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

Formation and Decomposition of Nitrocyanamide in Strong Mineral Acids

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Abstract—Nitrourea is the major product of acid-catalyzed decomposition of nitrocyanamide. Study of the kinetics of this process in aqueous sulfuric and nitric acid unexpectedly revealed a fairly high resistance of nitrocyanamide to acids, so that it can be synthesized not only in alkaline but also in strongly acid media.
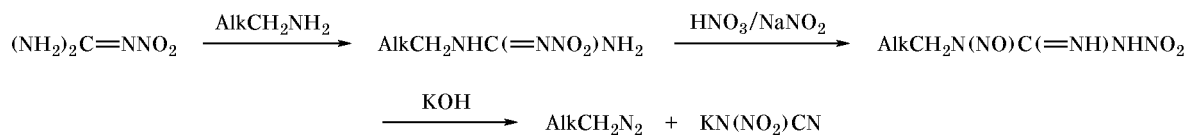
Nitrocyanamide $HN(NO_2)CN$ is the closest analog of dinitramide $HN(NO_2)_2$; salts of the latter are extensively studied as components of various high-energy compositions [1]. Unlike dinitramide, properties of nitrocyanamide salts have been studied very poorly. It is known that some nitrocyanamide salts with heavy metals are relatively safe and heat-resistant initiating explosives [2]; barium and ammonium nitrocyanamide salts were proposed as components of gas-generating compositions [3]. The silver salt was studied in most detail. Some its physicochemical parameters were determined [4], and its combustion was examined [5]. Electrolytic reduction of nitrocyanamide salts at a mercury cathode was shown [6] to give cyanamide and nitrous acid. Treatment of nitrocyanamide salts with alkyl halides in organic solvents leads to formation of both N- and O-alkylation products [7–9], and the reaction with triorganostannyl chlorides yields the corresponding stannyl derivative of nitrocarbodiimide [10]. The ^{13}C NMR spectrum of nitrocyanamide was reported in [11]. Jaeger *et al.* [12] determined the crystalline

structure of potassium and silver salts of nitrocyanamide, and the crystalline structure of nitrocyanamide complexes with copper, cobalt, and nickel was studied in [13, 14]. Free nitrocyanamide isolated as monohydrate is an unstable compound which decomposes on storage [2].
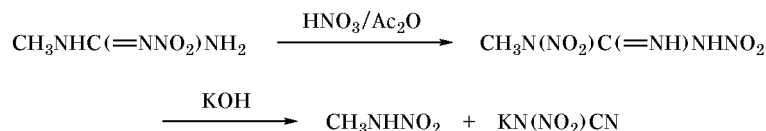
The lack of more detailed published data on the properties of nitrocyanamide and its salts is explained primarily by difficulties in the preparation of these compounds. Prior to our present work, nitrocyanamide still remained among the series of "exotic" compounds having no chance to find practical application.

Nitrocyanamide (as potassium salt) was synthesized for the first time in 1950 by decomposition of *N*-alkyl-*N*-nitroso-*N'*-nitroguanidines with potassium hydroxide [15] according to Scheme 1. Caltress *et al.* [16] performed a detailed study of the mechanism of this process using *N*-methyl-*N*-nitroso-*N'*-nitroguanidine as an example. Nitrocyanamide potassium salt was described as a colorless crystalline substance, soluble in water and polar organic solvents. The same salt was obtained by decomposition of *N*-alkyl-*N*,*N'*-

Scheme 1.

$$(NH_2)_2C{=}NNO_2 \xrightarrow{\text{AlkCH}_2\text{NH}_2} AlkCH_2NHC(=NNO_2)NH_2 \xrightarrow{\text{HNO}_3/\text{NaNO}_2} AlkCH_2N(NO)C(=NH)NHNO_2$$

$$\xrightarrow{\text{KOH}} AlkCH_2N_2 \ + \ KN(NO_2)CN$$

Scheme 2.

