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SOME AMMONO-CARBONIC ACIDS AND THEIR REACTIONS IN LIQUID AMMONIA[1]

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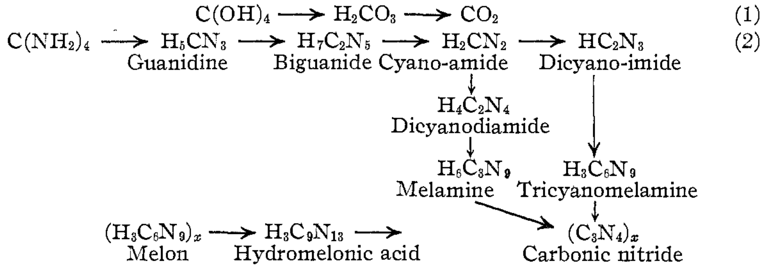
The ammono-carbonic acids are compounds related to ammonia as ordinary carbonic acid is related to water. Among the substances which may be looked upon as ammono-carbonic acids are the well-known substances guanidine, biguanide, cyano-amide, dicyanodiamide and melamine. Others less familiar are dicyano-imide, tricyanomelamine, melon and hydromelonic acid.

Starting in each series with the hypothetical ortho acid of its respective system, Franklin[2] has shown the analogy between the aquo-carbonic acids and the ammono-carbonic acids as follows.



In the first series we find the well-known dehydration products of orthocarbonic acid. In the second series in passing from guanidine to dicyano-imide each compound may be considered as a deammonation product of the preceding member. Experiment[3] has shown, however, that this de-

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[1] From a thesis submitted to the Department of Chemistry of Stanford University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Franklin, THIS JOURNAL, **44,** 486 (1922).

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

ammonation does not take place successively owing to the ease with which cyano-amide polymerizes, first to dicyanodiamide and then to melamine.

The foregoing brief discussion of the ammono-carbonic acids shows that in contrast to the occurrence of only one aquo-carbonic acid we have many more or less familiar members of the ammono-carbonic acid group, all of which are solids.

The present work was undertaken for the purpose of completing the above series by the preparation of dicyano-imide, tricyanomelamine, hydromelonic acid and carbonicnitride. A study was made of certain of their reactions in liquid ammonia.

Dicyano-imide, HC_2N_3

Madelung and Kern[4] have prepared salts of dicyano-imide as well as aqueous solutions of the acid. In attempting to obtain the free acid, however, they found that evaporation of the acid solution gave amorphous deposits of undetermined composition.

To obtain a solution of dicyano-imide several grams of sodium dicyanoimide was prepared following the method of Madelung and Kern.[5] Analysis of the samples showed close agreement with that given by these investigators. In each case, however, the low sodium content indicated that impurities were present. When the salt is dissolved in liquid ammonia a white insoluble residue separates. The analysis of the salt recrystallized from liquid ammonia gave consistently higher values for sodium. This indicated a purer product than that obtained from aqueous solutions.

Anal. Subs., 0.3155, 0.1525: Na_2SO_4, 0.2495, 0.1204. Calcd. for NaC_2N_3: Na, 25.8. Found: 25.6, 25.6.

An aqueous solution of dicyano-imide was prepared by decomposing silver dicyano-imide, in suspension in water, with hydrogen sulfide. After the silver sulfide had been filtered off the evaporation of the strongly acid solution was allowed to proceed at low pressure. Deposits of flocculent material were filtered off from time to time. As the concentration increased a crystalline solid separated. At this point the solution was placed in a crystallizing dish and transferred to a vacuum desiccator. White, needle-shaped crystals were deposited.

The analyses indicate a crystallized hydrate of the formula, $HC_2N_3.H_2O$. I and II represent separate preparations.

Anal. Subs. (I) 0.0670, (II) 0.0722: H_2O, (I) 0.0233, (II) 0.0253; CO_2, (I) 0.0692, (II) 0.0735. Calcd. for $HC_2N_3.H_2O$: H, 3.5; C, 28.2. Found: H, (I) 3.9, (II) 3.9; C, (I) 28.1, (II) 27.8.

