Summary

Nitrourea dearranges into cyanic acid and nitroamide. It has been prepared from these two substances, and they have been prepared from it.

The products from the decomposition of nitrourea by heat are those which would be expected from the two possible modes of its dearrangement.

Nitrous oxide and cyanic acid are produced quantitatively when nitrourea is heated with water.

A solution of nitrourea in concd. sulfuric acid contains nitroamide and may be used as a reagent for nitrations.

Alkalies promote the decomposition of nitrourea; acids hinder it. A very slight alkalinity in the presence of a trace of moisture is sufficient to cause its spontaneous decomposition.

An aqueous solution of nitrourea, being a source of cyanic acid, reacts with ammonia and with primary and secondary amines to form urea and substituted ureas. The yields are excellent, the manipulation is simple and the other products of the reaction are gaseous. The method is especially advantageous for the preparation of those substituted ureas which cannot be heated in water without decomposition. A number of urea derivatives, a few of them new, have been prepared by this method.

ω,ω-Di-*n*-propylbiuret and ω-*n*-propyl-ω-phenylbiuret have been obtained as by-products in the preparation of urea derivatives from nitrourea and the corresponding amines.

Moist alcohols react with nitrourea to produce carbamic and allophanic esters.

CAMBRIDGE, MASSACHUSETTS

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THE DEARRANGEMENT OF NITROBIURET AND ITS APPLICATION IN SYNTHESIS

BY TENNEY L. DAVIS AND KENNETH C. BLANCHARD

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A study of the dearrangement of nitrobiuret is especially interesting for the reason that it might be expected to produce the unknown dimer of cyanic acid, dicyanic acid, NH_2CONCO (or $HOC(NH)\text{-}NCO$). Nitrobiuret might be expected to dearrange in four modes, as indicated below. The known or expected decompositions of the nitro-amines from the four modes of dearrangement are also shown.

$$NH_2CONHCONHNO_2 \rightleftarrows NH_2CONCO + NH_2NO_2 \longrightarrow N_2O + H_2O \tag{1}$$

$$NH_2CONHCONHNO_2 \rightleftarrows NH_2CONH_2 + OCNNO_2 \longrightarrow N_2O + CO_2 \tag{2}$$

$$NH_2CONHCONHNO_2 \rightleftarrows NH_3 + OCNCONHNO_2 \longrightarrow N_2O + CO_2 + HNCO \tag{3}$$

$$NH_2CONHCONHNO_2 \rightleftarrows HNCO + NH_2CONHNO_2 \longrightarrow N_2O + H_2O + HNCO \tag{4}$$

We find that a freshly prepared cold aqueous solution of nitrobiuret does not give the biuret test. If the solution is boiled, nitrous oxide and carbon dioxide come off, and the liquid now gives a strong biuret test but shows no evidence of cyanic acid by Werner's sensitive test with copper sulfate, pyridine and chloroform. The solution, however, contains no biuret, for it yields a residue of urea along with some cyanuric acid when it is evaporated to dryness. Although the boiled solution at the beginning does not contain cyanic acid, it develops cyanic acid during the evaporation—but this is normal behavior of urea solutions. Since the solution immediately after dearrangement does not contain cyanic acid, we conclude at once that dearrangements of the third and fourth sorts (as indicated above) do not occur.

The evolution of nitrous oxide and carbon dioxide from the hot solution and the production of urea, as originally observed by Thiele and Uhlfelder,[1] suggest strongly that dearrangement occurs in the second of the above-indicated modes. The biuret test in the absence of biuret indicates some other reaction—and is, we believe, evidence of the presence of dicyanic acid in the solution. Moreover, solutions of nitrobiuret act with ammonia, amines and alcohols as if they contained dicyanic acid and yield with those reagents the products which that substance would be expected to yield. We conclude, therefore, that dearrangement occurs in the first two modes, namely, to form nitroamide and dicyanic acid, and urea and nitrocyanic acid.

A solution of nitrobiuret in concd. sulfuric acid gives up its nitro group quantitatively in the nitrometer and is a suitable reagent for the nitration of substances such as aniline and acet-*p*-toluide which are not injured by contact with strong sulfuric acid.

Nitrobiuret with alcoholic potash yields potassium allophanate. By boiling with alcohols and a little water, it produces allophanic and carbamic esters.

