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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RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

DICYANIC ACID

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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.

$$\mathrm{H{-}\underset{\vdots}{N}{=}\underset{\vdots}{C}O + H{-}\vdots{-}NCO \longrightarrow NH_2{-}CO{-}NCO}$$

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 these substances. (4) It dimerizes to form dicyanic acid.[1] Dicyanic acid either depolymerizes during the evaporation of the solution or undergoes hydrolysis—for an aqueous solution of cyanic acid yields only urea and a little cyanuric acid when it is evaporated to dryness.

The dimerization of cyanic acid is obviously due to the affinity of one molecule of cyanic acid for another molecule of the same kind. Different solvents would probably have different effects upon it, some causing more dimerization or association, some less. The affinity of cyanic acid for the solvent itself would also come into play. Thus, cyanic acid gas passed into a solvent which has a great affinity for it would react with the solvent and might not dimerize at all. Passed into a solvent for which it has little or no affinity, it would be more likely to dimerize. When cyanic acid gas is passed into an alcohol, one portion may combine with the alcohol to form a carbamic ester, another portion may dimerize to form dicyanic acid which then combines with the alcohol to form an allophanic ester. Evidently the associating action of the solvent and the relative affinities of cyanic acid for cyanic acid and of cyanic acid for the solvent are both to be considered. These matters are now under investigation in this Laboratory.

The formation of allophanic ester from cyanic acid and alcohol was long ago explained by Hofmann[2] as being due to the direct combination of one molecule of cyanic acid with one of alcohol to produce carbamic ester and to the subsequent addition of a second molecule of cyanic acid to this substance. He claimed indeed to have prepared allophanic ester by the action of cyanic acid on urethan. Béhal[3] more recently was unable to obtain any allophanic ester by this method. He prepared an extensive series of aliphatic and aromatic allophanates by passing into the corresponding alcohols cyanic acid gas from the thermal depolymerization of cyanuric acid.[4] Carbamates were formed at the same time. He supposed that the allophanates probably resulted from the combination of the alcohols with dicyanic acid produced during the depolymerization. We think it more likely that the dicyanic acid is produced by dimerization in the liquid phase—and have found that the cyanic acid which results from the acidification of a solution of potassium cyanate dimerizes in part and yields both carbamic and allophanic esters with alcohols.

Lane[5] refluxed urea with *n*-butyl alcohol for three hours and obtained both allophanate and carbamate. After six hours' boiling he found only carbamate. He heated *n*-butyl carbamate with urea and with nitrourea,

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[1] The dimer of phenylisocyanate has been prepared by Hoffmann, *Ber.*, **4,** 246 (1871), by the action of triethylphosphine on phenylisocyanate, and by Snape, *Trans. Chem. Soc.*, **49,** 254 (1886), by the action of pyridine.

[2] Hofmann, *Ber.*, **4,** 268 (1871).

[3] Béhal, *Bull. soc. chim.*, **25,** 477 (1919).

[4] Liebig and Wöhler, *Ann.*, **39,** 29 (1846).

[5] Lane, Bachelor's "Thesis," Massachusetts Institute of Technology, **1925.**

and failed to produce any allophanate. Bishop[6] obtained both allophanate and carbamate by refluxing *n*-butyl alcohol with biuret for a short time, and on longer refluxing less of the allophanate. We conclude that the allophanate is formed directly and independently of the carbamate, and hence that dicyanic acid is present in the solution.

Carbamic ester when heated in alcohol solution evidently dissociates in part, reversing its formation from cyanic acid and alcohol. The cyanic acid which results associates in part to form dicyanic acid, which then combines with the alcohol to form allophanic ester. By heating ethyl carbamate with alcohol in a sealed tube at 100° we have converted a portion of it into ethyl allophanate.

An aqueous solution of potassium cyanate in a warm room hydrolyzes rapidly and contains both cyanic acid and urea. We have isolated urea from such a solution. The liquid however fails to give a biuret test, even after standing for several hours. It is evident that cyanic acid and urea do not combine to form biuret under these conditions.

