrates. *N,N'*-Dinitrourea dipotassium



salt (**IV**) readily reacts in water with ammonia, methylamine, butylamine, hydrazine, and hydroxylamine. In the UV spectra of the reaction mixtures we observed fast displacement of the absorption maximum at λ 274 nm, which is typical of dinitrourea, to the region 250 – 260 nm. These data indicate decomposition of the dinitrourea anion (Fig. 2) with formation of the corresponding potassium salts (Table 2).

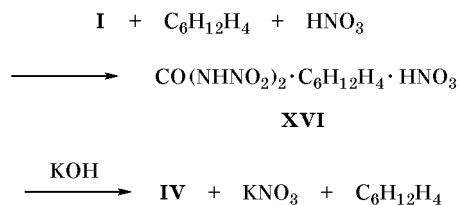
The amine basicity is the most important factor affecting the reactions of amines with dinitrourea salts; on the other hand, steric factor should also be taken into account. For example, no products were obtained in reactions of dinitrourea salts with secondary amines. Using dinitrourea monopotassium salt as starting compound, we isolated fairly pure samples of the target products which required no additional purification.

It is not recommended to carry out reactions with dinitrourea in alcohols as solvents. *N,N'*-Dinitrourea (**I**) readily reacts with alcohols even at low temperature to give the corresponding *N*-nitrocarbamates. On the other hand, this reaction provides a very simple and convenient procedure for preparation of *N*-nitrocarbamates.



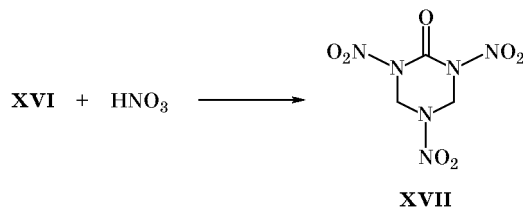
R = Me (a), Et (b), Pr (c).

Dinitrourea reacts with urotropin in the presence of nitric acid, yielding hexamethylenetetraammonium dinitrourea nitrate (**XVI**); treatment of the latter with potassium hydroxide leads to decomposition with formation of urotropin, *N,N'*-dinitrourea dipotassium salt, and potassium nitrate.



It is interesting that product **XVI** has structural fragments favoring formation of cyclic compounds.

Dissolution of **XVI** in concentrated nitric acid or its mixture with H_2SO_4 results in formation of 1,3,5-trinitrohexahydro-1,3,5-triazin-2-one (**XVII**). The synthesis of compound **XVII** will be discussed in more detail in our next communication.



EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer in KBr. The UV spectra of aqueous solutions were measured on Specord UV-Vis and Specord M-40 spectrophotometers. The concentration of crystallization water in crystal hydrates was determined by the thermogravimetric method on a Paulik–Paulik–Erdey derivatograph. Determination of metal cations (K^+ , Na^+ , Ba^{2+} , Cu^{2+}) in dinitrourea salts was performed by potentiometric titration in glacial acetic acid with a 0.1 N solution of perchloric acid in dioxane. Determination of Ag^+ in **III** was performed by indicator titration with a 0.1 N solution of ammonium thiocyanate in water. Potassium and silver cations in compound **III** were determined by potentiometric titration of its solution in AcOH with a 0.1 N solution of perchloric acid in dioxane (both K^+ and Ag^+ cations were titrated simultaneously within a single wave), followed by titration of a solution of **III** in water with 0.1 N ammonium thiocyanate (only Ag^+ was thus determined). The concentration of K^+ was determined from the difference between the experimental volume of 0.1 N perchloric acid (found in the titration in AcOH) and that calculated from the already known amount of silver. Nickel and copper cations were determined by complexometric titration with Trilon B.

N,N'-Dinitrourea (**I**), *N,N'*-dinitrourea monopotassium salt, and *N,N'*-dinitrourea dipotassium salt were prepared by the procedure described in [2].

