

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE AMMONO CARBONIC ACIDS

BY EDWARD C. FRANKLIN

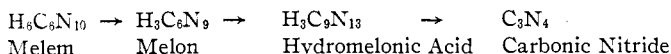
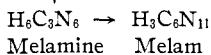
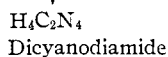
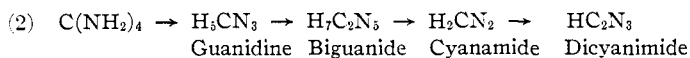
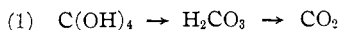
Received November 23, 1921

Introduction

Ammono acids are compounds related to ammonia as the ordinary oxygen acids are related to water.¹ It follows therefore that the familiar substances guanidine, biguanide, cyanamide, dicyanodiamide and melamine as well as the less well known melam, melem, melon and hydromelonic acid, which many years ago were objects of intensive study,² are to be looked upon as ammono carbonic acids.

Aquo Carbonic Acids and Ammono Carbonic Acids

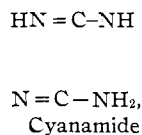
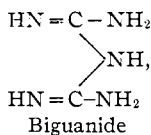
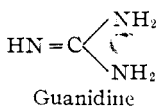
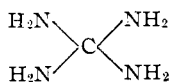
The formal analogy between the carbonic acids of the water or oxygen system on the one hand and the carbonic acids of the ammonia or nitrogen system on the other is shown by the following schemes which represent (1) aquo ortho carbonic acid and its dehydration products and (2) the compounds enumerated above represented as de-ammonation products of a purely hypothetical ammono ortho carbonic acid.³



¹ Cf. *Am. Chem. J.*, **47**, 285 (1912); *Proc. Eighth Int. Cong. App. Chem.*, **6**, 119 (1912).

² Liebig, *Ann.*, **10**, 1 (1834); **50**, 337 (1844); **53**, 330 (1845); **95**, 257 (1855). Laurent and Gerhardt, *Ann. chim. phys.*, [3] **19**, 85 (1847).

³ The following structural formulas are printed in the belief that the relations between the members of the group of compounds under consideration will thereby be made clearer. Those given for guanidine, biguanide, cyanamide, dicyanodiamide and melamine are the generally accepted formulas. The remaining compounds are represented as successive de-ammonation products of melamine which for this purpose is formulated as the amide of the trivalent nucleus, C_3N_3 .



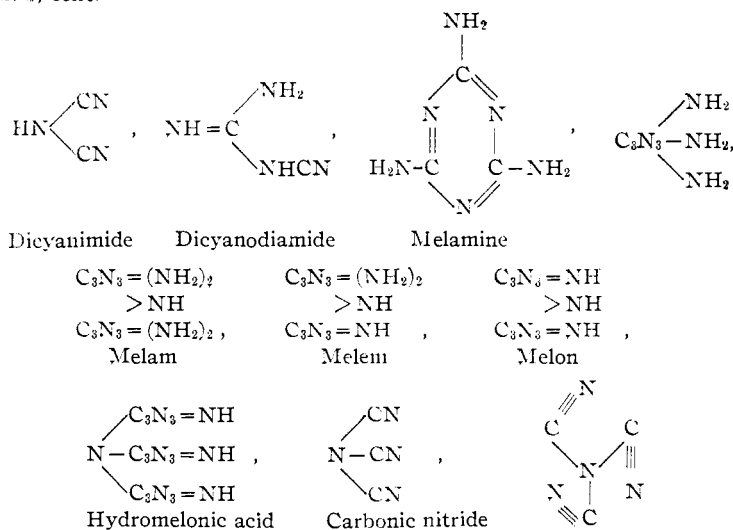
The first scheme, familiar for its frequent use to show the relations between ortho carbonic acid, ordinary carbonic acid and carbonic anhydride, calls for no comment other perhaps than to contrast the very limited number of compounds in this series of dehydration products with the much larger number of ammono carbonic acids listed in the second, and to note that the end product in the former is a gas, while all the compounds in the latter group are solids. Melon, the best known compound towards the end of the second scheme, is an insoluble, infusible substance which withstands without change a temperature approaching redness.

In the second scheme guanidine, biguanide, cyanamide and dicyanamide are represented as stepwise de-ammonation products of ammono ortho carbonic acid, dicyanodiamide and melamine as a dimer and a trimer, respectively, of cyanamide, while the remaining members of the group appear as successive de-ammonation products of melamine. For the most part the transformations indicated have been experimentally established.

Guanidine to Melon.—The action of water and ammonia, respectively, on chloropicrin or ethyl ortho carbonate might be expected to yield compounds of the respective formulæ $C(OH)_4$ and $C(NH_2)_4$. As a matter of fact, the products obtained are, in the first case, carbon dioxide, in the second, guanidine.⁴ Guanidine thus appears as a de-ammonation product of an hypothetical ammono ortho carbonic acid just as carbon dioxide is usually assumed to be the dehydration product of the primarily formed ortho carbonic acid.

The second step in this process of de-ammonation, namely, the conver-

Ref. 3, cont.



Hofmann, *Ann.*, **139**, 107 (1866); *Ber.*, **1**, 145 (1868).

sion of guanidine into biguanide has been accomplished by carefully heating guanidine hydrochloride.⁵

Apparently neither guanidine nor biguanide has been converted into cyanamide by simple loss of ammonia. When guanidine carbonate,⁶ or free guanidine⁷ is heated melamine, a trimer of cyanamide, is obtained instead of cyanamide itself. However, the transformation of guanidine into cyanamide is easily accomplished by dissolving guanidine in fused sodium amide⁸ or by heating it with quicklime.⁹ It is safe to assume that biguanide may also be converted into cyanamide by the action of fused sodium amide.

In the table given above, cyanamide is represented either as losing ammonia to form dicyanimide or as undergoing polymerization to dicyandiamide. When cyanamide is heated it does not lose ammonia as might be expected to form dicyanimide. Instead, it undergoes polymerization first to dicyanodiamide¹⁰ and thence to melamine.¹¹ The transformation of cyanamide into dicyanimide takes place when melon is dissolved in fused disodium cyanamide.¹²

At a higher temperature melamine loses ammonia to form melam which in turn is finally converted into melon. Further de-ammonation of melon to hydromelonic acid or to pure carbonic nitride has not been accomplished.

Returning to dicyanimide it is interesting to note that this substance on being heated is polymerized to melon instead of losing ammonia to form carbonic nitride.

Melon to Guanidine.—Among the inverse transformations but one case of simple addition of ammonia seems to be known. Rathke¹³ found that melamine is formed when melam is heated with aqueous ammonia.

Cyanamide, in the form of its disodium salt, is formed when sodium melonate, sodium dicyanimide, melon, crude melam, melamine or dicyandiamide is dissolved in fused sodium amide. The ammono carbonic acids,¹⁴ hydromelonic acid, dicyanimide, melon and melam are thus ammonated, while melamine and dicyanodiamide are depolymerized to cyanamide, the only ammono carbonic compound which is stable in the presence of an excess of the fused ammono base.

The simple stepwise ammonation of cyanamide through biguanide to

⁵ Bamberger and Dieckmann, *Ber.*, **25**, 543 (1892).

⁶ Nencke, *J. prakt. Chem.*, [2] **17**, 235 (1878); Smolka and Friedreich, *Monatsh.*, **10**, 91 (1889).

⁷ Rathke, *Ber.*, **12**, 778 (1879).

⁸ Observations made in this laboratory.

⁹ Emich, *Monatsh.*, **10**, 334 (1889).

¹⁰ Beilstein and Geuther, *Ann.*, **108**, 99 (1858); **123**, 241 (1862).

¹¹ Drechsel, *J. prakt. Chem.*, [2] **13**, 331 (1876).

¹² See p. 497.

¹³ Rathke, *Ber.*, **23**, 1675 (1890).

¹⁴ See p. 497.

guanidine has apparently never been realized. Cyanamide, however, is ammonated to guanidine when heated with ammonium chloride in alcoholic solution¹⁵ and in a similar manner dicyandiamide is converted into biguanide.¹⁶ Dicyanodiamide is also ammonated to biguanide when heated with ammoniacal cupric hydroxide solution.¹⁷

The final step in this ammonation series, namely, the formation of guanidine from biguanide has not been accomplished.

Hydrolysis of the Ammono Carbonic Acids and the Ammonolysis of Aquo Carbonic Acid.—In harmony with the view that compounds under consideration are ammono carbonic acids is the behavior of the ammono carbonic acids toward water, on the one hand, and the action of ammonia on aquo carbonic acid, or more generally, on the metallic carbonates, on the other. The ammono carbonic acids without exception when heated to a high temperature in the presence of water are hydrolyzed, usually through various mixed aquo ammono carbonic acids to carbon dioxide and ammonia in accordance with the general equation $x\text{NH}_3 \cdot y\text{C}_3\text{N}_4 + 6y\text{H}_2\text{O} = 3y\text{CO}_2 + (x + 4y)\text{NH}_3$ in which $x\text{NH}_3 \cdot y\text{C}_3\text{N}_4$ represents any one of the known ammono carbonic acids.¹⁸

The equation given above, read from right to left, represents the ammonolysis of aquo carbonic acid, or strictly speaking, carbonic anhydride, to an ammono carbonic acid. In experiments¹⁹ in this direction, however, the ammonolysis has been carried only so far as the formation of urea, a mixed aquo ammono carbonic acid. The action of ammonia on ethyl ortho carbonate to form guanidine mentioned above and on calcium carbonate to form calcium cyanamide²⁰ are, in principle, reactions represented by the equation given above read from right to left.