$$CH_3NHC(=NNO_2)NH_2 \xrightarrow{HNO_3/Ac_2O} CH_3N(NO_2)C(=NH)NHNO_2$$

$$\xrightarrow{KOH} CH_3NHNO_2 + KN(NO_2)CN$$

dinitroguanidines [17] (Scheme 2). The syntheses of nitrocyanamide salts according to Schemes 1 and 2 are quite laborious and low efficient (the yield does not exceed ~30%, calculated on the nitroguanidine), and intermediate products exhibit a strong carcinogenic and skin irritant activity. Alkaline decomposition of 1-nitroamidino-1,2,4-triazole [16], leading to the corresponding nitrocyanamide salt (Scheme 3), is absolutely inadmissible for practical use.

Scheme 3.

$$\xrightarrow[-H_2O]{KOH} + KN(NO_2)CN$$
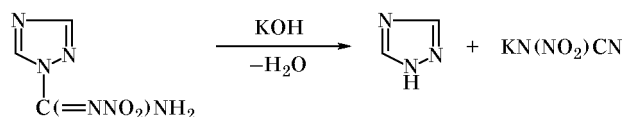
No other, simpler procedures for preparation of nitrocyanamide salts have been proposed so far.

Our studies were aimed at developing a radically new method for preparation of nitrocyanamide salts from relatively cheap and accessible initial compounds. The simplest procedure could be nitration of cyanamide or its salt with nitric acid in sulfuric acid, e.g., according to Scheme 4.

Scheme 4.

$$NH_2CN \xrightarrow[-H_2O]{HNO_3/H_2SO_4} NCNHNO_2$$
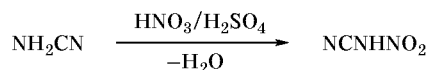
As far as we know, no attempts were made to obtain nitrocyanamide in such a way. A probable reason is supposedly low resistance to strong acids of both nitrocyanamide itself and its possible direct precursor, cyanamide. The kinetics of acid-catalyzed hydrolysis of cyanamide to urea were studied in sufficient detail [18–21]. The rate of this reaction in aqueous nitric acid regularly increases as the concentration of HNO_3 rises. The apparent energy of activation does not depend on the acidity of the medium and is about 80 kJ/mol [18]. No data have so far been reported on the stability of nitrocyanamide in acid media.

The UV spectrum of an aqueous solution of a nitrocyanamide salt contains an absorption maximum at λ 265 nm (ε = 8900 l mol^{-1} cm^{-1}) which does not change over a wide acidity range (from the pH region to $H_0 \approx -2$); this maximum corresponds to absorption of the $[NCNNO_2]^-$ ion. In aqueous sulfuric acid (containing more than ~30 wt % of H_2SO_4) the molar absorption coefficient at λ 265 nm regularly and reversibly decreases due to displacement of the anion protonation equilibrium (Scheme 5) to the right.

Scheme 5.

$$NCNNO_2^- + H \rightleftharpoons NCNHNO_2$$
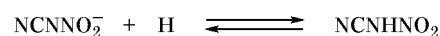
The fact that displacement of the above equilibrium requires a fairly high concentration of H_2SO_4 indicates a relatively strong acidity of nitrocyanamide, which is comparable with the acidity of dinitramide ($pK_a = -5.62$ [22]).

Dissolution of nitrocyanamide salts in aqueous sulfuric acid with a concentration of more than ~55 wt % leads to their decomposition, as follows from irreversible changes in the UV spectra. The rate of these variations increases with rise in the medium acidity and temperature. With the goal of estimating the stability of nitrocyanamide toward strong acids, we have studied the kinetics and mechanism of its acid-catalyzed decomposition. Linear relations between the reaction rate and acidity of the medium in the coordinates $\log k_{ap}$—H_0 ($r > 0.99$, $s < 0.05$) were obtained in the range of sulfuric acid concentrations from 61 to 82 wt % (Fig. 1). The parameters of correlation equations describing the plots shown in Fig. 1 are given in Table 1. The slopes of the $\log k_{ap}$—H_0 plots are similar to those typical of acid-catalyzed decomposition of primary aliphatic N-nitroamines (-0.4 to -0.6 [24, 25]) but are strongly different from the corresponding values for denitration of various