With ammonia it yields biuret along with some cyanuric acid and urea. With primary and secondary amines it gives ω-substituted biurets, substances which are evidently produced by the direct combination of the amine with dicyanic acid, thus

$$R_2NH + NH_2CONCO \longrightarrow NH_2CONHCONR_2$$

In this manner we have prepared ω-methyl-, ω-ethyl-, ω-*n*-propylbiuret (new), ω-*n*-butylbiuret (new), ω-benzylbiuret (new), ω-phenyl-, ω-*p*-tolyl-, and ω-α-naphthylbiuret (new), and from secondary amines a number (all new) of ω,ω-disubstituted biurets, namely, ω,ω-dimethyl-, ω,ω-diethyl-, ω,ω-di-*n*-propyl-, ω,ω-di-*n*-butyl-, ω-ethyl-ω-phenyl- and ω-*n*-propyl-ω-phenylbiuret.

The dicyanic acid from the dearrangement of nitrobiuret in water solu-

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[1] Thiele and Uhlfelder, *Ann.*, **303,** 93 (1898).

tion does not combine with urea to form carbonyldiurea or triuret,[2] but does combine with biuret to form tetruret.

Experiments

Preparation of Nitrobiuret.—Nitrobiuret was prepared by a method essentially that of Thiele and Uhlfelder.[1] Our first crude product from the drowning of the nitration mixture, purified by dissolving it in water with the addition of sodium hydroxide and precipitating with hydrochloric acid, yielded, from 100 g. of biuret with water of crystallization, 95 g., 70% of the theoretical, of very small white crystals which decomposed at 175–180°. Thiele and Uhlfelder report a decomposition temperature of 165°. Two recrystallizations from water (52 cc. per gram) at 65–67° raised the decomposition temperature to 223°. It was found necessary to carry out the crystallization below 70°, for at that temperature the solution begins to decompose with the evolution of gas. The nitrobiuret was identified by conversion to benzalaminobiuret and by analysis with the nitrometer; nitro group nitrogen: found, 9.50, 9.37; calcd. for $C_2H_4O_2N_3NO_2$, 9.42.

Tests for Nitrobiuret.—Nitrobiuret gives no color with ferrous sulfate and sodium hydroxide solution, in which respect it differs from nitroguanidine.[3] One-tenth of a gram of nitrobiuret in 5 cc. of water, treated with 1 g. of zinc dust and 1 cc. of 50% acetic acid, allowed to stand for fifteen minutes, and filtered, yielded a solution which did not reduce silver acetate in the cold (as does the corresponding solution from nitroguanidine) but reduced ammoniacal silver nitrate instantly. When a small drop of benzaldehyde was added to such a solution, a crystalline precipitate of benzalaminobiuret was formed within a few minutes.

Decomposition of Nitrobiuret in Aqueous Solution.—Portions of about 1 g. each of nitrobiuret were dissolved in 10 cc. of water, warmed until gassing ceased and evaporated to dryness on the water-bath. The weight of residue in several experiments varied between 44.8 and 47.2% of the weight of the nitrobiuret which was taken. About 80% of the residue consisted of urea; about 20% of cyanuric acid. No other substance was found.

Nitrations with Nitrobiuret.—A solution of 3 g. of nitrobiuret in 30 cc. of concd. sulfuric acid at 2–3° was added slowly and with stirring to a cold solution of 1.96 g. of aniline in 7 cc. of concd. sulfuric acid. The mixture was stirred continuously for six hours while cooled with ice, then poured onto cracked ice, made alkaline with ammonia and extracted with chloroform. The chloroform solution yielded 2.34 g. of mixed nitranilines, 85% of the theoretical. This was analyzed by the melting-point method of Holleman, Hartogs and van der Linden[4] and found to consist of 30.3% *p*-, 42.0% *o*- and 27.7% *m*-nitraniline.

Three grams of nitrobiuret in 30 cc. of concd. sulfuric acid and 3 g. of acet-*p*-toluide in 10 cc. were mixed and warmed in the boiling water-bath for fifteen minutes. The mixture was drowned in ice water and the product, recrystallized from water, gave 1.5 g. of *m*-nitro-acet-*p*-toluide as pale yellow needles, m. p. 94–94.3°.

Potassium Allophanate from Nitrobiuret.—Five and six-tenths grams of nitrobiuret and 2 g. of potassium hydroxide were refluxed together for two hours in 60 cc. of 80% alcohol. Small plates of potassium allophanate separated from the cold liquid. These, after washing with alcohol and ether, weighed 0.95 g., 32% of the theoretical.

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[2] Cyanic acid from nitrourea in water solution does not combine with urea to form biuret. A solution of urea and nitrourea on evaporation to dryness yields only urea along with some cyanuric acid and ammonium cyanurate.

[3] Davis, Ashdown and Couch, This Journal, **47**, 1063 (1925).