Subs., 0.0671: H_2O, 0.0144 (180°). Calcd. for $HC_2N_3.H_2O$: H_2O, 21.2. Found: 21.4.

Calcd.: N, 49.5. Found (Kjeldahl): 49.2.

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[4] Madelung and Kern, *Ann.*, **427**, 1 (1922).

[5] Ref. 4, p. 15.

Mercuric Dicyano-imide, $Hg(C_2N_3)_2$.—Mercuric dicyano-imide was prepared by adding a solution of mercuric nitrate to a solution of sodium dicyano-imide. The heavy white precipitate was washed by decantation in a tall beaker and filtered by suction on a hard filter. The product was placed in an oven and dried at 110°. At this temperature the salt puffs up, giving a bulky, yellow residue. Other samples were prepared and dried in a vacuum desiccator.

Anal. Subs., 0.1011: HgS, 0.0705. Calcd. for $Hg(C_2N_3)_2$: N, 25.3; Hg, 60.2. Found. N (Kjeldahl), 25.0; Hg, 60.1.

Of special interest in connection with this salt is the effect caused by heating small pieces or touching them with sulfuric acid. In either case the salt instantly increases in bulk forming a homogeneous yellow mass which takes the form of a slug or snake. At the same time a squeaky noise is emitted. In its interesting and spectacular effect this reaction may well be classed with that in which the so-called Pharaoh's serpents are formed when mercuric thiocyanate is decomposed.

The constitution of the yellow material formed in the decomposition of mercuric dicyano-imide has not been determined. Small amounts have been heated for days in a vacuum at 400° but traces of mercury still persisted. No concordant analytical results have been obtained. Further work will be done to prove whether or not carbonic nitride, C_3N_4, is formed according to the following reaction: $3Hg(C_2N_3)_2 = 3Hg + N_2 + 4C_3N_4$.

Tricyanomelamine, $H_3C_6N_9$

In attempts to prepare tricyanomelamine Franklin[6] has prepared solutions of the acid by treating the silver salt, suspended in water, with hydrogen sulfide. Kern[7] treated the copper salt, suspended in alcohol, in like manner. Each investigator found that the evaporation of the acid solution on a water-bath gave flocculent deposits of undetermined composition.

A solution of tricyanomelamine was prepared by treating silver tricyanomelamine, suspended in water, with pure hydrogen sulfide for several hours. The precipitated sulfide was filtered off and the clear acid solution evaporated in a vacuum at room temperature. After several days, depending on the amount of solution present, crystals separate. The final evaporation was carried out in a vacuum desiccator. The residue consisted of small white crystals. The following analyses indicated a hydrate with the formula, $H_3C_6N_9.3H_2O$. I and II are samples of the same preparation; III is a second preparation.

Anal. Subs., (I) 0.1311, (II) 0.0804, (III) 0.1061: CO_2, (I) 0.1325, (II) 0.0877, (III) 0.1108; H_2O, (I) 0.0400, (II) 0.0259, (III) 0.0317. Subs., (I) 0.1143: 51.93 cc. of N_2 (over water, 25.5°, 761.3 mm.). Subs., (II) 0.1290, (III) 0.0848, heated to 180°: H_2O, (II) 0.0258, (III) 0.0176. Calcd. for $H_3C_6N_9.3H_2O$: C, 28.2; H, 3.5; N, 49.5; H_2O, 21.1. Found: C, (I) 27.6, (II) 28.8, (III) 28.0; (I) H, 3.4, (II) 3.6, (III) 3.4; N, (I) 50.4, (II) (Kjeldahl) 49.4, (III) (Kjeldahl), 49.2; H_2O, 20.0, 20.8.

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[6] Ref. 2, p. 497.

[7] Ref. 4, p. 34.

Sodium Tricyanomelamine, $Na_3C_6N_9.3H_2O$.—Franklin[6] has prepared sodium tricyanomelamine by the action of fused sodium amide on melon, also by heating a mixture of sodium cyanide and mercuric cyanide. Kern[7] has prepared the salt by heating sodium dicyano-imide to redness.