Spectrophotometric study of reactions of *N,N'*-dinitrourea dipotassium salt (IV**) with amines.** To a solution of 2.26 g (0.01 mol) of dipotassium salt **IV** in 100 ml of water we added at $30 \pm 1^\circ\text{C}$ under continuous stirring 0.01 mol of appropriate amine. Samples were withdrawn immediately after mixing the reactants and then every 5 min. A 0.1-ml portion was placed in a 200-ml volumetric flask and was

weighed with an accuracy of ± 0.0001 g, the solution was adjusted to a required volume by adding distilled water, and the optical density at $\lambda = 274$ nm was measured. The concentration of **IV** in the reaction mixture g (g) was calculated by the formula

$$g = (M V a D) / (\epsilon a_0 \times 1000),$$

where M is the molecular weight of dinitrourea (226); V is the volume of the flask (200 ml); a_0 is the weight of the reaction mixture, g; D is the optical density; ϵ is the molar absorption coefficient of salt **IV** in water, $12400 \text{ l mol}^{-1} \text{ cm}^{-1}$; and a is the sample weight, g.

***N,N'*-Dinitrourea calcium salt (**Ic**, $M = \text{Ca}$).** To a solution of 5.52 g (0.03 mol) of dinitrourea diammonium salt in 20 ml of water we added at $20 \pm 2^\circ\text{C}$ under continuous stirring a solution of 7.08 g (0.03 mol) of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 15 ml of water, the mixture was kept for 30 min at $0\text{--}2^\circ\text{C}$, and the precipitate was filtered off, washed with water, ethyl alcohol, and ether, and dried at room temperature. Yield 1.69 g (30%). Decomposes at 212°C with explosion. Found, %: Ca^{2+} 15.3. $\text{Ca}[\text{CO}(\text{NNO}_2)_2] \cdot 3\text{H}_2\text{O}$. Calculated, %: Ca^{2+} 16.53.

***N,N'*-Dinitrourea potassium ammonium salt (**II**).** To a solution of 1.67 g (0.01 mol) of *N,N'*-dinitrourea monoammonium salt in 5 ml of water we added at 20°C under continuous stirring a solution of 0.56 g (0.01 mol) of potassium hydroxide in 5 ml of water. Ethyl alcohol, 10 ml, was then added, and the precipitate was filtered off, washed with ethyl alcohol and ether, and dried at room temperature. Yield 2.05 g (100%). Decomposes at 194°C with explosion. Found, %: K^+ 19.0; NH_4^+ 8.5. $\text{CH}_4\text{KN}_5\text{O}_5$. Calculated, %: K^+ 19.02; NH_4^+ 8.78.

***N,N'*-Dinitrourea potassium silver salt (**III**).** To a solution of 1.88 g (0.01 mol) of *N,N'*-dinitrourea monopotassium salt in 50 ml of water we added at 20°C under continuous stirring a solution of 1.7 g (0.01 mol) of silver nitrate in 50 ml of water. The precipitate was filtered off, washed with water, ethyl alcohol, and ether, and dried at room temperature. Yield 3.31 g (100%). Decomposes at 143°C with explosion. Found, %: Ag^+ 31.5; K^+ 10.7. $\text{CAgKN}_4\text{O}_5 \cdot 2\text{H}_2\text{O}$. Calculated, %: Ag^+ 32.63; K^+ 11.78.

***N,N'*-Dinitrourea copper(II) salt (**V**).** To a suspension of 1.105 g (5 mmol) of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ in 10 ml of water we added at 20°C under continuous stirring 1.5 g (0.01 mol) of dinitrourea. The mixture was stirred for 30 min, diluted with 40 ml of acetone, and filtered, and the filtrate was evaporated to dryness. Yield of salt **V** (trihydrate) 2.0 g (75%), blue crystals,

decomp. point 171°C. IR spectrum, ν , cm^{-1} : 3440 (H_2O); 1688 ($\text{C}=\text{O}$); 1608, 1600 (NNO_2); 1525, 1495, 1425, 1382, 1335, 1295 (NNO_2); 1185, 1075, 1025, 960, 880, 830, 790, 775, 750, 685. Found, %: Cu^{2+} 23.9; K^+ 10.7. $\text{Cu}[\text{CO}(\text{NNO}_2)_2] \cdot 3\text{H}_2\text{O}$. Calculated, %: Cu^{2+} 24.1.