[4] Holleman, Hartogs and van der Linden, *Ber.*, **44**, 704 (1911).

The material was recrystallized from alcohol and a portion of it was converted to potassium sulfate by evaporation with sulfuric acid; 0.4632 g. yielded 0.5637 g. of K_2SO_4; calcd. for $C_2H_3O_3N_2K$, 0.5676.

In a similar experiment with absolute alcohol, no potassium allophanate was obtained. The fact that no gas was given off showed that dearrangement did not take place in the anhydrous solution.

In an experiment with 50% alcohol, urea was produced but no potassium allophanate could be isolated. The dicyanic acid was apparently hydrolyzed.

Reaction with Alcohols.—Portions of nitrobiuret were refluxed, respectively, with absolute ethyl, absolute *n*-propyl, absolute *n*-butyl and absolute *tert.*-butyl alcohols. The nitrobiuret was recovered unchanged and no evidence was found of carbamic or allophanic ester.

When nitrobiuret was refluxed with a 1% solution of water in the various alcohols, dearrangement evidently occurred, for nitrous oxide was evolved. The solutions were evaporated to dryness and the residues were extracted with boiling aviation gasoline and with boiling benzene, but neither of the extracts contained any dissolved substance—and we conclude that no carbamate or allophanate was formed. The material insoluble in gasoline and benzene was found in each case to be urea and cyanuric acid.

Five cc. of the alcohol and 1.4 g. of nitrobiuret in a small flask under reflux were heated in the boiling water-bath until no more air was driven out of the apparatus. Water was then admitted through a dropping funnel until the evolution of nitrous oxide commenced. The heating was continued for fifteen or twenty minutes until gas production had ceased. The solutions were evaporated to dryness; the residues were dried in vacuum and extracted with hot gasoline and hot benzene. The resulting carbamates and allophanates were identified, after recrystallization, by mixed melting points with samples of known purity. The yields are tabulated below.

TABLE I

PRODUCTS (GRAMS) FROM 1.4 GRAMS OF NITROBIURET AND 5 CC. OF ALCOHOL

Alcohol	Ethyl	*n*-Propyl	*n*-Butyl	*Tert.*-butyl	*Iso*-amyl
Carbamate	0.05	0.10	0.13	0.16	None
Allophanate	0.23	0.12	0.30	None	0.25

The carbamates are not formed first, for nitrobiuret does not dearrange to produce cyanic acid which could form them directly by combination with the alcohols. Undoubtedly the dicyanic acid from the dearrangement first combines with the alcohols to form allophanates, and these react with the alcohols to produce carbamates. We have found in fact that allophanates are converted to carbamates by refluxing with alcohols.

Reaction with Ammonia.—Twenty-five cc. of strong ammonia water and 1.4 g. of nitrobiuret, heated together in a sealed tube at 100° for four hours, yielded 0.7 g. of biuret, 60% of the theoretical, and small amounts of cyanuric acid and urea.

Substituted Biurets.—Nitrobiuret and an equivalent quantity of the amine were brought together in water, generally enough to dissolve both reagents, and the mixture was warmed gently until gas evolution had ceased. The liquid was then refluxed for fifteen or twenty minutes and allowed to cool for crystals—or concentrated and cooled—or evaporated to dryness, in which case the substituted biuret was extracted with an organic solvent which did not dissolve the cyanuric acid. All of the products were recrystallized to constancy of melting point; yields, etc., are shown in Table II.

The low yields in the cases of methyl- and ethylbiuret are evidently due to loss of the amines by volatilization. An experiment in which nitrobiuret, methylamine and water

TABLE II

SUBSTITUTED BIURETS

Substance, -biuret	Yield, %	% Nitrogen, Found	Calcd.	M. p., °C.	Habit
ω-Methyl	12.5	...	...	166.5–167	Prisms from alcohol
ω-Ethyl	23.9	...	...	154–154.5	Fine needles from alcohol
ω-*n*-Propyl	45.0	27.67	27.58	147.2–147.6	Recrystallized from water
ω-*n*-Butyl	70.0	26.33	26.41	129.1–129.5	Irregular shiny plates from water
ω-Benzyl	43.0	21.33	21.24	174.5–175	Tufts of microscopic prisms from water
ω-Phenyl	80.0	...	...	165	Silky needles from water
ω-*p*-Tolyl	62.0	...	...	199	Fine needles from water
ω-α-Naphthyl	52.0	18.28	18.34	217.3–217.6	Very fine needles from 50 per cent. alcohol
ω,ω-Dimethyl	33.6	32.18	32.06	141–141.5	Thick needles from water
ω,ω-Diethyl	80.0	26.50	26.41	139–139.2	Thick pointed leaflets from water
ω,ω-Di-*n*-propyl	62.0	22.54	22.46	129–129.4	Fine sharp needles from water
ω,ω-Di-*n*-butyl	50.0	19.37	19.53	144.8–145	Small glistening plates from water
ω-Ethyl-ω-phenyl	71.0	20.41	20.29	155.2–155.8	Thin glistening plates from alcohol
ω-*n*-Propyl-ω-phenyl	45.3	18.96	19.00	151–151.5	Thin glistening rectangular plates from alcohol