When a concentrated aqueous solution of potassium cyanate is acidified with acetic acid and allowed to stand for a few minutes, the resulting liquid gives a biuret reaction. Werner[7] supposes that a portion of the cyanic acid undergoes hydrolysis, that urea is formed and that this combines with cyanic acid to form biuret. We find that the solution contains no biuret. By a colorimetric method the amount of biuret necessary to give a biuret reaction of the observed intensity was determined. The solution was worked up for biuret and none was found. An amount of actual biuret corresponding to the colorimetric determination was added to a similar solution; the liquid was worked up for biuret and four-fifths of that which had been added was recovered. An acidified solution of potassium cyanate, after standing for a short time, gave with aniline both phenylurea and ω-phenylbiuret.

The aqueous solutions which result, respectively, from the passage of cyanic acid (from the depolymerization of cyanuric acid) into water, and from warming a solution of nitrourea until gas evolution ceases, both give the biuret test. They contain cyanic acid and dicyanic acid—and, after standing, urea—but contain no biuret and yield on evaporation residues which consist of urea along with a little cyanuric acid. The liquid which results from warming an aqueous solution of nitrobiuret contains at first dicyanic acid but no cyanic acid; it gives the biuret test and yields a similar residue on evaporation.

Experiments

Allophanates and Carbamates from Potassium Cyanate.—Thirty cc. of ethyl alcohol was added to a solution of 16.2 g. of potassium cyanate in 30 cc. of water; the mixture

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[6] Bishop, Bachelor's "Thesis," Massachusetts Institute of Technology, **1925.**

[7] Werner, "The Chemistry of Urea," London, **1923,** p. 25.

was acidified with hydrochloric acid, allowed to stand for an hour and evaporated to dryness. The residue was extracted first with aviation gasoline and then with benzene, and the extracts yielded, respectively, 0.3 g. of ethyl carbamate, m. p. 49–50° after sublimation, and 1.4 g. of ethyl allophanate, m. p. 197–198° after recrystallization from benzene, both further identified by mixed melting points with known samples.

Similar experiments with 0.2 mole of potassium cyanate, 25 cc. of water and 0.1 mole of *n*-butyl and of *iso*-amyl alcohol yielded, respectively, 0.2 g. of *n*-butyl carbamate, m. p. 51–52°, and 0.4 g. of *n*-butyl allophanate, m. p. 149–149.5°; and 0.3 g. of *iso*-amyl carbamate, m. p. 64–65° after sublimation and 0.1 g. of *iso*-amyl allophanate, m. p. 161.8–162.5°.

Ethyl Allophanate from Ethyl Carbamate.—Several experiments were tried in which urethan was refluxed for different intervals of time with different amounts of alcohol, but no allophanate was found in the residues when the liquids were evaporated to dryness. It was believed that whatever cyanic acid may have been produced escaped through the condenser. Ten cc. of alcohol was therefore heated with 8.9 g. of urethan in a sealed tube at 100° for half an hour. The residue from the evaporation of the liquid yielded 0.4 g. of material insoluble in gasoline which was identified as ethyl allophanate by mixed melting point.

The Biuret Test in an Acidified Solution of Potassium Cyanate.—Six cc. of glacial acetic acid was added very slowly to a well-stirred solution of 8.1 g. of potassium cyanate in 20 cc. of water. The mixture was brought to neutrality with barium carbonate, filtered and diluted to 50 cc. The intensity of color in the biuret reaction of a 5-cc. portion of this liquid was found to be equal to that produced by 0.03 g. of actual biuret—which would correspond to 0.27 g. of biuret in the remaining 45 cc. of solution. The remaining solution was evaporated to dryness and the residue was refluxed with 5 cc. of alcoholic potash (in which biuret is soluble while cyanuric acid is almost insoluble). The filtrate, acidified with hydrochloric acid and filtered for the removal of potassium chloride, was evaporated to a small volume. This solution gave no biuret reaction and on chilling in a freezing mixture deposited a few crystals of potassium acetate. Three repetitions of the experiment gave identical results. A similar experiment, in which 0.3 g. of actual biuret was added to the water in which the potassium cyanate was dissolved, gave a final residue which gave the biuret reaction with an intensity of color which corresponded to 0.24 g. of biuret or four-fifths of the amount which had been added.