The Acid Properties of Guanidine and its De-ammonation Products.—Among the members of the group of compounds under consideration it happens that only dicyanamide and hydromelonic acid are endowed with distinct acid properties. Cyanamide and dicyanodiamide are neutral in reaction. The first forms an unstable hydrochloride; both form metallic derivatives which, excepting certain highly insoluble salts of heavy metals, are practically completely hydrolyzed in the presence of water. Guanidine and biguanide show not the slightest acid properties in water solution. On the contrary, they behave as strong bases.²¹ Mel-

¹⁵ Erlenmeyer, *Ann.*, **146**, 259 (1868); Bannow, *Ber.*, **4**, 162 (1871).

¹⁶ Smolka and Friedreich, *Monatsh.*, **9**, 288 (1888); **10**, 87 (1889); Ref. 5, p. 545.

¹⁷ Herth, *ibid.*, **1**, 94 (1880).

¹⁸ For example, according to Knapp [*Ann.*, **21**, 256 (1837)] melamine is hydrolyzed first to ammeline, thence to ammelide and finally to cyanuric acid.

¹⁹ Mixter, *Am. Chem. J.*, **4**, 35 (1882). Bourgeois, *Bull. soc. chim.*, [3] **7**, 48 (1892); [3] **17**, 474 (1897).

²⁰ Ger. pat. 138,456; *Zentr.*, **1903**, I, 677.

²¹ They are bases in the sense that ammonia is a base.

amine is a weak base. Melam, melon and melon are insoluble substances, concerning the acid properties of which practically nothing is known.

Conclusion.—The formal analogy existing between the two carbonic acids as derivatives of water on the one hand and the group of compounds under consideration, looked upon as derivatives of ammonia, on the other; the readiness with which one may pass stepwise from guanidine to melon by processes of de-ammonation and polymerization and, beginning with melon, return to guanidine by reactions of ammonation and depolymerization, the fact that each of these compounds may be hydrolyzed into carbon dioxide and ammonia are considerations which certainly lend support to the view that guanidine and its de-ammonation products are carbonic acids of the ammonia system.

This view is established, as it would seem, by the experimental work described below which shows that all the soluble members of this group of compounds are capable of forming metallic salts when liquid ammonia²² instead of water is used as solvent in which to carry out the necessary reactions.

Guanidine



Without going into details it will serve present purposes to point out that the large majority of methods listed in Beilstein's "Handbuch" for the preparation of guanidine involve processes of ammonolysis, ammonation or de-ammonation, while none is in disagreement with the view that it is an ammono carbonic acid.

The acid properties of guanidine are demonstrated by the following described reactions which have been carried out in liquid ammonia solutions.²³

Dipotassium Guanidine, $\text{K}_2\text{H}_3\text{CN}_3$.—It has been found that potassium amide in excess added to a solution of guanidine nitrate²⁴ results in the formation of dipotassium guanidine which is insoluble and potassium ni-

²² Compounds which, dissolved in ionizing solvents give a very low hydrogen-ion concentration, are not recognizable as acids in water solution because of the relatively high degree of ionization of water itself into hydrogen and hydroxyl ions. In liquid ammonia the very much lower degree of auto-ionization, which characterizes this solvent as compared with water, permits the acid properties of compounds which as acids are much too weak to be recognized as such in aqueous solutions to show themselves.

²³ For descriptions of methods of manipulating liquid ammonia solutions, cf. *THIS JOURNAL*, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913); *J. Phys. Chem.*, **15**, 915 (1911); **16**, 694 (1912).

²⁴ It is a matter of very considerable difficulty to prepare pure guanidine, and once obtained it is so very hygroscopic that the exclusion of water and carbon dioxide from its liquid ammonia solution would be a tedious undertaking. It was therefore decided to make use of guanidine nitrate which is easily obtained in a pure dry state. This compound dissolved in liquid ammonia may be looked upon as a solution containing a mixture of nitric acid and guanidine.

trate which is soluble. The reaction is represented by the equation, $\text{H}_5\text{CN}_3 \cdot \text{HNO}_3 + 3\text{KNH}_2 = \text{K}_2\text{H}_3\text{CN}_3 + \text{KNO}_3 + 3\text{NH}_3$. The salt was obtained in the form of a non-crystalline powder which was vigorously hydrolyzed by the action of water into guanidine and potassium hydroxide.

Preparation I.—Half a gram of guanidine nitrate in solution in liquid ammonia added to a solution of 3 equivalents of potassium amide gave a bulky, amorphous precipitate which after standing for some time became denser and then settled fairly well. After the manner described in an earlier paper the precipitate was washed, dried in a vacuum and weighed. Preparatory to analysis the salt was treated first with water. Hydrochloric acid was then added which gave an aqueous solution of guanidine hydrochloride and potassium chloride. The specimen dried in a vacuum at 20° weighed 0.5397 g. One half gave 0.3333 g. of potassium sulfate. An accident prevented the determination of nitrogen. 0.50 g. of guanidine nitrate and 0.48 g. of potassium gave 0.54 g. of dipotassium guanidine and 0.42 g. of potassium nitrate. Calc. for $\text{K}_2\text{H}_3\text{CN}_3$, 0.55 g.; for KNO_3 , 0.41 g.

Preparation II.—With the possibility in mind of obtaining a monopotassium salt a solution containing 2 equivalents of potassium amide was added to a solution of 0.30 g. of guanidine nitrate. No precipitate was formed. On concentrating the solution a crop of mixed crystals of potassium nitrate and, presumably, the monopotassium salt of guanidine separated from the solution. The isolation of the monopotassium salt from the mixture appearing impracticable, the reaction tube was opened and somewhat more than 4 additional equivalents of metallic potassium were introduced with the object in view of determining whether a salt could be obtained containing more than two atoms of potassium in the molecule. The solution of potassium amide formed by the action of ammonia on the potassium (in the presence of platinum black) was then added to the solution of the monopotassium salt with the result that a white amorphous precipitate was formed. The precipitate was washed and prepared for analysis in the usual way. The preparation dried in a vacuum at 20° weighed 0.3538 g. One half gave 0.2155 g. of K_2SO_4 ; the other half gave 0.0580 g. of N.

It is to be noted that in the presence of a large excess of potassium amide only two of the acid hydrogen atoms were replaced.

Preparation III.—In a third experiment the potassium amide from 0.38 g. of potassium, and 0.30 g. of guanidine nitrate were used. The preparation dried in a vacuum at 20° weighed 0.3250 g. One half gave 0.2082 g. of K_2SO_4 .

Analysis. Calc. for $\text{K}_2\text{H}_3\text{CN}_3$: K, 57.7; N, 31.0. Found: K, (I) 55.3, (II) 54.7, (III) 57.5; N, (II) 32.8.

Monosilver Guanidine, AgH_4CN_3 .—This salt was obtained by the action of guanidine nitrate on silver amide in accordance with the equation $\text{H}_5\text{CN}_3 \cdot \text{HNO}_3 + 2\text{AgNH}_2 = \text{AgH}_4\text{CN}_3 + \text{AgNO}_3 + 2\text{NH}_3$. The salt is insoluble in liquid ammonia. It was not obtained in crystalline form.

Preparation I.—The silver amide obtained from 0.50 g. of silver nitrate was transferred in suspension to a solution containing 0.179 g. of guanidine nitrate, a quantity slightly in excess of the amount required for the formation of a monosilver salt. The first portions of the silver amide dissolved in the guanidine nitrate solution,²⁵ the later portions failed to dissolve, nor could any marked change in the appearance of the insoluble residue be observed. The mixture was allowed to stand for 36 hours with occasional shaking with the object in view of transforming the insoluble silver amide

²⁵ The solution of the first portions of the silver amide is the result of the action of nitric acid on silver amide to form silver nitrate which is soluble.

as completely as possible into the guanidine salt. Digestion was followed by a thorough washing of the precipitate. From the washings 0.245 g. of silver nitrate was recovered (calc. 0.250). The salt dried at 20° in a vacuum, was prepared for analysis by treatment, first with water, then with dil. sulfuric acid. The specimen weighed 0.3106 g. One half gave 0.1334 g. of AgCl. The other half gave 0.0322 g. of N. Calc. for AgH_4CN_3 : Ag, 65.1; N, 25.4. Found: Ag, 64.8; N, 20.7. The low result for nitrogen is probably due to incomplete recovery of nitrogen by the Kjeldahl process.

Triphenylguanidine

Accepting guanidine as an ammono carbonic acid, then the readily accessible triphenylguanidine is an ammono ester; and since the ammono-ester contains amide hydrogen it is an acid ester and should react with metallic amides to form salts. Moreover, in view of the fact that typically organic compounds are in a general way readily soluble in liquid ammonia, it was anticipated that the alkali metal salts of triphenylguanidine would be found to be sufficiently soluble to permit their crystallization from liquid ammonia.

Dipotassium Triphenylguanidine, $\text{K}_2(\text{C}_6\text{H}_5)_3\text{CN}_3$.—A well crystallized specimen of this salt has been prepared by the action of potassium amide on triphenylguanidine in accordance with the equation, $\text{H}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + 2\text{KNH}_2 = \text{K}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + 2\text{NH}_3$.

Preparation I.—One g. of triphenylguanidine in solution in liquid ammonia was added to a solution of potassium amide prepared from 0.50 g. of metallic potassium. After a short time and without concentrating the solution beautiful crystals began to separate on the walls and bottom of the tube. Without recrystallization the crop of crystals was washed several times with small quantities of the solvent and then dried in a vacuum at laboratory temperature. After drying the product took on the appearance of a salt which has undergone efflorescence. The salt therefore probably separates from solution with ammonia of crystallization. For analysis the salt was first hydrolyzed by the introduction of a small quantity of water, then dissolved in dilute alcohol and hydrochloric acid. The weight of the specimen was 0.2814 g. One half gave 0.0667 g. of K_2SO_4 . The other half gave 0.0169 g. of N.