Table 1. Parameters of correlation equations $\log k_{ap} = a \times H_0 + b$ for decomposition of nitrocyanamide in aqueous sulfuric acid

| [H$_2$SO$_4$], wt %	Temperature, °C	$-a$	$-b$
69.1–81.9	10	0.64	7.9
61.4–77.7	25	0.54	6.3
62.8–73.2	40	0.52	5.4
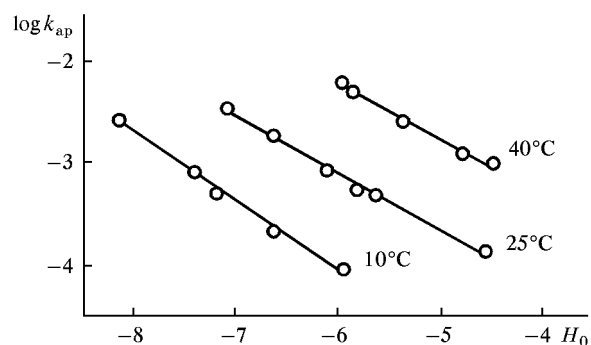
Fig. 1. Semilog plots of the apparent rate constants for decomposition of nitrocyanamide versus acidity of the medium; [H_2SO_4] = 61.4–81.9 wt %; values of H_0 were taken from [23].
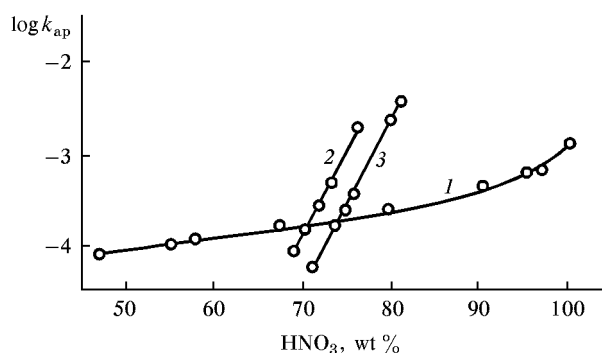
Fig. 2. Semilog dependences of the apparent rate constants of acid-catalyzed decomposition of (*1*) nitrocyanamide, (*2*) 6-fluoro-2,4-dinitrophenyl-*N*-nitroamine [27], and (*3*) dinitramide [26] on the concentration of HNO_3; 25°C.

N-nitro compounds (–1.1 to –1.4 [26]). The dependence of the rate of nitrocyanamide decomposition in aqueous nitric acid on the concentration of the latter also sharply differs from those found for denitration of 6-fluoro-2,4-dinitrophenyl-*N*-nitroamine and dinitramide (Fig. 2). Thus, the kinetic data indicate that decomposition of the nitroamide fragment in the molecule of nitrocyanamide does not follow the denitration pathway (which begins with protonation of the nitrogen atom in the nitroamino group as shown in Scheme 6).
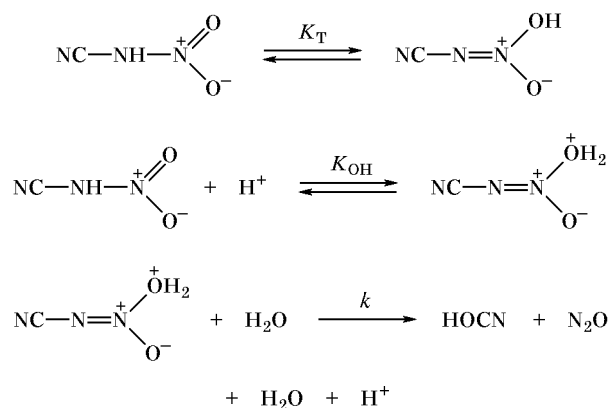
Scheme 6.
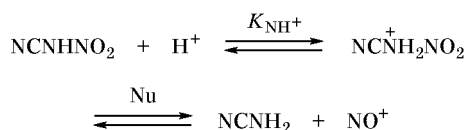
Mechanism of this reaction may be analogous to the mechanism of decomposition of primary aliphatic