Phenylbiuret from Potassium Cyanate.—A solution of 8.1 g. of potassium cyanate in 25 cc. of water was chilled and acidified with 6 cc. of glacial acetic acid. After five minutes, 9.3 g. of aniline was added. The mixture was stirred for five minutes, diluted with 100 cc. of hot water, filtered, freed from excess aniline and refluxed for two hours to convert the phenylurea into insoluble carbanilide. The filtrate on chilling yielded silky needles of phenylbiuret along with a small quantity of phenylurea. The product, recrystallized from water, amounted to 0.6 g., 3.3% of the theoretical, of ω-phenylbiuret, m. p. 165°.

Summary

Chemical evidence is presented which shows that cyanic acid in solution dimerizes in part to form dicyanic acid.

Allophanic esters and biuret are formed directly from the alcohols and from ammonia, respectively, not by the addition of cyanic acid to intermediate carbamic esters and urea.

Aqueous solutions of cyanic acid contain some substance, not biuret,

which gives a biuret test, which reacts with aniline to form phenylbiuret and with alcohols to form allophanic esters.

CAMBRIDGE, MASSACHUSETTS

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EFFECT OF ANILINE ON CELLULOSE TRIACETATE

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Introduction

The action of aniline and similar compounds on cellulose triacetate has been studied but little by investigators in the field of cellulose chemistry. In a paper by E. Knoevenagel,[1] published in 1914, however, mention is made that triacetylcellulose may be heated with aniline without saponification of the ester. It is pointed out that marked differences in solubility result, which the author ascribes as possibly due to a stereoisomeric change of the cellulose acetate molecule, similar to that which produces mutarotation in the sugars. No polarimetric data are given.

That an ester like cellulose acetate could be kept in contact with a base like aniline at a high temperature for a protracted period of time without saponification seemed somewhat incongruous. Therefore, a study was made of the effect of aniline at various temperatures on cellulose triacetate.

Experimental

General Procedure.—The general procedure employed in these experiments was as follows. Fifteen grams of finely-divided cellulose acetate, containing 43.9% of acetyl (theoretical cellulose triacetate, 44.8% acetyl), and 300 cc. of aniline (b. p. 88–90° at 15 mm.) were placed in a 500-cc. ring-necked Pyrex flask equipped with an air condenser.

Three series of experiments were made. The first of these at the boiling point of the aniline–cellulose acetate solution (approx. 183°) was done in an oil-bath, the solution being refluxed continuously. The second at 148–151° was carried out by placing the flask in an air-bath, the temperature of which was maintained by the vapors of boiling cyclohexanol (b. p. 157–162°) and the third series was conducted at room temperature, 20–25°.

In the series in which elevated temperatures were employed, the solutions were cooled to approximately zero degrees and the mixtures were poured into 3 liters of ethyl alcohol. The products were washed with alcohol until free from aniline; this was followed by washing with ether. They were dried at 35°, after which the samples for analyses were dried at 105° for fifteen to twenty hours. Acetyl determinations were made according to the method of Eberstadt[2] as described by Knoevenagel,[3] with slight modifications. Optical rotations were determined using a Hilger polarimeter (accuracy 0.01°) employing the 546.1 mμ line of the mercury spectrum as illuminant. Readings

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[1] Knoevenagel, *Z. angew. Chem.*, **27**, 505 (1914).

[2] Eberstadt, "Dissertation," Heidelberg, **1909**.

[3] Knoevenagel, *Cellulosechemie*, **3**, 119 (1922).