Preparation II.—The above described experiment was repeated, excepting that 1.00 g. of triphenylguanidine and the potassium amide from 0.31 g. of metallic potassium (2.2 equivalents of potassium amide per molecule of triphenylguanidine) were used and the product obtained was recrystallized. The light yellow, effloresced, crystals, when dried in a vacuum finally to 100°, weighed 0.9226 g. One half gave 0.2149 g. of K_2SO_4 . The other half gave 0.0555 g. of N. Calc. for $(\text{C}_6\text{H}_5)_3\text{K}_2\text{CN}_3$: K, 21.5; N, 11.6. Found: K, (I) 21.3, (II) 21.0; N (I) 12.0, (II) 12.0.

A third preparation was undertaken with the object in view of determining the ammonia of crystallization. An unfortunate breakage in the apparatus put an end to the experiment, which was not repeated.

Monopotassium Triphenylguanidine.—One g. of triphenylguanidine and one equivalent of potassium amide were brought together in liquid ammonia solution. After the expenditure of much time in fruitless attempts to crystallize the salt a crop of extremely soluble crystals was finally obtained which was unfortunately lost while being prepared for analysis. There is little doubt of the existence of a monopotassium salt.

In view, however, of the time-consuming operations involved it did not seem worth while to repeat the experiment.

Disodium Triphenylguanidine, $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3$ and $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot 3\text{NH}_3$.—Sodium amide, which is but slightly soluble in liquid ammonia, dissolves readily in a solution of triphenylguanidine. The disodium salt separates well crystallized from very concentrated cold solutions. The disodium salt has also been prepared by the action of metallic sodium on the acid ester in accordance with the equation $\text{H}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + 2\text{Na} = \text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + \text{H}_2$.

Preparation I.—A solution containing 1.00 g. of triphenylguanidine was poured upon about 1.2 equivalents of sodium amide. The ammono base dissolved readily in the acid, forming a solution which on concentration at laboratory temperature, and even at -33° , is converted into a viscous mass. When, however, the highly concentrated solution was cooled to a temperature near the freezing point of the solvent a crop of very soluble crystals was obtained. The mother liquor, in small quantity, was drained from the crystal mass, and the latter was then recrystallized from a small quantity of solvent. The preparation, dried at -33° , and blackened as a result of the inadvertent entrance into the tube of a small quantity of air, weighed 0.3300 g. One half gave 0.0612 g. of Na_2SO_4 . The other half gave 0.0298 g. of N. Losses of nitrogen were known to have occurred. Calc. for $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot 3\text{NH}_3$: Na, 12.0; N, 22.0. Found: Na, 12.0; N, 18.0.

Preparation II.—To a solution containing 1.00 g. of triphenylguanidine portions of a solution containing 0.24 g. (3 equivalents) of metallic sodium were successively added. The blue color of the sodium solution was rapidly discharged as a result of the action of the acid on the metal. After the addition of approximately $\frac{2}{3}$ of the metal solution the disappearance of the color of further small portions became very slow. The hydrogen was not collected and measured. The resulting salt solution was evaporated to high concentration and cooled to -78° when a crop of crystals separated. The product was drained of mother liquor, dissolved in pure solvent and recrystallized. The specimen was dried at -33° in a vacuum. Then, maintaining a low pressure within the tube to prevent the melting of the salt in its ammonia of crystallization, the temperature was gradually raised to 70° , the ammonia given off, collected and determined. The amount was 0.0840 g. When dried the specimen weighed 0.5265 g. One half gave 0.1181 g. of Na_2SO_4 . The other half gave 0.0333 g. of N. Calc. for $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3$: Na, 13.9; N, 12.7. Found: Na, 14.5; N, 12.7. Calc. for $\text{Na}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot 3\text{NH}_3$: 13.4. Found: 13.9.

Monosilver Triphenylguanidine, $\text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3$ and $\text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot \text{NH}_3$.—A monosilver salt of triphenylguanidine has been obtained by the action of a solution of the acid ester on silver amide as represented by the equation, $\text{H}_2(\text{C}_6\text{H}_5)_3\text{CN}_3 + \text{AgNH}_2 = \text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3 + \text{NH}_3$. The salt separates from solution with one molecule of ammonia of crystallization which is lost in a vacuum at 20° .

Preparation I.—To 1.00 g. of silver nitrate in solution in liquid ammonia potassium amide prepared from 0.23 g. of metallic potassium was gradually added. The pure white precipitate of silver amide was thoroughly washed and then treated with a solution containing 1.13 g.²⁶ of triphenylguanidine. A considerable quantity of the silver

²⁶ It had been intended to use equimolecular quantities which would have required 1.69 g. of triphenylguanidine. The smaller quantity was used inadvertently.

amide dissolved but the solution becoming supersaturated, crystals of the salt began to separate before all the silver amide had gone into solution. The saturated solution was poured into the second leg of the reaction tube and evaporated to small volume. Crystals of the salt were deposited. The solvent distilled into the first leg of the tube was shaken up with the crude salt, the undissolved portion allowed to settle, after which the supernatant solution was poured into the second leg and evaporated to small volume. Additional pure salt was thus transferred to the second leg. This operation, once more repeated, gave an adequate specimen for analysis. The dried salt was treated first with water and then dissolved in a dilute alcohol sulfuric acid mixture preparatory to analysis. Dried in a vacuum at 20°, the preparation weighed 0.5373 g. One half gave 0.1101 g. of AgCl. The other half gave 0.0290 g. of N.

Preparation II.—In this experiment the silver amide prepared from 0.50 g. of silver nitrate was dissolved in a solution of 0.90 g. of triphenylguanidine or about 106% of the equivalent quantity. Soon after the amide had dissolved, beautiful crystals began forming on the walls and bottom of the reaction tube. The preparation was not recrystallized but was simply washed several times with pure solvent. The salt was then dried in a vacuum at -33°. On warming to laboratory temperature it lost 0.0231 g. of ammonia. Dried at 20° the specimen weighed 0.5565 g. One half gave 0.1069 g. of AgCl. The other half gave 0.0302 g. of N.

Preparation III.—0.50 g. of silver nitrate and 0.90 g. of triphenylguanidine were brought together in liquid ammonia solution in order to determine whether a silver salt might be formed in accordance with the equation $\text{AgNO}_3 + \text{C}_6\text{H}_5\text{NC}(\text{NHC}_6\text{H}_5)_2 = \text{C}_6\text{H}_5\text{NC}(\text{NHC}_6\text{H}_5)(\text{NAgC}_6\text{H}_5) + \text{HNO}_3$. The failure to obtain a crop of crystals from this solution was interpreted as showing that the silver salt of triphenylguanidine is soluble in a liquid ammonia solution of nitric acid. Neutralization of the acid (ammonium nitrate) by addition of potassium amide was followed by the immediate deposition of a crop of crystals. The crystals were washed and dried as described above for analysis. The salt was dried first at -33°. Heated at 70° in a vacuum it weighed 0.5529 g. It lost 0.0316 g. of ammonia between -33° and 70°. One half of the specimen gave 0.1134 g. of AgCl. The other half gave 0.0292 g. of N. The filtrate from AgCl gave 0.0298 g. of N. Calc. for $\text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3$: Ag, 27.6; N, 10.7. Found: Ag, (I) 30.9, (II) 28.9, (III) 30.9; N, (I) 10.8, (II) 10.8, (III) 10.6. Calc. for $\text{HAg}(\text{C}_6\text{H}_5)_3\text{CN}_3 \cdot \text{NH}_3$: NH_3 , 4.1. Found: NH_3 , (II) 4.0, (III) 5.4. The high silver content in these preparations is probably due to the presence of disilver salt.

Cuprous Triphenylguanidine, $\text{HCu}(\text{C}_6\text{H}_5)_3\text{CN}_3$.—Monocuprous triphenylguanidine is formed as a brown insoluble powder without ammonia of crystallization by the action of a solution of the acid ester on cuprous amide. The pure salt is undoubtedly colorless.

Preparation I.—A portion of cuprous amide precipitated from a solution containing 1.00 g. of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3^{27}$ was treated with a solution containing 1.13 g. of triphenylguanidine. The amide was not dissolved and there was no evidence of any action excepting some change in the appearance of the precipitate. The cuprous amide was left in contact with the solution overnight after which it was thoroughly washed in the usual manner. After drying in a vacuum at 20° the specimen weighing 0.7885 g. was dissolved in alcohol hydrochloric acid mixture for analysis. One half taken for the determination of nitrogen was lost. One fourth gave 0.0493 g. of CuO. Another fourth gave 0.0246 g. of N. A second portion of the salt which had stood longer in

²⁷ The action of potassium amide on a solution of cupric nitrate gives cuprous amide; cf. *THIS JOURNAL*, 29, 657 (1907); 43, 1501 (1921).

contact with the solution gave 19.9% of Cu. Calc. for $\text{HCu}(\text{C}_6\text{H}_5)_3\text{CN}_3$: Cu, 18.2; N, 12.0. Found: Cu, 20.0; N, 12.4.

The high copper content may very well be due to the presence of copper amide which escaped conversion into the salt.