N-nitroamines [28–30]. As applied to nitrocyanamide, the corresponding processes can be represented by Scheme 7.
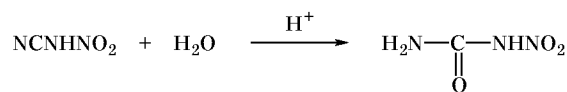
Scheme 7.

However, neither in aqueous sulfuric acid nor in aqueous nitric acid the decomposition of nitrocyanamide was accompanied by evolution of nitrogen(I) oxide or any other gaseous products. Solutions of the decomposition products in concentrated sulfuric acid possess an appreciable nitrating activity which suggests the presence of nitric acid. The yield of HNO_3 in the decomposition of nitrocyanamide in 92% sulfuric acid (measured by nitration of benzene according to the procedure described in [31]) is not quantitative and is ~0.6 mol per mole of nitrocyanamide. When the decomposition product was isolated by dilution of a solution of nitrocyanamide potassium salt in 72% H_2SO_4, a colorless crystalline solid was obtained. Its elemental composition and melting point were fully consistent with the corresponding parameters of nitrourea $H_2NCONHNO_2$.

Comparison of the UV spectra of solutions of nitrocyanamide potassium salt, its decomposition products in aqueous sulfuric acid, and an authentic sample of nitrourea (Fig. 3) showed that the yield of the latter in the decomposition of nitrocyanamide is nearly quantitative. The nitrating ability of solutions of nitrocyanamide decomposition product in concentrated sulfuric acid is explained by partial denitration of nitrourea, which was noted in [32]. Thus the acid-catalyzed decomposition of nitrocyanamide involves the cyano group rather than the *N*-nitroamino moiety (Scheme 8).

Scheme 8.

According to the results of kinetic studies (Figs. 1, 2), nitrocyanamide is fairly resistant to strong acids; therefore, there exists the possibility of synthesizing this compound not only in alkaline (Schemes 1–3) but also in strongly acid media. The cheapest and most accessible initial compound for the synthesis of nitrocyanamide could be either cyanamide or its salts with metals, which recover cyanamide in acid medium. Taking into account possible side processes, Scheme 9 illustrates the formation of nitrocyanamide by treatment of cyanamide with nitrating mixtures.

Scheme 9.
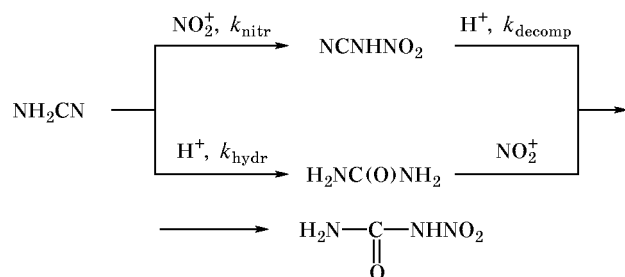
It follows from Scheme 9 that the yield of nitrocyanamide is determined by the ratio of rate constants for its formation (k_{nitr}) and decomposition (k_{decomp}) and rate constant for hydrolysis of initial cyanamide (k_{hydr}). Therefore, the optimal composition of nitrating mixture should ensure a sufficiently high nitrating activity and as low as possible acidity of the medium. Such conditions are met through the use of mixtures of nitric and sulfuric acids with a high concentration of nitric acid and a low concentration of water [33]. Anhydrous nitrating agents including sulfuric anhydride in the form of nitronium hydrogen sulfate (NO_2HSO_4) or pyrosulfate ($NO_2HS_2O_7$) and other nitronium salts are even better in the above respect.