Potassium bis(*N,N'*-dinitrocarbamido)cuprate(II) (VI). To a solution of 2.26 g (0.01 mol) of salt **IV** in 25 ml we added at 20°C under continuous stirring a solution of 1.25 g (5 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 5 ml of water. The precipitate was filtered off, washed with water, ethyl alcohol, and ether, and dried at 50–60°C under reduced pressure. Yield 2.1 g (95%). Decomposes at 182°C with explosion. IR spectrum, ν , cm^{-1} : 1645 ($\text{C}=\text{O}$), 1420, 1310, 1180, 970, 905, 775, 740. Found, %: C 5.3; Cu^{2+} 14.6; K^+ 17.25; N 24.9. $\text{C}_2\text{CuK}_2\text{N}_8\text{O}_{10}$. Calculated, %: C 5.48; Cu^{2+} 14.61; K^+ 17.81; N 25.57.

Potassium bis(*N,N'*-dinitrocarbamido)diamminecuprate(II) (VII) was synthesized in a similar way from salt **IV** and 1 ml (0.01 mol) of 26.7% aqueous ammonia. Yield 1.9 g (80%). Decomposes at 238°C with explosion. IR spectrum, ν , cm^{-1} : 3300–3160 (NH_3), 1650 ($\text{C}=\text{O}$), 1400, 1310, 1170, 970, 775, 735. Found, %: C 4.6; H 1.8; Cu^{2+} 12.5; K^+ 16.0; N 29.3; (NH_3) 7.0. $\text{C}_2\text{H}_6\text{CuK}_2\text{N}_{10}\text{O}_{10}$. Calculated, %: C 5.08; H 1.27; Cu^{2+} 13.56; K^+ 16.52; N 29.66; (NH_3) 7.20.

Potassium bis(*N,N'*-dinitrocarbamido)(urea)cuprate(II) (VIII) was synthesized in a similar way with the difference that 0.6 g (0.01 mol) of urea in 5 ml of water was additionally added to a solution of salt **IV**. Yield 1.9 g (76%). Decomposes at 179°C with explosion. Found, %: C 7.2; H 1.0; Cu^{2+} 11.5; K^+ 14.9; N 26.0. $\text{C}_3\text{H}_4\text{CuK}_2\text{N}_{10}\text{O}_{11}$. Calculated, %: C 7.22; H 0.80; Cu^{2+} 12.85; K^+ 15.66; N 28.11.

***N*-Nitrourea ammonium salt (XI).** Compound **I**, 3 g (0.02 mol), was added at 20–25°C to 25 ml of 26% aqueous ammonia under continuous stirring. The mixture was kept for 24 h and was evaporated under reduced pressure. Yield 0.9 g (73%), mp 120–121°C (decomp.). UV spectrum (H_2O): λ_{max} 260 nm, ϵ 9700 $\text{l mol}^{-1} \text{cm}^{-1}$. Found, %: C 9.68; H 5.00; N 44.90; NH_4^+ 13.55. $\text{CH}_6\text{N}_4\text{O}_3$. Calculated, %: C 9.84; H 4.92; N 45.90; NH_4^+ 14.75.

***N*-Methyl-*N'*-nitrourea (XII).** Compound **I**, 1.5 g (0.01 mol), was added at a temperature not exceeding 20°C to 12.4 g (0.1 mol) of 25% aqueous methylamine under continuous stirring. The mixture was kept for 16 h at 20°C and extracted with ethyl acetate (3 × 20 ml), and the extract was evaporated under reduced pressure. Yield 0.95 g (80%), mp 162°C [5].

Found, %: C 20.0; H 4.8; N 29.0. $\text{C}_2\text{H}_5\text{N}_3\text{O}_3$. Calculated, %: C 20.17; H 4.20; N 30.25.