Biguanide



Attempts have not yet been made to prepare biguanide salts using liquid ammonia as a solvent principally because of the prospective difficulties in the way of preparing a pure, dry specimen of the acid. It is practically certain that salts may be so prepared. The existence of a copper compound of the formula $(\text{C}_2\text{H}_6\text{N}_3)_2\text{Cu}\cdot 2\text{H}_2\text{O}$ is recorded in the literature.

Cyanamide



The acid properties of cyanamide are so well established—first by the recorded existence of a considerable number of metallic salts;²⁸ second, by the work of Franklin and Stafford²⁹ in preparing beautifully crystallized specimens of the magnesium salt by the action of a liquid ammonia solution of cyanamide on metallic magnesium; and third, by the observation of Franklin and Kraus³⁰ to the effect that liquid ammonia solutions of cyanamide are fair conductors of electricity—that it was not considered necessary to the present purpose to prepare further salts in liquid ammonia solution by the action of cyanamide on ammono bases. It may be assumed as a matter of course that salts may be so made.

Every one of the numerous methods collected in Beilstein for the formation of cyanamide and its salts is in harmony with the view that cyanamide is a carbonic acid of the ammonia system. Since however a detailed discussion of all the reactions involved would lead too far, a limited number which show clearly and simply the strict analogy between cyanamide and its salts on the one hand and carbonic acid and the metallic carbonates on the other will be briefly considered.

The best known reaction for the formation of a salt of cyanamide is that involved in the commercial preparation of calcium cyanamide. When calcium carbide is heated in the presence of nitrogen nitridation takes place with the result that calcium cyanamide is formed in accordance with the equation, $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$, just as similar treatment with oxygen converts calcium carbide into aquo carbonate of calcium as represented by the equation $\text{CaC}_2 + 3\text{O} = \text{CaCO}_3 + \text{CO}_2$. The analogy between the two processes is obvious.

Of considerable importance in its bearing on the view that cyanamide

²⁸ Beilstein, "Handbuch der organischen Chemie,," Deutsche Chemische Gesellschaft, 4th Ed., III, 28 (1921).

²⁹ Franklin and Stafford, *Am. Chem. J.*, **28**, 105 (1902).

³⁰ Franklin and Kraus, *THIS JOURNAL*, **27**, 195 (1905).

is an ammono acid is the reaction represented by the equation, $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$, whereby ammonia is obtained from calcium cyanamide. This equation represents a well-known type of reaction, namely, the hydrolysis of an ammono acid to an aquo acid. For example, the mixed aquo ammono acetic acid, acetamide, is easily hydrolyzed to aquo acetic acid and ammonia as represented by the equation, $\text{CH}_3\text{-CONH}_2 + \text{H}_2\text{O} = \text{CH}_3\text{COOH} + \text{NH}_3$. Moreover, just as aquo acetic acid may be ammonolyzed to aquo ammono acetic acid and water as represented by the above equation read from right to left, so also has the ammonolysis of aquo carbonate of calcium to the ammono carbonate been accomplished as represented by the second equation above read from right to left,³¹ in accordance with the specifications of a German patent.

In the abstract of this patent it is stated that barium and lead carbonates have in this manner been converted into the respective cyanamide salts. These results have been confirmed in this laboratory and it has also been found that cyanamide salts of calcium, sodium, potassium and lithium are formed when the carbonates of these metals are heated in a platinum crucible in an atmosphere of ammonia. The formation of cyanamide in each experiment was shown by dissolving the melt in water, adding aqua ammonia and obtaining the characteristic yellow precipitate of disilver cyanamide by the addition of ammoniacal silver nitrate.

This formation of cyanamide by the action of ammonia on the alkali carbonates has apparently never been observed before but such formation was certainly to be expected in view of recorded facts. Siepermann³² found that ammonia acts on hot potassium carbonate in accordance with the equation $\text{K}_2\text{CO}_3 + \text{NH}_3 = \text{KCNO} + \text{KOH} + \text{H}_2\text{O}$. Since Drechsel³³ observed the formation of alkali cyanamide on fusing a mixture of potassium cyanate and sodium hydroxide as represented by the equation $2\text{KNCO} + 2\text{KOH} = \text{K}_2\text{CN}_2 + \text{K}_2\text{CO}_3^{33a} + \text{H}_2\text{O}$, it necessarily follows that Siepermann's reaction mixture must have contained cyanamide.

Siepermann's equation represents the ammonolysis of an aquo carbonate to an aquo ammono carbonate; Drechsel's represents the conversion of a mixed aquo ammono carbonate into a mixture of an aquo carbonate and an ammono carbonate.

Drechsel³⁴ found that calcium cyanate, when heated, decomposes

³¹ Ger. pat. 139,456; *Zentr.*, 1903, I, 577.

³² Siepermann, Ger. pat. 38,012; *Ber.*, 20, Ref., 180 (1887).

³³ Drechsel, *J. prakt. Chem.*, [2] 21, 89 (1880).

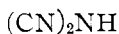
^{33a} This reaction rather takes the course represented by the equation $3\text{KNCO} + 3\text{KOH} = \text{K}_2\text{CN}_2 + 2\text{K}_2\text{CO}_3 + \text{NH}_3$, for it has been found in this Laboratory that ammonia is liberated during the reaction.

³⁴ Drechsel, *J. prakt. Chem.*, [2] 16, 206 (1877).

into calcium cyanamide and carbon dioxide. The equation $\text{Ca}(\text{NCO})_2 = \text{CaCN}_2 + \text{CO}_2$ represents the conversion of a mixed aquo ammono-carbonate into an ammono carbonate by the elimination of carbonic anhydride, a reaction which is analogous to that which takes place on similarly exposing potassium pyrosulfate to a high temperature.

The fusion of any carbonic acid or carbonate whatever with excess of sodium amide, the caustic soda of the ammonia system, results in the formation of the disodium salt of cyanamide. This general statement includes the action of sodium amide on carbon dioxide and sodium carbonate, the anhydride and sodium salt, respectively, of aquo carbonic acid; on urea, a mixed aquo ammono carbonic acid, and on sodium cyanate and sodium carbamate, salts of aquo ammono carbonic acids; on thio-urea, a thio ammono carbonic acid and on sodium thiocyanate, a salt of a thio ammono carbonic acid and on any one of the ammono carbonic acids listed in the scheme at the beginning of this paper.

Dicyanimide



Aqueous solutions of dicyanimide^{34a} have been prepared by decomposing silver dicyanimide, in suspension in water, by means of hydrogen sulfide. On evaporation of the strongly acid solution thus obtained continuously deposited white, flocculent material of undetermined composition. The moderately concentrated solution solidified to a jelly-like mass which dried to an amorphous colorless powder. Analyses failed to identify this powder as a pure compound.

Calc. for HC_2N_3 : C, 35.8; H, 1.5; N, 62.5. Found: C, 30.2 to 32.2; H, 2.2 to 3.0, in 5 different preparations; N, 56.1 and 59.3.

That the product thus obtained was nevertheless composed largely of dicyanimide was shown by the preparation of the potassium and barium salts of dicyanimide from the crude acid in the manner described below.

The impure acid dissolves readily in warm water. When such a solution is heated in a closed tube to 150° for a time, the acid is completely hydrolyzed to carbon dioxide and ammonia. On heating the crude material in a dry state considerable quantities of ammonia and other volatile products are driven off, leaving a yellow residue of melon.

Calc. for $(\text{HC}_2\text{N}_3)_x$: C, 35.8, H, 1.5. Found: C, 35.7; H, 1.9.

Sodium Dicyanimide, NaC_2N_3 and $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$.—This ammono carbonate of sodium has been prepared by two independent methods, first by the action of fused sodium amide on melon, and second, by heating a mixture of sodium cyanide and mercuric cyanide.

First Method.—On the assumption that the ammono carbonic acids may be looked upon as carbonic nitride ammonated in successive steps

^{34a} This ammono carbonic acid has not hitherto been prepared.

from hydromelonic acid, $\text{NH}_3 \cdot 3\text{C}_3\text{N}_4$, through to guanidine, $5\text{NH}_3 \cdot \text{C}_3\text{N}_4$, just as in accordance with the binary theory of Berzelius the phosphoric acids are phosphorus pentoxide combined respectively with 1, 2 and 3 molecules of water, it appeared reasonable to expect that the action of fused sodium amide on carbonic nitride would result in the formation of the sodium salt of hydromelonic acid, dicyanimide or cyanamide, depending upon the relative quantities of the two substances entering into the reaction. Since carbonic nitride is an unknown compound, melon was used in its stead in the experiments described (p. 506).

Melon dissolves readily in fused sodium amide. With the latter in excess disodium cyanamide is formed. When the reaction is carried out by dissolving an amount of melon slightly less than that required by the equation, $x\text{NaNH}_2 + (\text{HC}_2\text{N}_3)_x = x\text{NaC}_2\text{N}_3 + x\text{NH}_3$, a good yield of sodium dicyanimide has been obtained. Attempts to prepare the sodium salt of Liebig's hydromelonic acid by adding melon to fused sodium amide in the proportion required by the equation, $6\text{NaNH}_2 + 3\text{HC}_3\text{N}_9 = 2\text{Na}_3\text{C}_9\text{N}_{13} + 7\text{NH}_3$ have given unsatisfactory results. From the aqueous solution of such melts the reaction product separated in a bulky non-crystalline form of variable sodium content. Some of the solutions solidified to a gelatinous mass on cooling.

The following described procedure has been found to give a satisfactory yield of pure sodium dicyanimide.