The dependence of the yield of nitrocyanamide on the reaction time should have an extremal character due to the occurrence of irreversible decomposition stage. Therefore, the reaction time should not exceed the optimal value, i.e., that sufficient to attain the maximal yield of nitrocyanamide. Prolonged reaction should inevitably result in reduced yield because of the transformation of nitrocyanamide into nitrourea. The nitration temperature should be sufficiently low to ensure nitrocyanamide "lifetime" within the limits determined by the reaction time.

With the above in mind, the nitration of cyanamide and its salts was effected with strong nitrating mixtures at fairly low temperatures. In each experiment, the yield of nitrocyanamide was measured in order to determine the optimal reaction time. Even first
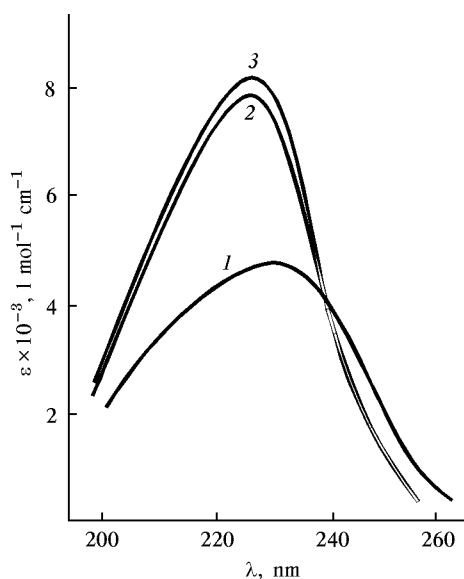
Fig. 3. UV spectra of (*1*) nitrocyanamide, (*2*) products of its decomposition, and (*3*) nitrourea in 69% H_2SO_4; 25°C.

experiments on the nitration of cyanamide calcium salt with concentrated nitric acid or its mixtures with sulfuric acid showed that these systems are suitable, in principle, for the synthesis of nitrocyanamide. Insofar as the rate of formation of nitrocyanamide was fairly low (the process was heterogeneous) and was comparable with the rate of its decomposition, the maximal yield of nitrocyanamide did not exceed ~20% (calculated on the initial cyanamide). We failed to improve the nitration results using dipotassium (K_2NCN) or disodium (Na_2NCN) cyanamide salts which are better soluble in water in mineral acids. In all cases, addition of these salts to nitrating mixture, even under vigorous

Table 2. Reaction conditions and yields of nitrocyanamide potassium salt in the nitration of crystalline cyanamide (10 g)

Amounts of reactants, ml		Temp., °C	Time,[a] min	Yield, %
98% HNO_3	94% H_2SO_4			
40	0	0	10	85
15	0	0	10	55
28	2	0	12	82
30	10	−10	20	87
30	10	0	10	83
30	10	10	5	75
30	10	20	5	68
30	10	30	3	51

[a] Depended only on the conditions of heat removal.

Table 3. Reaction conditions and yields of nitrocyanamide in the nitration of cyanamide as a 90% aqueous solution[a]

Weight of solution, g	Amounts of reactants, ml		Nitration number[b]	Yield, %
	98% HNO$_3$	94% H$_2$SO$_4$		
16	64	0	6	86
18	60	0	5	80
16	42	0	4	67
15	54	5	6	89
15	45	4	5	87
19	45	4	4	73
15	49	10	6	92
18	49	10	5	92
23	49	10	4	82
16	47	15	6	91
20	47	15	5	88
24	47	15	4	82

[a] Temperature 15–20°C, reaction time 4–5 min.
[b] Weight ratio of the nitrating mixture to the solution of nitrocyanamide subjected to nitration.

stirring, resulted in violent decomposition in the site of contact.