In the present investigation sodium tricyanomelamine has been prepared by fusion of weighed amounts of dicyanodiamide and sodium cyanoamide in a gold crucible. The following reaction takes place: $6Na_2CN_2 + 9H_4C_2N_4 = 4Na_3C_6N_9 + 12NH_3$. After the mass had cooled it was extracted with boiling water. Impurities were filtered off. A bulky crop of white, needle-shaped crystals separate from the cooled solution.

Anal. Subs., 0.4178: H_2O, 0.0697; Na_2SO_9, 0.2784. Calcd. for $Na_3C_6N_9.3H_2O$: H_2O, 16.8; Na, 21.5. Found: H_2O, 16.7; Na, 21.6.

Silver Tricyanomelamine, $Ag_3C_6N_9.3NH_3$.—Weighed amounts of silver nitrate and anhydrous sodium tricyanomelamine were placed in separate legs of a reaction tube, dissolved in liquid ammonia and the solutions slowly mixed. After a short time, large, colorless crystals were obtained.

Anal. Subs., 0.0712, 0.0227: Ag, 0.0407, 0.0227. Calcd. for $Ag_3C_6N_9.3NH_3$: Ag, 57.1. Found: 57.2, 57.2. Calcd.: N, 29.6. Found (Dumas): 28.7, 28.5.

The low nitrogen value is due to loss of ammonia when the salt is exposed to air.

Copper Tricyanomelamine, $Cu_3(C_6N_9)_2.12NH_3$.—When a few drops of a solution of ammonated cupric nitrate in liquid ammonia are added to a solution of anhydrous sodium tricyanomelamine a white precipitate is first formed. Upon further addition of the copper solution the precipitate is dissolved. After a few minutes bright blue crystals are deposited. Repeated washing of these crystals showed that they are only slightly soluble in liquid ammonia. The dried salt, heated to redness, decomposes quietly.

Anal. Subs. (I), 0.0495: CuO, 0.0154. Calcd. for $Cu_3(C_6N_9)_2.12NH_3$: N, 52.2; Cu, 25.0. Found: N (Kjeldahl), 51.5, 51.8; Cu, (I) 24.9.

Lead Tricyanomelamine, $Pb_3(C_6H_9)_2.6NH_3$.—Addition of a few drops of lead nitrate in liquid ammonia to a solution of anhydrous sodium tricyanomelamine produces a white precipitate which is soluble in an excess of the sodium salt. An excess of the lead solution produces a white precipitate.

Anal. Subs., (I) 0.2490: $PbSO_4$, 0.1944. Calcd. for $Pb_3(C_6N_9)_2.6NH_3$: N, 7.5; Pb, 55.5. Found: N (distillation with alkali), 7.4; Pb, 55.3.

Hydromelonic Acid, $H_3C_9H_{13}$

Hydromelonic acid is the final known member of the series of ammonocarbonic acids. Metallic salts of the acid have been prepared by Liebig.[8] The acid has not been known in the free state.

In attempts to prepare free hydromelonic acid an aqueous solution

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[6] Liebig, *Ann.*, **95**, 257 (1855).

of sodium melonate was treated with silver nitrate solution. The white, gelatinous precipitate was heated to boiling, washed by decantation, suspended in water and treated with hydrogen sulfide. After removal of the excess of hydrogen sulfide a solution was obtained which gave a strong acid reaction. Evaporation of this solution gave a white amorphous powder. The dried product is difficultly soluble in cold water but readily soluble in hot water. At low red heat the material decomposes. A solution of the dried powder gives the gelatinous precipitate of silver melonate. The analytical results given herewith, though not conclusive, indicate a hydrate of the formula, $H_3C_9N_{13}.2H_2O$.

Anal. Subs., 0.0953: CO_2, 0.1149; H_2O, 0.0325. Subs., 0.0240: 11.8 cc. of N_2 (over water, 23°, 761 mm.). Calcd. for $H_3C_9N_{13}.2H_2O$: C, 32.7; H, 2.1; N, 55.4. Found: C, 32.9; H, 3.8; N, 55.2.