In a capacious gold crucible 10 g. of sodium amide and 10 g. of melon are heated together out of contact with the air (conveniently in an atmosphere of ammonia) until the reaction mixture is completely fluid. Heating is continued until all the melon is dissolved but no longer, for the reason that the yield is thereby diminished. After cooling the cake is placed in water in which it gradually disintegrates. The product is then transferred to a filter and separated by suction into a solution containing sodium cyanamide and sodium cyanide, and a solid residue of crude sodium dicyanimide. The latter is dissolved in hot water and the solution thus formed set aside to crystallize. A bulky crop of fine needle-like crystals separates after a time. Further quantities of the salt separate from the mother liquor on the addition of alcohol. In one experiment the salt separated from solution in the form of colorless, granular crystals.

The empirical composition of sodium dicyanimide is established by the analytical results given herewith.

I. Of a specimen of the salt crystallized once from the crude product 0.2017 g. heated to 160° lost 0.0327 g. of water and gave 0.1360 g. of Na_2SO_4 . II. Four separate preparations were united and recrystallized. Of this specimen 0.2423 g. lost 0.0402 g. of water at 160° and gave 0.1607 g. of Na_2SO_4 . III. Another preparation purified by recrystallization was heated in a vacuum to the temperature at which the soft glass container began to collapse. The specimen, which weighed 0.6002 g., lost during this treatment 0.1008 g. of water; 0.2052 g. of this dry salt on combustion gave 0.0050 g. of H_2O and 0.2042 g. of CO_2 . IV. A nitrogen determination by the absolute method of Dumas was made on still another preparation; 0.1072 g. of the hydrated salt gave 37.4 cc. of N measured over water at 22° and 762 mm. barometric pressure (uncorr.). Calc. for $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$: Na, 21.5; C, 22.4; N, 39.3; H_2O ,

16.8. Found: Na, (I) 21.8, (II) 21.5; N, (IV) 39.3; H₂O, (I) 16.2, (II) 16.6, (III) 16.8. Calc. for NaC₂N₃: C, 27.0. Found: C, (III) 27.2; H, (III) 0.3.

Second Method.—The reaction upon which the second method for the preparation of sodium dicyanimide is based is represented by the scheme $\text{NaNC} + \text{C}_2\text{N}_2 \longrightarrow \text{NaN}(\text{CN})_2$. When sodium cyanide is heated in contact with cyanogen the former is nitridized to sodium dicyanimide while the latter undergoes reduction probably to carbon, possibly to carbonous nitride, although as a matter of fact the products of such reduction have not been isolated.

The clue to this method for the preparation of sodium dicyanimide goes back to Bannow³⁵ who, by extracting the melt formed by heating a mixture of potassium cyanide and mercuric cyanide, obtained a solution from which ammoniacal silver nitrate precipitated a compound of the formula AgC_2N_3 . Bannow apparently also had the potassium salt of dicyanimide in his hands but no analytical data appear in his papers in support of this supposition.

After several unsuccessful attempts to isolate the potassium salt, following Bannow's directions, the following procedure was found to give a satisfactory yield of sodium dicyanimide.

Thirty g. of mercuric cyanide and 15 g. of sodium cyanide were thoroughly ground together and the mixture thus formed was heated in a glass retort until all the mercury was driven off. The residue was placed in a deep porcelain crucible and heated to complete fusion out of contact with the air. The cooled melt covered with water rapidly disintegrated. The solution, rich in sodium cyanide, was separated from the undissolved portion which latter was then dissolved in hot water. To the filtered solution alcohol was added until turbidity appeared. Then on standing a crop of yellow crystals separated, of which 0.1713 g. dried at 200° gave off 0.0272 g. of water and on treatment with sulfuric acid yielded 0.1099 g. of Na₂SO₄. Calc. for NaC₂N₃.H₂O: Na, 21.5; H₂O, 16.8. Found: Na, 20.9; H₂O, 15.9.

The yellow salt was then heated to fusion in a platinum crucible, cooled and re-crystallized. A crop of well-formed colorless crystals resulted; 0.1331 g. of the salt dried at 200° gave 0.1044 g. of Na₂SO₄. Calc. for NaC₂N₃: Na, 25.8. Found: 25.5. 0.1901 g. of the crystallized salt lost 0.0320 g. of H₂O on heating to 200° and gave 0.1227 g. of Na₂SO₄. Calc. for NaC₂N₃.H₂O: Na, 21.5; H₂O, 16.8. Found: Na, 21.0; H₂O, 16.8.

Sodium dicyanimide is moderately soluble in cold water and abundantly soluble in the hot solvent. It is also readily soluble in liquid ammonia. It is insoluble in alcohol. At temperatures around 160° it loses its water of crystallization. The anhydrous salt then resists further change up to the temperature at which soda glass begins to soften. Heated to dull redness out of contact with air it is decomposed into sodium cyanide, cyanogen and nitrogen. In contact with air it is converted into sodium carbonate. Boiled with aqueous sodium hydroxide solution it yields as final products sodium carbonate and ammonia. Heated with water alone in a sealed tube it is converted into sodium carbonate, carbon dioxide and ammonia.

Monosodium Tri-dicyanimide, $\text{NaH}_2(\text{C}_2\text{N}_3)_3$ and $\text{NaH}_2(\text{C}_2\text{N}_3)_3 \cdot 2\text{H}_2\text{O}$.—Monomolecular formulas for dicyanimide and its sodium salt have been

³⁵ Bannow, *Ber.*, **4**, 253 (1871); **13**, 2201 (1880).

used in the preceding discussion for the simple reason that the real molecular weights of these substances are unknown. It appears, however, with the preparation of an acid salt of the composition represented by the formula $\text{NaH}_2\text{C}_6\text{N}_9$ that the free acid is a trimer of dicyanimide. In view of the ease with which cyanamide undergoes polymerization to dicyanodiamide and thence to melamine it would not be surprising to find an even greater tendency to characterize the nearly related dicyanimide.

Preparation I.—A solution of 2 g. of $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$ in about 10 cc. of water was poured into an equal volume of glacial acetic acid. After standing for a short time a crop of beautiful crystals was obtained. 0.2752 g. of the salt dried in an desiccator lost 0.0378 g. of H_2O at 200° and gave 0.0780 g. of Na_2SO_4 .

Preparation II.—In a second experiment carried out in the same manner excepting that hydrochloric acid was substituted for glacial acetic acid, a crop of crystals was obtained, 0.1753 g. of which lost 0.0235 g. of H_2O at 200° and gave 0.0483 g. of Na_2SO_4 . Calc. for $\text{NaH}_2\text{C}_6\text{N}_9 \cdot 2\text{H}_2\text{O}$: Na, 8.9; $2\text{H}_2\text{O}$, 13.9. Found: Na, (I) 9.2, (II) 8.9; H_2O , (I) 13.7, (II) 13.4.

Other Metallic Salts of Dicyanimide.—Although the acid properties of dicyanimide are presumably established with a sufficient degree of certainty by the work just described, it nevertheless seemed worth while to confirm this conclusion by the preparation of a limited number of salts of other metals.

Potassium Dicyanimide, KC_2N_3 .—A portion of a solution of dicyanimide prepared by the action of hydrogen sulfide on silver dicyanimide was neutralized with potassium hydroxide. On adding alcohol until a slight turbidity appeared and allowing the the solution to stand for a time a bulky crop of crystals of the potassium salt of dicyanimide was obtained. 0.1087 g. of the salt dried at 200° gave 0.0902 g. of K_2SO_4 .

In a second experiment a portion of the dry crude acid was dissolved in water and neutralized by potassium hydroxide. By manipulating this solution as described above a crop of well-formed crystals was obtained. 0.1235 g. dried at 200° gave 0.1014 g. of K_2SO_4 . Calc. for KC_2N_3 : K, 37.2. Found: (I) 37.2, (II) 36.9.

Silver Dicyanimide, AgC_2N_3 .—On adding silver nitrate to a solution of sodium dicyanimide the silver salt separates as a pure white, very bulky precipitate insoluble either in aqua ammonia or dil. nitric acid. When dried the precipitate shrinks to hard, more or less strongly discolored masses. The composition of the salt is shown by the observations, first, that somewhat more than an equivalent quantity of silver nitrate added to a solution of 2 g. of sodium dicyanimide gave a precipitate which, after thorough washing and drying, weighed 3.21 g. (calc. 3.26 g.), and second, that 0.2106 g. of the salt on ignition left 0.1297 g. of silver. Calc. for AgC_2N_3 : Ag, 62.0. Found: 61.7.

Magnesium Dicyanimide, $\text{Mg}(\text{C}_2\text{N}_3)_2$ and $\text{Mg}(\text{C}_2\text{N}_3)_2 \cdot 6\text{H}_2\text{O}$.—To a solution containing 1 g. of sodium dicyanimide, an equivalent amount of magnesium sulfate was added. From the concentrated solution well-formed crystals separated. 0.1085 g. of the salt heated to 160° lost 0.0441 g. of H_2O and gave 0.0454 g. of $\text{Mg}_2\text{P}_2\text{O}_7$. Calc. for $\text{Mg}(\text{C}_2\text{N}_3)_2 \cdot 6\text{H}_2\text{O}$: Mg, 9.2; $6\text{H}_2\text{O}$, 40.8. Found: Mg, 9.1; H_2O , 40.7.

Barium Dicyanimide, $\text{Ba}(\text{C}_2\text{N}_3)_2$ and $\text{Ba}(\text{C}_2\text{N}_3)_2 \cdot 3\text{H}_2\text{O}$.—Half a g. of sodium dicyanimide and an equivalent quantity of barium bromide were brought together in aqueous solution. After a short time the solution set to a solid mass of needle-like crystals. Of the air-dried salt 0.1509 g. lost 0.0249 g. of H_2O at 160° and gave 0.1069

g. of BaSO₄. Calc. for Ba(C₂N₃)₂·3H₂O: Ba, 42.4; H₂O, 16.7. Found: Ba, 41.8; H₂O, 16.5.