***N*-Methyl-*N'*-nitrourea potassium salt (XIIa).** Compound **I**, 15 g (0.1 mol), was added at a temperature not exceeding 20°C to 37.2 g (0.3 mol) of 25% aqueous methylamine under continuous stirring. The mixture was stirred for 120 min at 30°C and cooled to 20°C, and 300 ml of ethyl alcohol was added. The mixture was allowed to settle down, and the layers were separated. A 30% aqueous solution of KOH (5.6 g) was added to the organic phase, the resulting solution was evaporated under reduced pressure, and the solid residue was washed with ethyl alcohol and ether and dried at room temperature. Yield 15.2 g (97%), mp 156°C (decomp.); published data [6]: mp 145°C (decomp.). Found, %: K^+ 24.5. $\text{C}_2\text{H}_3\text{KN}_3\text{O}_3$. Calculated, %: K^+ 24.68.

4-Nitrosemicarbazide (XIII', neutral). A 1.5-g (0.01-mol) portion of compound **I** (prepared by passing hydrogen chloride through a suspension of dinitrourea monopotassium salt in ether; method *a* in [2]) was dissolved in 5 ml of water under continuous stirring, maintaining the temperature below 20°C. Hydrazine hydrate, 0.5 g (0.01 mol), was added to the solution at a temperature not exceeding 30°C. The mixture was kept for 60 min at 30°C and cooled to 5°C, and the precipitate was filtered off, washed with cold water, and dried at room temperature. Yield of 4-nitrosemicarbazide monohydrate 0.62 g (45%), mp 227–235°C (decomp.). IR spectrum, ν , cm^{-1} : 3460 s, 3400 s, 3110 br.s, 3000, 2760 br.s, 2700, 1660 ($\text{C}=\text{O}$), 1620 m, 1570 s, 1540 s (NNO_2), 1500, 1400 s, 1330 s, 1290 s (NNO_2), 1200 s, 1155 s, 1035 m, 970, 790, 750, 610, 500, 365. Found, %: C 8.1; H 4.2; N 45.6. $\text{CH}_4\text{N}_4\text{O}_3 \cdot \text{H}_2\text{O}$. Calculated, %: C 8.70; H 4.35; N 40.10.

4-Nitrosemicarbazide (XIII'', zwitterionic). A 1.88-g portion of compound **I**, prepared by nitration of urea in a mixture of nitric and sulfuric acids (method *b* in [2]), was dissolved in 5 ml of water under continuous stirring, maintaining the temperature below 20°C. Hydrazine hydrate, 1.25 g (0.025 mol), was added at a temperature not exceeding 30°C, the mixture was kept for 60 min at 30°C and cooled to 5°C, and the precipitate was filtered off, washed with cold water, and dried at room temperature. Yield 0.3 g (27%), mp 230–231°C (decomp.). IR spectrum, ν , cm^{-1} : 3400 br.w, 3180 s, 3100 s, 3010, 2920 br.s, 2680, 1660 ($\text{C}=\text{O}$), 1585 m, 1540, 1500, 1410 s, 1320 m, 1260 s (NNO_2), 1190 w, 1140 s, 1025 s, 975, 820, 790, 765, 750, 675, 580, 505, 440, 365. Found, %: C 10.5; H 2.9; N 46.1. $\text{CH}_4\text{N}_4\text{O}_3$. Calculated, %: C 10.00; H 3.33; N 46.67.

4-Nitrosemicarbazide hydrazinium salt (XIIIa). Compound **I**, 1.5 g (0.01 mol), was dissolved in 5 ml of water under continuous stirring, maintaining the temperature below 20°C. Hydrazine hydrate, 5.0 g (0.1 mol), was added to the solution at a temperature not exceeding 30°C, the mixture was kept for 30 min at 30±1°C and cooled to 5°C, 50 ml of ethyl alcohol was added, and the precipitate was filtered off, washed with alcohol and ether, and dried at room temperature. Yield 1.2 g (80%), mp 130°C (DSC). IR spectrum, ν , cm⁻¹: 3310, 3180, 3000, 2640, 1660 (C=O), 1615, 1540, 1515, 1380, 1350, 1330, 1260 (NNO₂), 1190, 1110, 975, 960, 775, 765, 745, 675, 610, 510, 450, 419, 395, 385. Found, %: C 7.3; H 4.8; N 55.0. CH₈N₆O₃. Calculated, %: C 7.89; H 5.26; N 55.26.