Sodium Melonate, $Na_3C_9N_{13}.5H_2O$.—Since sodium melonate has not, hitherto, been prepared it may be well to show in what ways its preparation differs from that of the potassium salt as prepared by Liebig.[8]

When melted antimony trichloride is added to melted sodium thiocyanate a violent reaction takes place. Several different mixtures were tried but the best results were obtained with amounts corresponding to the following reaction: $39NaSCN + 10SbCl_3 = 3Na_3C_9N_{13} + 5Sb_2S_3 + 12CS_2 + 30NaCl$.

Sodium thiocyanate was added in small portions and carefully heated until each fresh portion was melted. As soon as the last addition was melted, liquefied antimony trichloride was poured in slowly. After each successive addition of the antimony salt the mixture was stirred until the violence of the reaction had subsided. It was found necessary to protect the face and hands from the spattering fusion mixture. Fusions for 20 to 30 minutes gave good results. The cooled mass was extracted with hot water and treated with lead hydroxide to remove soluble sulfides. Upon cooling, the sodium salt crystallized. The crystals were filtered off and any excess of sodium thiocyanate was washed out with alcohol. The salt was finally recrystallized from hot solutions.

Anal. Subs., 0.2121, 0.2184: H_2O, 0.0413, 0.0432; Na_2SO_4, 0.0997, 0.1019. Calcd. for $Na_3C_9N_{13}.5H_2O$: N, 40.5; Na, 15.4; H_2O, 20.1. Found: N (Kjeldahl), 40.6; Na, 15.2, 14.1; H_2O, 19.5, 19.8.

Silver Melonate, $Ag_3C_9N_{13}.6NH_3$.—When a solution of sodium melonate in liquid ammonia is added to a solution of silver nitrate a clear, colorless, crystalline precipitate is formed. The salt is much less soluble than silver tricyanomelamine. It is insoluble in water and dilute acids.

Anal. Subs., 0.1238: Ag (ignition) 0.0561. Calcd. for $Ag_3C_9N_{13}.6NH_3$: N, 37.2; Ag, 45.2. Found: N, 36.8; Ag, 45.3.

In conclusion I wish to express my sincere appreciation of the coöperation which Dr. E. C. Franklin has given during this investigation.

Summary

It has been shown at the beginning of this paper that the substances dicyano-imide, tricyanomelamine, and hydromelonic acid may be looked upon as ammono-carbonic acids. In the present paper the preparation of these acids, as well as certain of their metallic salts, has been described. The preparation and properties of mercuric dicyano-imide have been recorded.

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THE SPECIFIC HEATS OF BINARY MIXTURES

By John Warren Williams and Farrington Daniels

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A method for measuring the specific heats of liquids has been described in previous communications from this Laboratory.[1] In carrying the investigations to solutions, binary mixtures of nearly ideal liquids have been studied first, and in this paper are presented the results on mixtures of benzene and toluene; bromobenzene and chlorobenzene; carbon tetrachloride and chloroform; benzene and carbon tetrachloride; and of chloroform and acetone. The fourth pair is described in the literature as showing a minimum boiling point, the fifth as showing a maximum boiling point, but the other three pairs are generally classed as illustrations of ideal solutions. In such solutions, properties may be expressed in terms of the mole fractions of the components and the properties of the pure substances by simple addition.

Few solutions, if any, are strictly ideal and it becomes of interest to study the mechanism underlying the deviations from the ideal solution. One of the best approaches appears to be through investigations of specific heats at different temperatures.

The apparatus used in this work has been described before.[1a] The input of electrical energy (in international units) was converted into calories by dividing by 4.182. In weighing out the liquid to make solutions of definite composition the usual correction for the buoyancy of the air was made. A given solution (160 cc.) was used but once, for the evaporation of the warm liquid after completing an experiment caused a change in composition. In nearly every case the experimental points fall on a smooth curve within 0.001 calorie per degree.

Purification of Materials

The benzene, toluene, carbon tetrachloride and chloroform were purified in the manner described in the preceding papers and their physical constants were essentially

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[1] (a) Williams and Daniels, This Journal, **46**, 903 (1924); (b) **46**, 1569 (1924).