A second specimen of the salt was prepared by neutralizing a solution of crude dicyanamide, prepared in the manner already described, with barium hydroxide solution. 0.1455 g. of the salt dried at 160° gave 0.1228 g. of BaSO₄. Calc. for Ba(C₂N₃)₂: Ba, 51.0. Found: 49.7.

Cupric Dicyanamide, Cu(C₂N₃)₂ and Cu(C₂N₃)₂·3H₂O.—Addition of cupric sulfate to a solution of sodium dicyanamide gave a dark green insoluble precipitate. 0.1024 g. of the salt dried at 100° gave 0.0328 g. of CuO. A second portion weighing 0.1004 g. lost 0.0216 g. of H₂O on heating to 160° and gave 0.0324 g. of CuO. Calc. for Cu-(C₂N₃)₂·3H₂O: Cu, 25.5; 3H₂O, 21.6. Found: Cu, (I) 25.6, (II) 25.8; H₂O, (II) 21.5.

Nickel Dicyanamide, Ni(C₂N₃)₂·3H₂O.—Addition of an equivalent quantity of nickel sulfate to a solution of 0.50 g. of sodium dicyanamide gave a beautiful green insoluble precipitate. 0.1084 g. of the vacuum-dried salt gave 0.0335 g. of NiO; a second portion of 0.1590 g. gave 0.0486 g. of NiO. Calc. for Ni(C₂N₃)₂·3H₂O: Ni, 24.0. Found: Ni, 24.2, 24.0. The salt could not be satisfactorily dehydrated by heating.

Dicyanodiamide



In view of its position in the series of ammono carbonic acids, cyanamide might be expected to undergo de-ammonation to form dicyanamide and possibly even carbonic nitride. As a matter of fact, however, the reactions which take place when cyanamide is heated, follow another course, namely, polymerization successively to dicyanodiamide and melamine, the latter then losing ammonia after the manner already described. The dimerization of cyanamide to dicyanodiamide may be looked upon as a process analogous to the hydration of cyanamide to urea or its ammonation to guanidine. In the formation of dicyanodiamide a second molecule of cyanamide functions as water does in the formation of urea and as ammonia does in the formation of guanidine. Dicyanodiamide is a neutral substance which does not form salts in aqueous solution though indications of its acid nature are on record to the extent that a sodium³⁶ and a silver salt are known. The reactions described below, carried out in liquid ammonia as solvent, bring out clearly the acid properties of this ammono carbonic acid.

Dipotassium Dicyanodiamide, K₂H₂C₂N₄.—This salt is formed in accordance with the equation $\text{H}_4\text{C}_2\text{N}_4 + 2\text{KNH}_2 = \text{K}_2\text{H}_2\text{C}_2\text{N}_4 + 2\text{NH}_3$, when potassium amide in excess and dicyanodiamide are brought together in liquid ammonia solution. It was obtained as a very slightly soluble crystalline product.

Preparation I.—In order to replace as much of the hydrogen as possible in the tetrabasic acid a solution containing 0.40 g. of dicyanodiamide was added to a solution containing a generous excess of potassium amide. An amorphous precipitate was formed

³⁶ The sodium salt was obtained by bringing together sodium ethylate and dicyanodiamide in absolute alcohol solution (Bamberger, *Ber.*, **16**, 1461 (1883)).

which, after standing over night in contact with the mother liquor, changed to a crystalline product. The salt was washed sparingly with the object in view of avoiding possible ammonolysis of a hypothetical tri- or tetrapotassium salt. The salt was dried at 20° in a vacuum. The dry salt was treated first with water, then dissolved in dil. hydrochloric acid preparatory to analysis. The specimen weighed 0.4452 g. One half gave 0.2430 g. of K_2SO_4 . The other half gave 0.0777 g. of N. Calc. for $K_2H_3C_2N_4$: K, 48.8; N, 35.0. Found: K, 48.8; N, 35.0.

Since the dipotassium salt of sharply definite composition was obtained in the presence of a large excess of potassium amide it is obvious that in liquid ammonia solution not more than two atoms of hydrogen are replaceable by metals.

Monopotassium Dicyanodiamide, $KH_3C_2N_4$.—The monopotassium salt of dicyanodiamide is formed when equimolecular quantities of dicyanodiamide and potassium amide are brought together in liquid ammonia solution. The salt crystallizes beautifully and is fairly soluble.

Preparation I.—To a solution containing 0.40 g. of dicyanodiamide the potassium amide from 0.19 g. of potassium (1 equivalent) was added. The precipitate which formed on the addition of each portion of potassium amide solution dissolved completely to a clear colorless solution. On evaporating the solution to a fairly high concentration the monopotassium salt separated as a crop of well-formed crystals. The product was drained of mother liquor and washed twice with small quantities of pure solvent. Dried at 20° the specimen weighed 0.5107 g. One half gave 0.1810 g. of K_2SO_4 . The other half gave 0.1170 g. of N. Calc. for $KH_3C_2N_4$: K, 32.0; N, 45.8. Found: K, 31.8; N, 45.7.

Magnesium Dicyanodiamide, $Mg(H_3C_2N_4)_2 \cdot 2NH_3$.—The magnesium salt of dicyanodiamide has been prepared by the action of a solution of the acid on metallic magnesium in accordance with the equation, $Mg + 2H_4C_2N_4 = Mg(H_3C_2N_4)_2 + H_2$.

Preparation I.—A solution of 0.60 g. of dicyanodiamide was poured upon 0.070 g. of magnesium metal. The metal was immediately attacked with the evolution of hydrogen and was completely dissolved after the lapse of half an hour. The solution was poured from a small quantity of white insoluble material and evaporated to a rather high degree of concentration when well-formed crystals separated. Once formed, the crystals seemed to be practically insoluble. The crop of crystals was washed, then dried in a vacuum at 20°. The weight of the specimen was 0.5132 g. One half gave 0.1372 g. of $MgSO_4$. The other half gave 0.1600 g. of N. Calc. for $Mg(H_3C_2N_4)_2 \cdot 2NH_3$: Mg, 10.8; N, 62.4. Found: Mg, 10.8; N, 62.5.

Calcium Dicyanodiamide, $Ca(H_3C_2N_4)_2 \cdot NH_3$ and $Ca(H_3C_2N_4)_2 \cdot 4NH_3$.—This salt is formed by the action of a liquid ammonia solution of dicyanodiamide on either metallic calcium or calcium amide. It separates from very concentrated solutions at low temperatures with 4 molecules of ammonia of crystallization, three of which are lost on heating to 50°.

Preparation I.—The blue color of a solution of metallic calcium in liquid ammonia solution was instantly discharged when the calcium solution was poured into one of dicyanodiamide. The products of the reaction were an insoluble white portion and an extremely soluble salt which remained as a viscous mass when the solvent was distilled at laboratory temperature. The specimen was lost by the explosion of the reaction tube.

Preparation II.—In the presence of platinum black 0.133 g. of metallic calcium was converted into calcium amide which is practically insoluble in liquid ammonia.

On pouring a solution containing 0.56 g. of the acid upon the amide the latter went rapidly into solution excepting a white insoluble residue, the nature of which was not determined. The solution was poured from this residue and evaporated at low temperature to crystallization. A bulky crop of crystals was obtained. The salt, which is very soluble, exhibits the phenomenon of supersaturation to a surprising degree. The mother liquor in considerable quantity was drained from the crop of crystals which were then dried in a vacuum at -33° . The weight was 0.4444 g. After heating to 50° the weight was 0.3574 g. One fifth gave 0.0395 g. of N. Four fifths gave 0.1764 g. of CaSO_4 . Calc. for $\text{Ca}(\text{H}_3\text{C}_2\text{N}_4)_2\cdot\text{NH}_3$: Ca, 17.9; N, 56.4. Found: Ca, 18.1, N, 55.3. Calc. for $\text{Ca}(\text{H}_3\text{C}_2\text{N}_4)_2\cdot\text{NH}_3\cdot 3\text{NH}_2$: 3NH_3 , 18.6. Found: 19.5.

The high degree of solubility and the bulky nature of this salt made its separation and proper drying a matter of considerable difficulty. The attempt was not made to obtain an ammonia-free salt.

Monosilver Dicyanodiamide, $\text{AgH}_3\text{C}_2\text{N}_4$, $\text{AgH}_3\text{C}_2\text{N}_4\cdot\text{NH}_3$ and $\text{AgH}_3\text{C}_2\text{N}_4\cdot 2\text{NH}_3$.—Monosilver dicyanodiamide is formed by the action of a solution of the acid on either silver amide or silver oxide. It was obtained well-crystallized with two molecules of ammonia. It loses one molecule of ammonia at 40° , melts at about 60° and gives up all its ammonia at a somewhat higher temperature.

Preparation I.—Silver amide prepared from 0.42 g. silver nitrate dissolved rapidly and completely in a solution containing 0.21 g. of dicyanodiamide. On evaporating the solution to proper concentration a crop of crystals separated on the walls and bottom of the tube. After washing the crystals with several small portions of pure solvent they were dried in a vacuum at -33° . Heated to 45° the specimen lost 0.0204 g. of ammonia and weighed 0.2707 g. It gave 0.0938 g. of N and 0.1768 g. of AgCl . Calc. for $\text{AgH}_3\text{C}_2\text{N}_4\cdot 2\text{NH}_3$: Ag, 48.0; 5N, 31.2; 1NH_3 , 7.5. Found: Ag, 45.8, N, 32.2; NH_3 , 7.0.