4-Nitrosemicarbazide potassium salt (XIIIb). Compound **XIII**, 1.19 g (0.01 mol), was dissolved in 20 ml of water at 20°C under continuous stirring, and 0.56 g (0.01 mol) of potassium hydroxide in 5 ml of water was added. The mixture was diluted with 50 ml of ethyl alcohol, and the precipitate was filtered off, washed with ethyl alcohol and ether, and dried at room temperature. Yield 1.5 g (95%), mp 130°C (decomp.). UV spectrum (H₂O): λ_{\max} 258 nm, ϵ 8100 l mol⁻¹ cm⁻¹. Found, %: K⁺ 23.8. CH₃KN₄O₃. Calculated, %: K⁺ 24.68.

4-Nitrosemicarbazide nickel salt (XIIIc). Compound **XIIIa**, 1.58 g (0.01 mol), was dissolved in 20 ml of water at 20°C under continuous stirring, and 1.45 g (0.005 mol) of Ni(NO₃)₂·6H₂O was added. The mixture was stirred for 10 min, and the precipitate was filtered off, washed with water, alcohol, and ether, and dried at room temperature. Yield 1.55 g (99% on Ni[O₂NNCONHNH₂]₂·H₂O), mp 254°C (decomp., DSC). IR spectrum, ν , cm⁻¹: 3400, 3345, 3320, 1660 (C=O), 1445, 1375, 1310, 1285 (NNO₂), 1165, 1110, 1085, 985, 785, 755, 665, 615, 590, 510. Found, %: Ni 17.8. CH₃N₄NiO₃. Calculated, %: Ni 18.6.

N-Hydroxy-N'-nitrourea (XIV). Compound **I**, 15 g (0.1 mol), was dissolved in 20 ml of water under continuous stirring, maintaining the temperature below 20°C, and 9.9 g (0.3 mol) of hydroxylamine in 20 ml of water was added at a temperature not exceeding 30°C. The mixture was kept for 30 min at 30°C and cooled to 5°C, and 70 ml of concentrated sulfuric acid was added at a temperature not exceeding 10°C. The precipitate was filtered off, washed with glacial acetic acid, and dried at room temperature. Yield 8.4 g (69%), mp 189°C (decomp.); after recrystallization from water, mp 151°C (decomp.). IR spectrum, ν , cm⁻¹: 3320 (NH), 3220, 3100, 2980,

2810, 1705, 1685 (C=O), 1630, 1490, 1460, 1420, 1340, 1275 (NNO₂), 1125, 1065, 960, 805, 760, 735, 715, 575, 475, 455, 435, 340, 300. Found, %: C 10.0; H 2.5; N 34.5. CH₃N₃O₄. Calculated, %: C 9.91; H 2.48; N 34.71.

N-Hydroxy-N'-nitrourea hydroxylammonium salt (XIVa). Compound **I**, 15 g (0.1 mol), was dissolved in 20 ml of water under continuous stirring, maintaining the temperature below 20°C, and 9.9 g (0.3 mol) of hydroxylamine in 20 ml of water was added to the solution at a temperature not exceeding 30°C. The mixture was kept for 30 min at 30°C, cooled to 5°C, and diluted with 50 ml of ethyl alcohol. The precipitate was filtered off, washed with alcohol and ether, and dried at room temperature. Yield 12.3 g, mp 155°C (decomp.). Found, %: C 7.8; H 3.9; N 36.3. CH₆N₄O₅. Calculated, %: C 7.79; H 4.00; N 36.36.

Methyl nitrocarbamate (XVa). A solution of 3 g (0.02 mol) of compound **I** in 50 ml of methyl alcohol was heated to the boiling point, kept for 30 min under reflux, cooled to 20°C, and evaporated under reduced pressure. The residue was recrystallized from ether-hexane. Yield 0.6 g (85%), mp 86–88°C [7].

Ethyl nitrocarbamate (XVb) was synthesized in a similar way using ethyl alcohol. Yield 2.68 g (100%), mp 62–63°C [8].