Much greater yield of nitrocyanamide was obtained in the nitration of crystalline cyanamide (Table 2), and addition of the latter to the nitrating mixture was considerably quieter, although vigorous stirring was necessary. The best results in the nitration were obtained with the use of concentrated aqueous solutions of cyanamide. The addition of a 90% aqueous solution of cyanamide to the nitrating mixture was not accompanied by visible decomposition in the site of contact, so that requirements to the intensity of stirring can be strongly reduced. Nitrocyanamide potassium salt was formed in more than 90% yield at fairly high temperatures (Table 3). The data in Tables 2 and 3 indicate that, in keeping with Scheme 9, raising the amount of nitric acid enhances the nitrating activity and considerably increases the yield. The same effect is observed on addition of sulfuric acid to the nitrating mixture.
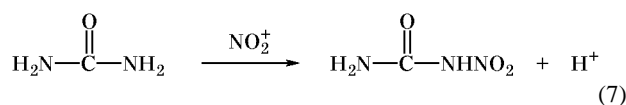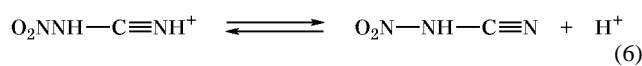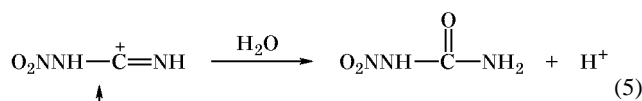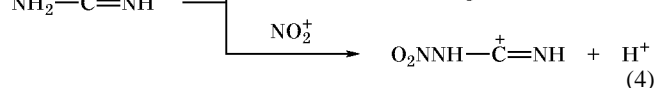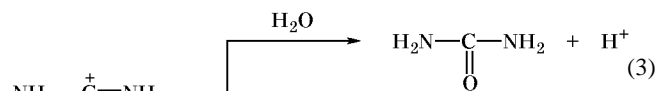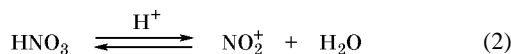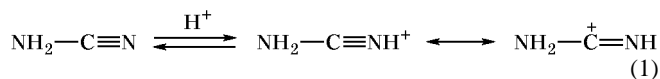
As follows from the dependence of the yield of nitrocyanamide potassium salt on the reaction time, the rate of nitration of cyanamide with mixtures of sulfuric and nitric acids remains immeasurably high at any composition of nitrating mixture and temperatures up to –35°C. According to published data, the basicity of cyanamide is relatively high. Potentiometric titration of cyanamide with hydrochloric acid

at 29°C gave a pK_{BH^+} value of 1.1 [34]; pK_{BH^+} values of –1.2 [35] and –1.12 [36] were obtained by spectrophotometric measurements. The concentration of protonated form of cyanamide in strongly acidic [37] mixtures of nitric and sulfuric acids is quite insufficient to ensure the observed rate of nitration. Therefore, the reactive species may be only the conjugate acid. Peips *et al.* [35] believed that the protonation center in cyanamide is the nitrogen atom of the amino group. According to our data, the protonation center may be only the cyano group nitrogen atom, otherwise nitration of the protonated form of cyanamide would be impossible. Analogous conclusion on the site of protonation in cyanamide was drawn by Kallies and Mitzner [38]; on the basis of the results of quantum-chemical calculations, the authors showed that both in the gas phase and in aqueous solution proton should be attached to the nitrogen atom of the cyano group. The basicity of cyanamide with respect to the amino group nitrogen atom should be several orders of magnitude lower than with respect to the cyano group [38]. The basicity of nitrocyanamide with respect to the *N*-nitroamino group should be even lower due to strong electron-acceptor effect of the nitro group. According to Scheme 6, the first stage in denitration of *N*-nitro compounds is protonation just at the nitrogen atom of the nitroamino group; therefore, no denitration of nitrocyanamide occurs in strong acids. Assuming that the hydrolysis mechanisms of nitrocyanamide and cyanamide [19] are similar, the processes occurring in the nitration of cyanamide with mixtures of sulfuric and nitric acids can be summarized by Scheme 10.

