[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

MIXED AQUO-AMMONOCARBONIC ACIDS. II. SALT FORMATION IN LIQUID AMMONIA SOLUTION

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The status of the mixed aquo-ammonocarbonic acids,[1] as acids, is in many cases not generally recognized. While some of them, such as cyanic and carbamic acids, have gained recognition as such, others, such as urea, biuret, guanylurea, etc., are ordinarily called bases. They are bases, however, only in the sense in which ammonia itself is a base, namely in being capable of forming a base by the addition of water. This property, together with the fact that salts of such very weak acids as many of these are would be completely hydrolyzed in water solution, is undoubtedly accountable for the prevalent failure to recognize many of these compounds as acids.

The work described in this paper was done for the purpose of extending and amplifying the experimental basis upon which the right to call these compounds "acids" depends. To this end the potassium salts of several representative members of this class of compounds were prepared in liquid ammonia solution.

Liquid ammonia is a solvent which is excellently suitable for this purpose, for three reasons. The tendency for solvolysis of a salt in liquid ammonia solution is much less than in water since the degree of auto-ionization of ammonia is much less than that of water. Furthermore, the tendency to form bases of the "ureanium hydroxide" type, such as H_2NCONH_3OH, is absent. Finally, it was found that while the acids themselves are, as a rule, readily soluble in liquid ammonia, their salts are only slightly soluble thus rendering the preparation of the salts an easy matter.[2]

No salts other than potassium salts were made, for the reason that it was thought advisable to prepare salts of as many different acids as possible in the time available, rather than to prepare a larger number of salts of the individual acids.

The experimental method consisted in the use of 2-legged reaction tubes as described, in general, in previous contributions from this Laboratory.[3] For the sake of brevity, the general procedure will not be described here, but only the minor departures from it which were necessitated at various points during the work.

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[1] For a definition of a mixed aquo-ammonocarbonic acid, see the preceding paper, THIS JOURNAL, **48,** 87 (1926).

[2] However, the salts were in many cases too insoluble for best results. Efforts to purify a salt which was extremely insoluble usually proved fruitless, and this fact is largely responsible for the occasional variance in analytical results.

[3] THIS JOURNAL, **27,** 831 (1905); **29,** 1694 (1907); **35,** 1460 (1913). *J. Phys. Chem.*, **15,** 1915 (1911); **16,** 694 (1912).

Urea

The action of potassium amide on urea in liquid ammonia solution has already been investigated by Franklin and Stafford,[4] who reported the preparation of the monopotassium and dipotassium salts. The present work has confirmed their results. The remarkable formation of two liquid phases in the preparation of the monopotassium salt was also confirmed in the present investigation and found to result from the presence of the excess of urea. It was found that monopotassium urea, which is almost insoluble in liquid ammonia and can be precipitated from it only in a semi-gelatinous and impure form, is soluble in the denser of these two liquid phases and by careful work it may be caused to separate from this phase in beautifully crystalline form. For the sake of brevity the data for the monopotassium salt will be omitted.

On the basis of rather indirect evidence obtained from the behavior of urea with potassium ethylate in alcohol solution, E. A. Werner states[5] that he doubts the existence of the dipotassium salt of urea as reported by Franklin and Stafford. Whatever may be the case in alcohol solution, the formation of dipotassium urea by the action of potassium amide on urea in liquid ammonia solution was fully confirmed by the results of the present investigation, as is shown by the results of the analyses of three separate preparations.

Anal. Calcd. for $K_2H_2CON_2$: K, 57.4; N, 20.6. Found: K (I) 56.5, (II) 57.2, (III) 56.8; N (I) 20.5, (II) 21.9, (III) 20.4.

Carbamic Acid

Ammonium Carbamate.—The ammonium salt of carbamic acid is well known as the product of the action of ammonia on carbon dioxide in the absence of water. In addition, the sodium, potassium, calcium, strontium and barium salts have been prepared by Drechsel.[6] In all these compounds carbamic acid behaves as a monobasic acid. In the present work it was found possible, however, to prepare not only the monopotassium but also the dipotassium salt of carbamic acid, by the action of potassium amide upon ammonium carbamate in liquid ammonia solution.

In the preparation of ammonium carbamate a 2-legged reaction tube was used, fitted with a 2-way stopcock. The clean, dry tube was sealed off at the ends, evacuated and weighed. Dry carbon dioxide was introduced, the amount of which was ascertained by again weighing the tube. The subsequent introduction of dry ammonia served to form crystalline ammonium carbamate, further introduction of ammonia resulting in the condensation of liquid ammonia within the tube. The purpose of the

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[4] Franklin and Stafford, *Am. Chem. J.*, **28,** 98 (1902).

[5] Werner, "The Chemistry of Urea," Longmans, Green and Company, London, **1923,** p. 112.