Propyl nitrocarbamate (XVc) was synthesized in a similar way using 1-propanol. Yield 0.49 g (100%), oily substance, n_D^{20} 1.447.

Hexamethylenetetraaminium N,N'-dinitrourea nitrate (XVI). To 21 g of nitric acid ($d = 1.5$ g/cm³) we added 21 g of oleum (20% SO₃), and 6 g (0.1 mol) of urea was added in portions to the resulting mixture at –5 to 0°C under continuous stirring. The mixture was kept for 30 min at that temperature and was poured into 54 g of an aqueous solution of urotropin (14 g, 0.1 mol) at such a rate that the temperature did not exceed 20°C. The precipitate was filtered off, washed with alcohol and ether, and dried at room temperature. Yield 19.8 g (56%), mp 98°C. Found, %: C 24.8; H 4.4; N 34.9. C₇H₁₅N₉O₈. Calculated, %: C 23.80; H 4.25; N 35.69.

General procedure for preparation of nitrourea derivatives from N,N'-dinitrourea dipotassium salt (IV) and amines (Table 2). Salt **IV**, 2.26 g (0.01 mol), and appropriate amine, 0.01 mol, were added at 20°C to 10–20 ml of water under continuous stirring. The mixture was kept for 40–60 min at 30°C, cooled to 15–20°C, and diluted with 40–100 ml of ethyl alcohol. The precipitate was filtered off, washed with alcohol and ether, and dried at room temperature.

General procedure for preparation of nitrourea derivatives from *N,N'*-dinitrourea monopotassium salt and amines. The procedure is the same as above with the difference that 0.01 mol of *N,N'*-dinitrourea monopotassium salt and 0.02 mol of amine are used.

Nitrourea potassium salt. Decomposition point 126°C (decomposes on heating [8]). IR spectrum, ν , cm^{-1} : 3384, 3300 (NH_2), 3192, 1676 ($\text{C}=\text{O}$), 1640 (δNH_2), 1540, 1372, 1300, 1108, 800, 688, 592, 472, 312. Found, %: K^+ 27.8. $\text{CH}_2\text{KN}_3\text{O}_3$. Calculated, %: K^+ 27.27.

***N*-Butyl-*N'*-nitrourea potassium salt.** Decomposition point 190°C. Found, %: K^+ 20.08. $\text{C}_5\text{H}_{10}\text{KN}_3\text{O}_3$. Calculated, %: K^+ 19.60.

***N*-Butyl-*N'*-nitrourea.** A suspension of 1.99 g (0.01 mol) of *N*-butyl-*N'*-nitrourea in 100 ml of dry ether was saturated at 0°C with gaseous hydrogen chloride. The mixture was kept for 2–4 h, the precipitate of potassium chloride was filtered off, and the filtrate was evaporated to dryness under reduced pressure. Yield 1.34 g (83%), mp 74–76°C [9]. IR spectrum, ν , cm^{-1} : 3420 (NH), 3120, 3040, 2940, 2860, 2800, 1695 ($\text{C}=\text{O}$), 1600, 1550 (NNO_2), 1490, 1470, 1460, 1440, 1420, 1360, 1350, 1320, 1300, 1250 (NNO_2), 1200, 1160, 1140, 1040, 1000, 920, 900, 805, 780, 760, 750, 735, 720, 600, 520, 460, 430. Found, %: C 37.0; H 6.5; N 24.5. $\text{C}_5\text{N}_{11}\text{N}_3\text{O}_4$. Calculated, %: C 37.27; H 6.83; N 26.09.

***N*-Hydroxy-*N'*-nitrourea potassium salt.** Decomposition point 133°C. IR spectrum, ν , cm^{-1} : 3300

(NH), 3080, 1630 ($\text{C}=\text{O}$), 1580, 1550, 1520, 1450, 1370, 1340, 1210 s, 1120, 1060, 950, 850, 790, 610, 510, 455, 380. Found, %: K^+ 24.88. $\text{CH}_2\text{KN}_3\text{O}_3$. Calculated, %: K^+ 24.53.

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