The final product of nitration of cyanamide is nitrourea which is formed by both hydrolysis of nitrocyanamide [reaction (5) in Scheme 10] and nitration of urea (7), the latter resulting from hydrolysis of cyanamide in step (3). The maximal yield of nitrocyanamide depends on the rates of reactions (3) and (4), i.e., reactions of protonated cyanamide with water and nitronium ion, respectively. These rates depend in turn on the acidity of the medium, which determines the conversion of nitric acid into nitronium ion [equilibrium (2)], and on the concentration ratio of nitric acid and water in the nitrating system. Therefore, the greatest yields of nitrocyanamide are obtained only in the presence of sulfuric acid and a fairly large excess of nitric acid (nitration number 5 and larger; Tables 2, 3).

According to the laboratory procedure, nitrocyanamide salts are isolated by extraction with boiling acetone from the salt mixture obtained after dilution of the reaction mixture with water, neutralization,

Scheme 10.

$$NH_2{-}C{\equiv}N \;\xrightleftharpoons{H^+}\; NH_2{-}C{\equiv}NH^+ \;\longleftrightarrow\; NH_2{-}\overset{+}{C}{=}NH \qquad (1)$$

$$HNO_3 \;\xrightleftharpoons{H^+}\; NO_2^+ \;+\; H_2O \qquad (2)$$

$$NH_2{-}\overset{+}{C}{=}NH \;\xrightarrow{H_2O}\; H_2N{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \;+\; H^+ \qquad (3)$$

$$\xrightarrow{NO_2^+}\; O_2NNH{-}\overset{+}{C}{=}NH \;+\; H^+ \qquad (4)$$

$$O_2NNH{-}\overset{+}{C}{=}NH \;\xrightarrow{H_2O}\; O_2NNH{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \;+\; H^+ \qquad (5)$$

$$O_2NNH{-}C{\equiv}NH^+ \;\rightleftharpoons\; O_2N{-}NH{-}C{\equiv}N \;+\; H^+ \qquad (6)$$

$$H_2N{-}\underset{\underset{O}{\|}}{C}{-}NH_2 \;\xrightarrow{NO_2^+}\; H_2N{-}\underset{\underset{O}{\|}}{C}{-}NHNO_2 \;+\; H^+ \qquad (7)$$

and evaporation of the resulting solution to dryness. This procedure is quite inappropriate for large-scale preparations; however, Andreev *et al.* [39–41] showed that nitrocyanamide salts possess much stronger adsorptivity with respect to charcoal, as compared to nitrates and sulfates. Thus, salt mixtures containing nitrocyanamide potassium salt can be separated by dissolving them in water and passing the solution through a column charged with activated charcoal. The nitrocyanamide salt is retained in the column, whereas a mixture of nitrates and sulfates, which are weakly adsorbed by the charcoal surface, are washed off from the column with the eluate. Desorption of nitrocyanamide salt from charcoal is effected by washing with water or an organic solvent, acetone being the best, at elevated temperature [42].

EXPERIMENTAL

A sample of nitrocyanamide potassium salt for spectral studies, mp 135–136°C, was obtained by alkaline decomposition of methyldinitroguanidine [17] and was purified by recrystallization from alcohol. Calcium, dipotassium, and disodium salts of cyanamide, containing 87–90% of the main substance, were supplied by the Dzerzhinsk Branch of the State Institute of Nitrogen Industry and were used without additional purification. Crystalline cyanamide,

mp 43–44°C, was isolated from its calcium salt by the procedure described in [43]. Its 90% aqueous solution was prepared just before use. Aqueous solutions of H_2SO_4 for studying the kinetics of decomposition of nitrocyanamide were prepared by diluting concentrated sulfuric acid of chemically pure grade with distilled water. Aqueous solutions of nitric acid were prepared by diluting 98% HNO_3 which was obtained by distillation of technical-grade fuming nitric acid under reduced pressure. To remove lower nitrogen oxides, the solutions prepared were purged with air at 35–40°C. The concentration of aqueous solutions of sulfuric and nitric acids was determined by alkalimetric titration with an accuracy of no less than ±0.1%.