Preparation II.—Silver amide from 0.50 g. of silver nitrate was dissolved in a solution containing 0.25 g. of the ammono carbonic acid. On concentrating the solution a crop of crystals was obtained which was washed and dried in the usual manner. Since the analysis of the first preparation showed that not all the ammonia of crystallization was removed, the preparation was exposed to a higher temperature in this experiment. At 60° the crystals melted to a viscous frothy mass which lent itself illly to complete de-ammonation. Dried at -33° in a vacuum the salt weighed 0.4213 g. After heating to 70° it weighed 0.3613 g. and gave 0.1026 g. of N and 0.2685 g. of AgCl . Calc. for $\text{AgH}_3\text{C}_2\text{N}_4\cdot 2\text{NH}_3$: Ag, 48.0; 4N, 24.8; 2NH_3 , 15.1. Found: Ag, 48.0; N, 24.4; NH_3 , 14.3.

Preparation III.—A specimen of silver dicyanodiamide was also made by the action of a liquid ammonia solution of 0.20 g. of dicyanodiamide on 0.60 g. of silver oxide. Since silver oxide was in excess of the amount necessary for the formation of the monosilver salt, a portion only of the silver oxide went into solution. The solution was transferred to the second leg of the reaction tube and the residue then extracted several times with pure solvent. The crop of crystals obtained when dried at laboratory temperature weighed 0.1300 g. and gave 0.0824 g. of AgCl and 0.0473 g. of N. Calc. for $\text{AgH}_3\text{C}_2\text{N}_4\cdot 2\text{NH}_3$: Ag, 48.0; N, 47.5. Found: Ag, 47.7; N, 36.4.

Disilver Dicyanodiamide, $\text{Ag}_2\text{H}_2\text{C}_2\text{N}_4$.—The grayish residue from which the above preparation was extracted was in all probability impure disilver dicyandiamide, for after washing and drying it was found to contain Ag, 69.2; N, 18.1. Calc. for $\text{Ag}_2\text{H}_2\text{N}_4$: Ag, 72.5; N, 18.8.

Cuprous Dicyanodiamide, $\text{CuH}_3\text{C}_2\text{N}_4\cdot 2\text{NH}_3$.—Cuprous dicyanodiamide

is extremely soluble in liquid ammonia and crystallizes only from very concentrated solutions at low temperatures. It separates in the form of colorless crystals containing two molecules of ammonia of crystallization which are incompletely lost on heating. The merest trace of air gaining entrance to the preparation tube imparts a blue color to the salt.

Preparation I.—The cuprous amide obtained from 1.00 g. of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$ was treated with a solution containing for each atom of copper 2 molecules of the acid. The amide dissolved slowly giving a slightly blue solution. The color was completely discharged by allowing the solution to stand in contact with bits of copper foil for a few hours. The extremely soluble salt separated from the highly concentrated solution on cooling strongly. The crystals were merely drained from mother liquor for analysis. Adhering mother liquor readily accounts for the low content of copper and the high nitrogen found on analysis. The salt dried at 20° in a vacuum weighed 0.5198 g. One half gave 0.1092 g. of CuO . The other half gave 0.1237 of N. Calc. for $\text{CuH}_3\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$: Cu, 35.2; N, 46.6. Found: Cu, 33.6; N, 47.6.

Preparation II.—Again the cuprous amide from 1.00 g. of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$ was dissolved in a solution of excess of dicyanodiamide. The blue color due to the presence of a small amount of cupric salt was removed by the reducing action of copper foil. The crop of crystals obtained from the very concentrated cold solution was recrystallized for analysis. Dried in a vacuum at -33° the specimen weighed 0.2458 g. On heating slightly above laboratory temperature the crystallized salt fused to a viscous liquid which changed to a mass of froth as the escaping ammonia was pumped off. Dried finally at 40° the specimen weighed 0.2087 g. One half gave 0.0436 g. of N. The other half gave 0.0530 g. of CuO . Calc. for $\text{CuH}_3\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$: Cu, 35.2; total N, 46.7; 2NH_3 , 18.8. Found: Cu, 34.6; total N, 47.9; NH_3 , 15.1.

Melamine



Melamine, a trimer of cyanamide, is a basic substance which forms salts by direct union with acids. Contrary to the statements³⁷ frequently made to the effect that melamine is a strong monacid base, it is, as a matter of fact, a very weak base. Its aqueous solution has no effect on litmus or phenolphthalein while, as observed by Liebig,³⁸ its salts all show an acid reaction towards vegetable colors.

The specimen of melamine used for making the potassium salt described below was obtained in the form of beautifully developed crystals by heating a liquid ammonia solution of dicyanodiamide at a temperature of 100° for several hours.

The identity of the product as melamine was established by observations on its solubility in water and in liquid ammonia, on its crystal form and on its behavior on heating. Its purity was shown by a combustion. 0.2070 g. of substance gave 0.0872 g. of H_2O and 0.2169 g. of CO_2 . Calc. for $\text{H}_6\text{C}_3\text{N}_6$: H, 4.7; C, 28.6. Found: H, 4.7; C, 28.6.

³⁷ Beilstein "Handbuch der organischen Chemie," Leopold Voss, Hamburg and Leipzig, 1, 1443 (1893); Meyer and Jacobson, "Lehrbuch d. organischen Chemie," Veit and Company, Leipzig, 2nd Ed., 1, 2, 1337 (1913).

³⁸ Liebig, *Ann.*, 10, 19 (1834).

Melamine is moderately soluble in liquid ammonia at laboratory temperature. On cooling to -33° most of the solute separates from solution in the form of beautiful crystals.

Tripotassium Melamine, $K_3H_3C_3N_6$.—This salt has been obtained in the form of a practically insoluble microcrystalline powder by the action of potassium amide on melamine in solution in liquid ammonia in accordance with the reaction represented by the equation, $H_6C_3N_6 + 3KNH_2 = K_3H_3C_3N_6 + 3NH_3$. It is vigorously hydrolyzed into potassium hydroxide and melamine in the presence of water.

Preparation I.—In one leg of a reaction tube was contained 1.20 g. of melamine in solution in liquid ammonia, in the other a solution of a large excess of metallic potassium. A portion of the metal solution poured into the solution of melamine lost its blue color instantly, a behavior which shows the acid properties of melamine. The reaction tube was then allowed to stand until the metal in solution, in the presence of a trace of platinum black, was converted into a solution of potassium amide. Successive additions of melamine to this solution gave a colorless, bulky precipitate which changed rapidly to a microcrystalline powder. The washed salt dried in a vacuum at -33° showed no loss in weight on warming to laboratory temperature. The dried salt was hydrolyzed by the addition of water and the hydrolytic products resulting were dissolved in dil. hydrochloric acid preparatory to analysis. The preparation weighed 0.3897 g. One half gave 0.2120 g. of K_2SO_4 . The other half gave 0.0673 g. of N. Calc. for $K_3H_3C_3N_6$: K, 48.8; N, 34.9. Found: K, 48.8; N, 34.6.

Preparation II.—Tripotassium melamine prepared as described above not only has the same empirical composition as dipotassium dicyanodiamide but it is also very slightly soluble and was obtained as a microcrystalline product indistinguishable in appearance from the latter salt through the walls of the reaction tube. Since there thus appeared the possibility that melamine in the presence of potassium amide might be converted into dicyanodiamide or even into cyanamide (by fusion with sodium amide, it will be recalled, both of these substances are converted into sodium cyanamide) a second specimen of the tripotassium salt of melamine was prepared, decomposed by the action of water, the hydrolytic product other than potassium hydroxide recovered and identified as melamine. The potassium hydroxide solution was neutralized with sulfuric acid and evaporated to dryness. Ignition of the residue gave 0.1188 g. of potassium sulfate. The specimen weighed 0.1108 g. Calc. for $K_3H_3C_3N_6$: K, 48.8. Found: 48.2.

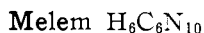
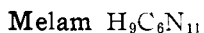
Monopotassium Melamine, $KH_5C_3N_6 \cdot NH_3$.—This salt separates as a very slightly soluble precipitate when potassium amide is added to an excess of melamine in liquid ammonia solution.

Preparation I.—To a solution containing 0.30 g. of melamine, a potassium amide solution prepared from 0.092 g. of metallic potassium was gradually added. Each addition of the amide gave a gelatinous insoluble mass which rapidly disintegrated and settled to the bottom of the tube in the form of a fairly compact precipitate. Five extractions of this precipitate carried out in the manner which has been described elsewhere gave a specimen of minute brilliant crystals covering the walls and bottom of the reaction tube. The specimen was washed, then dried in a vacuum at 20° . Its weight was 0.0950 g. For analysis the salt was treated with water, then dissolved in dil. hydrochloric acid. One half gave 0.0231 g. of K_2SO_4 . The other half was inadvertently lost.

Preparation II.—The precipitate from which the preceding preparation was extracted was washed in the usual manner and prepared for analysis as described above. From a portion of the precipitate the melamine was recovered and identified. The remaining portion was dried in a vacuum at 20° and submitted to analysis. One half of the specimen which weighed 0.1553 g. gave 0.0382 g. of K₂SO₄, the other half gave 0.0417 g. of N. Calc. for KH₅C₃N₆.NH₃: K, 21.6; N, 54.1. Found: K, (I) 21.8; (II) 22.1; N, (II) 53.7.

The ease with which these potassium salts have been obtained make it practically certain that melamine salts of other metals may be prepared.

Zimmermann³⁹ obtained a disilver salt of melamine by treating melamine disilver nitrate with aqua ammonia.