were heated in a sealed tube at 100° for half an hour gave a yield of 50% of the theoretical amount of ω-methylbiuret.

Nitrobiuret and Urea.—Two and eight-tenths grams of nitrobiuret and 1.2 g. of urea were dissolved in 25 cc. of water, allowed to stand for several days, diluted to 50 cc. and heated to boiling. On evaporation to 10 cc. and cooling, the mixture deposited crystals which did not melt at 260° and were identified as cyanuric acid. Schiff[5] reports that carbonyldiurea melts at 231–232° and is only sparingly soluble in water.

Nitrobiuret and Biuret. Tetruret.—One and four-tenths grams of nitrobiuret and 1.2 g. of biuret were dissolved in 50 cc. of warm water. After gassing had ceased, the mixture was evaporated to 10 cc. Six-tenths of a gram of crystals separated, m. p. 178–180°. Two recrystallizations from water raised the melting point to 186.2–187.1°. When treated with the reagents for the ordinary biuret test, the substance gave a beautiful blue-violet color such as Thiele and Uhlfelder[1] had found to be characteristic of tetruret. Those workers had prepared the substance by the action of ammonia on allophanic acid azide and reported the melting point as 186°.

Summary

Nitrobiuret appears to dearrange in two modes, to form nitroamide and dicyanic acid, and nitrocyanic acid and urea. When an aqueous solution is warmed, the nitroamide evidently breaks down into nitrous oxide and water, the nitrocyanic acid into nitrous oxide and carbon dioxide, and the liquid acts toward various reagents as if it contained dicyanic acid.

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[5] Schiff, *Ann.*, **291**, 374 (1896).

With moist alcoholic potash nitrobiuret yields potassium allophanate.

With moist alcohols it gives allophanic esters which react with the alcohols on refluxing to produce carbamic esters.

With aqueous ammonia it yields biuret; with biuret, tetruret; with primary and secondary amines, ω-substituted biurets.

A number of ω-mono-substituted biurets (several new) and of ω,ω-disubstituted biurets (all new) have been prepared and are described.

A solution of nitrobiuret in concd. sulfuric acid gives up its nitro group quantitatively in the nitrometer and is a suitable reagent for nitrations.

CAMBRIDGE, MASSACHUSETTS

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DICYANIC ACID

BY TENNEY L. DAVIS AND KENNETH C. BLANCHARD

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Cyanamide, which differs from cyanic acid in having an NH group in place of an oxygen atom, combines with itself in warm water solution, one molecule functioning as a derivative of cyanic acid and one as a derivative of ammonia, to form a dimer which is a urea derivative, namely, dicyandiamide or cyanoguanidine. When heated in the dry state cyanamide trimerizes to form melamine, a white crystalline solid, sparingly soluble in cold water, which sublimes without melting. Cyanic acid yields a similar trimer, cyanuric acid, of about the same physical properties as melamine. We have found evidence which shows that cyanic acid in solution dimerizes in part, one molecule evidently functioning in the usual manner of cyanic acid in urea formation and one as an ammonia derivative, namely, as carbonyl-ammonia, to form a urea derivative, carbonylurea or dicyanic acid.

$$H{-}N{=}CO + H{-}NCO \longrightarrow NH_2{-}CO{-}NCO$$

Dicyanic acid gives the biuret test; cyanic acid does not. Cyanic acid combines with amines to yield urea derivatives; dicyanic acid with amines to form biuret derivatives. An aqueous solution of cyanic acid in which some dimerization has occurred gives with aniline both phenylurea and phenylbiuret. With alcohols it yields both carbamic and allophanic esters.

Cyanic acid behaves in several different ways in aqueous solution. (1) It ionizes as a weak acid. (2) It trimerizes to cyanuric acid, which may precipitate out or may appear as a residue when the liquid is evaporated. (3) It undergoes hydrolysis to produce ammonia and carbon dioxide, and the ammonia combines with unchanged cyanic acid to form urea and ammonium cyanate in the ratio corresponding to the equilibrium between