The UV spectra of solutions of nitrocyanamide potassium salt in water and aqueous H_2SO_4 were recorded on a Specord UV-Vis spectrophotometer using 1-cm quartz cells. The optical densities of solutions at a given wavelength were measured on an SF-26 spectrophotometer.

Isolation of nitrourea from products of decomposition of nitrocyanamide potassium salt in aqueous sulfuric acid. Nitrocyanamide potassium salt, 10 g, was added with stirring at a temperature not exceeding ~20°C to 100 ml of 72% sulfuric acid. The mixture was stirred for 1 h at room temperature and was poured into 100 ml of water containing ice. The colorless precipitate was filtered off, thoroughly washed with water, and dried in air. After recrystallization from ethanol, the yield of the product was 5.8 g, mp 157–159°C (decomp.) [44]. No depression of the melting point was observed on mixing with an authentic sample of nitrourea. Found, %: C 11.37, 11.34; H 3.01, 2.89; N 40.12, 40.08. $CH_3N_3O_3$. Calculated, %: C 11.43; H 2.86; N 40.00.

The rate of acid-catalyzed decomposition of nitrocyanamide was measured following the reduction in the optical density of solutions (originating from absorption of the anion). A ~10-mg sample of nitrocyanamide potassium salt was added with stirring (with a magnetic stirrer) to ~30 ml of an aqueous acid solution with a required contcentration, which was placed in a cell maintained at a constant temperature (±0.1°C). After the salt dissolved (~0.5 min), a 0.5-ml sample of the mixture was withdrawn and was poured into 20 ml of distilled water. A stopwatch was activated at the moment of dilution, and the optical density D_0 was measured at λ 265 nm relative to distilled water (in experiments in aqueous H_2SO_4) or relative to dilute nitric acid with a similar concentration (in experiments in aqueous HNO_3). Samples of the reaction mixtures were withdrawn at specified

time intervals (τ) and diluted with water, and the optical density (D_τ) was measured. The apparent rate constants were calculated by the standard equation for first-order reactions:

$$k_{ap} = (1/\tau) \ln(D_0/D_\tau).$$

The accuracy of determination of the rate constants was within ±5%.

Nitration of cyanamide calcium salt. A 100-ml stainless-steel beaker equipped with a stirrer and a thermometer was charged with a known amount of nitrating mixture (±0.1 g), and powdered cyanamide calcium salt was added in small portions on cooling under vigorous stirring. When the entire amount of the salt was added, a 2–3-g sample of the reaction mixture was withdrawn and was placed in a beaker containing ~50 ml of distilled water. The contents were weighed with an accuracy of ±0.01 g and were quantitatively transferred into a 200-ml volumetric flask. The volume was adjusted to 200 ml by adding distilled water, the mixture was stirred, if necessary, calcium sulfate was filtered off, and the optical density at λ 265 nm was measured using as reference the initial nitrating mixture diluted in a similar way. The yield of nitrocyanamide was calculated assuming $\varepsilon = 8900 \ l\,mol^{-1}\,cm^{-1}$.

Nitration of crystalline cyanamide and its aqueous solutions. The nitration was carried out as described above (an aqueous solution of cyanamide was added dropwise), but, after the addition was complete, the mixture was immediately poured into a double volume of an ice–water mixture, neutralized with solid potassium carbonate or 50% aqueous KOH to a weakly alkaline reaction at a temperature not exceeding 20–25°C, and evaporated to dryness on a rotary evaporator under reduced pressure. The residue was treated for 10–15 min with two 75-ml portions of boiling acetone, and the combined extracts were filtered and evaporated. According to the spectrophotometric data, the residue was almost pure nitrocyanamide potassium salt containing a few percent of potassium nitrate. The yield was calculated with account taken of the KNO_3 concentration. Recrystallization from ethanol gave almost pure nitrocyanamide potassium salt. The results of nitration of cyanamide and its 90% aqueous solution are given in Tables 2 and 3.

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