These compounds are said to be present in Liebig's crude melam, the residue remaining after heating ammonium thiocyanate at a temperature around 300° to 360° so long as volatile products are given off. They are colorless, amorphous, insoluble substances, the existence of which as chemical individuals is open to some doubt.

Melon



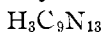
This name was given by Liebig to the yellow, amorphous, insoluble residue obtained by heating to redness the yellow precipitate formed by the action of chlorine on a solution of potassium thiocyanate. The compound was first observed by Berzelius who obtained it by heating mercuric thiocyanate. Formed in this manner it is familiar as the substance of the so-called Pharaoh's serpents. Melon⁴⁰ is left behind as the final de-ammoniation product on heating any one of the previously discussed ammono-carbonic acids. It is also formed by heating urea, ammonium thiocyanate and a large number of other mixed carbonic acids. Heated with water in a sealed tube to 200° for several hours it is hydrolyzed through a considerable number of aquo ammono carbonic acids finally to carbon dioxide

³⁹ Zimmermann, *Ber.*, **7**, 287(1874). (Not volume 9, as given in Beilstein.)

⁴⁰ Although Laurent and Gerhardt (*Ann. chim.*, [3] **19**, 89 (1847)) and Voelckel (*Pogg. Ann.*, **62**, 104 (1844)) have apparently shown melon to have the composition represented by the formula H₃C₆N₉, it is nevertheless a difficult matter to obtain the compound of sharply definite composition. Carbon and hydrogen determinations in 4 specimens of melon prepared from dicyandiamide and one from ammonium thiocyanate gave results varying from 34.9 to 36.9% of carbon and from 1.1 to 2.0 % of hydrogen. Nitrogen determinations by the method of Kjeldahl gave persistently low results varying from 61.0 to 62.8%. One nitrogen determination by the absolute method gave 62.8%. (Calc. for H₃C₆N₉: H, 1.5; C, 35.8; N, 62.7.) It is interesting to note in this connection that Liebig states in several places (*Ann.*, **50**, 341 and 354 (1844); *ibid.*, **95**, 258 (1855)) that he was unable to obtain melon of constant composition. Cf. Voelckel, *Pogg. Ann.*, **58**, 151 (1843).

and ammonia. Melon is to be looked upon as a highly polymerized form of dicyanamide.

Cyamelon or Hydromelonic Acid



Melon and the salts of hydromelonic acid are substances which were at one time of much theoretical importance. Their nature and, strange as it may seem, even their elementary composition were through years the subject of an acrimonious controversy between Liebig on the one side and Laurent and Gerhardt on the other,⁴¹ the outcome of which, insofar as our present interest is concerned, was to show that the metallic melonates are the salts of an acid, not known in the free state excepting in solution, of the composition represented by the formula given above. It is an acid of sufficient strength to form salts in water solution and is the final known member of the series of ammono carbonic acids.

Carbonic Nitride



One might expect to obtain carbonic nitride as the final de-ammonation product of the series of ammono carbonic acids by heating melon, but instead of losing ammonia at the high temperature required to effect any change at all it undergoes complete decomposition.⁴² Attempts have been made in this laboratory to prepare carbonic nitride by heating mercuric thiocyanate, with results which, while far from unequivocal, show that impure specimens of carbonic nitride have passed through our hands.

Specimens of mercuric thiocyanate prepared in the usual manner were dried by long standing in a vacuum over sulfuric acid, others by heating in a vacuum at 150°. The salt was then decomposed by heat and the extremely bulky residue heated in quartz in a vacuum until free from mercuric sulfide. Six separate specimens gave on combustion 2.4, 1.5, 0.6, 0.7, 1.5 and 1.7% of hydrogen; and 40.2, 39.7, 38.4, —, 35.9 and 35.9% of carbon respectively. Calc. for C_3N_4 : C, 39.1. Nitrogen determinations were more consistent. Four determinations on different specimens by the method of Dumas gave 60.4, 60.7, 58.0 and 60.6% of nitrogen, while one by the method of Kjeldahl gave 60.6%. Calc. for C_3N_4 : N, 60.9. Further attempts will be made to prepare the pure compound.

The Action of Fused Sodium Amide on the Ammono Carbonic Acids

The ammono carbonic acids constitute a series of compounds the members of which are related to each other as are the ortho-

⁴¹ In the older text-books and dictionaries of chemistry melon and related compounds were given a great deal of attention; cf. Liebig, "Traité de Chim. org.," 3rd Ed. 1845, Société Typographique Belge Adolphe Wahlenet Cie., p. 127; Gerhardt, "Traité de Chim. org.," Firman Didat Frères, Paris, 1853, vol. 1, 464, 473; Gmelin-Watts, "Handbook of Chemistry," The Cavendish Society, London, 1855, vol. 9, p. 378. In modern works of the same kind they are scarcely more than mentioned.

⁴² There is entire disagreement concerning the products of this decomposition. Cf. Liebig, *Ann.*, 10, 5 (1834); Laurent and Gerhardt, *Ann. chim. phys.*, [3] 19, 101 (1847); Voelckel, *Pogg. Ann.*, 61, 375 (1844). Gmelin-Watts, Ref. 41, p. 381.

pyro- and metaphosphoric acids within the group of phosphoric acids or the less well defined individuals within the group of silicic acids. Accordingly, sodium ammono carbonates of greater or less acidity⁴³ are formed by the action of fused sodium amide in excess or in dearth upon any one of the ammono carbonic acids just as the relative proportions in which sodium hydroxide and any one of the phosphoric acids are fused together determine which of the phosphates will be formed.

Experiment has shown that disodium cyanamide is formed when sodium melonate, melon, crude melam, melamine,⁴⁴ dicyandiamide,⁴⁴ sodium dicyanimide, cyanamide or guanidine⁴⁵ is dissolved in an excess of fused sodium amide and inversely that disodium cyanamide is converted into sodium dicyanimide by dissolving melon in the fused salt. Attempts to carry the process to the formation of trisodium melonate have so far resulted in the formation of gelatinous products of varying composition.

In successive experiments small amounts of each of the above named substances excepting that guanidine nitrate and guanidine carbonate were used instead of guanidine itself, were added to approximately 1 g. of sodium amide maintained in a state of fusion in an atmosphere of ammonia. Each substance was observed to dissolve readily with effervescence due to the escape of ammonia, one of the products of the reaction. Each cooled melt, together with the silver boat in which the reaction was carried out, was dropped into a beaker of water. To the solution formed, strongly alkaline from the presence of sodium hydroxide and ammonia resulting from the hydrolysis of excess of sodium amide, ammoniacal silver nitrate was added with the result that in each case an abundant precipitate of disilver cyanamide was formed. The precipitates were identified as disilver cyanamide by their characteristic yellow color confirmed in one instance by noting the ready solubility of the yellow substance in dil. nitric acid and by a determination of its silver content.

Hydrolysis of the Ammono Carbonic Acids

The hydrolysis of calcium cyanamide to calcium carbonate and the inverse reaction, namely, the ammonolysis of calcium carbonate to calcium cyanamide have been discussed above. There remains to be given here the results of experiments which show that all the ammono carbonic acids undergo hydrolysis to carbon dioxide and ammonia when heated in the presence of water.⁴⁶

Guanidine carbonate, dicyanodiamide, melamine, melon and crude dicyanimide in half gram portions together with 5 cc. of water were sealed in 5 respective glass tubes

⁴³ Acidity is here used in the sense in which the mineralogist uses the term in describing his silicates.

⁴⁴ Of course in the case of these two compounds the reaction is merely one of depolymerization.

⁴⁵ It is interesting to note that excess of sodium amide does not form a guanidine salt. The analogous situation in the case of the phosphates is that excess of sodium hydroxide does not form a salt of the composition Na_3PO_5 .

⁴⁶ Cf. Emich, *Monatsh.*, 9, 378 (1888).

and heated to a temperature of 200° for a day. On cooling and examining the contents of the tubes each substance was found to have been hydrolyzed completely into carbon dioxide and ammonia.

Summary

As is shown in the scheme at the beginning of this paper, guanidine, biguanide, cyanamide, dicyanimide, dicyanodiamide, melamine, melam, melem, melon and hydromelonic acid constitute a group of compounds which may be looked upon as ammono carbonic acids. That is to say, they are compounds related to ammonia as ordinary carbonic acid is related to water or in other words, they are carbonic acids in which nitrogen functions as oxygen does in ordinary carbonic acid.

It is pointed out that not only formally may these substances be looked upon as constituting a series of products resulting from the successive de-ammonation of an hypothetical ammono ortho carbonic acid of the formula $C(NH_2)_4$, but that also by processes of de-ammonation one may pass from guanidine to melon and inversely by processes of ammonation return to the first member of the group.

In face of the facts that guanidine and melamine are alkaline and dicyanodiamide is neutral in aqueous solution, it has been shown that these substances behave as acids when in solution in liquid ammonia. Guanidine for example, has been found to react with potassium amide, the caustic potash of the ammonia system, in accordance with the equation, $H_3CN_3 + 2KNH_2 = K_2H_3CN_3 + 2NH_3$ to form a dipotassium salt.

It has been shown that the reaction whereby atmospheric nitrogen is fixed in the cyanamide process is to be looked upon as the nitridation of calcium carbide to a calcium ammono carbonate and that the production of ammonia by the action of steam on calcium cyanamide consists in the hydrolysis of calcium ammono carbonate to calcium aquo carbonate.

Dicyanimide, a hitherto unknown member of the group of ammono carbonic acids, has been prepared together with a considerable number of its metallic salts. Attempts to prepare carbonic nitride, the theoretical final de-ammonation product of the series of ammono carbonic acids, are described.

STANFORD UNIVERSITY, CALIFORNIA