[6] Drechsel, *J. prakt. Chem.*, **16,** 181 (1877).

2-way stopcock was to allow a by-pass into the air, so that the gas supply line could be swept out with pure carbon dioxide or pure ammonia. In this way only pure, dry gases were introduced into the reaction tube.

The procedure after the preparation of ammonium carbamate was identical with that used in the experiments with other materials. It is perhaps worth recording that ammonium carbamate is not as soluble in liquid ammonia as might have been expected, its solubility being about 1.5 g. per liter.

Monopotassium Carbamate, KH_5CO_2N.—The reaction of potassium amide with ammonium carbamate to form monopotassium carbamate may be expressed by the equation $NH_4H_2CO_2N + KNH_2 = KH_2CO_2N + 2NH_3$.

The ammonium carbamate prepared from 0.301 g. of carbon dioxide was treated with the potassium amide from 0.251 g. of potassium, which is slightly less than one equivalent per molecule of carbamate. The monopotassium salt was precipitated as a microcrystalline powder the solubility of which in liquid ammonia was extremely slight.

After the addition of the whole of the potassium amide solution the tube was allowed to stand for three days at room temperature to allow the reaction, involving as it does the slightly soluble ammonium carbamate, to go to completion. The precipitate was then thoroughly washed with fresh solvent to remove the excess of ammonium carbamate, dried in a vacuum, and weighed; yield, 0.6612 g.

Anal. Subs., 0.6612: K_2SO_4 ($^1/_5$),[7] 0.1168; N (Kjeldahl) ($^1/_5$, $^1/_5$) 0.00196, 0.00197. Calcd. for KH_2CO_2N: K, 39.4; N, 14.2. Found: K, 39.6; N, 14.8, 14.9.

Dipotassium Carbamate K_2HCO_2N.—It was found that ammonium carbamate reacts with two equivalents of potassium amide in liquid ammonia solution according to the equation, $NH_4H_2CO_2N + 2KNH_2 = K_2HCO_2N + 3NH_3$.

PREPARATION I.—The ammonium carbamate from 0.282 g. of carbon dioxide was added to a solution of the potassium amide from 0.569 g., or three equivalents, of potassium. The ammonium carbamate was added in the form of a suspension in liquid ammonia and allowed to stand for several days in contact with the potassium amide solution. The gradual disintegration of the large ammonium carbamate crystals, forming the very insoluble microcrystalline potassium salt, could be visually observed. The sample was then thoroughly washed, dried in a vacuum, and weighed; yield, 0.6285 g.

Anal. Subs., 0.6285: K_2SO_4 ($^1/_5$, $^1/_{10}$), 0.1565, 0.0786; N ($^1/_5$, $^1/_5$), 0.00128, 0.00129.

PREPARATION II.—The ammonium carbamate from 0.312 g. of carbon dioxide was added to the potassium amide from 0.90 g. of the metal. This time the ammonium carbamate was added entirely as solution by repeated extraction of the solid material with fresh solvent. In this way any possible contamination of the sample with unchanged ammonium carbamate was avoided. The precipitated potassium salt was washed only thrice in order to avoid an ammonolysis of a possible tripotassium salt by too thorough washing. The absence of any tendency to form such a salt was attested by the fact that not only the potassium but also the nitrogen content of the sample

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[7] Refers to proportion of total substance used in analysis.

was found to be too high for the dipotassium salt. This indicates that the sample was dipotassium carbamate contaminated with potassium amide; yield, 0.7571 g.

Anal. Subs., 0.7571: K_2SO_4 (1/10), 0.0973; N (1/5, 1/5), 0.01704, 0.01704.

PREPARATION III.—The ammonium carbamate from 0.172 g. of carbon dioxide was treated with the potassium amide from 0.439 g. of the metal. The procedure was the same as in the previous preparation except that the material was this time thoroughly washed with fresh solvent; yield, 0.2857 g.

Anal. Subs., 0.2857: K_2SO_4 (1/10), 0.0562; N (1/5, 1/5), 0.01004, 0.01010. Calcd. for K_2HCO_2N: K, 57.0; N, 10.2. Found: K, (I) 55.8, 55.9, (II) 57.6, (III) 56.9; N, (I) 10.2, (II) 11.3, 11.3, (III) 10.6, 10.7.

Ethyl Carbamate (Urethan).—Since carbamic acid is a mixed aquo-ammonocarbonic acid containing three hydrogen atoms of which two have just been shown to be replaceable by a metal, it seemed probable that the ethyl ester of carbamic acid, urethan, might contain one or two hydrogen atoms replaceable by metal. It was found, however, that while there was some evidence of the formation of such a salt it was extremely unstable, decomposing to form potassium cyanate and alcohol. The ultimate reaction of ethyl carbamate with potassium amide in liquid ammonia solution may therefore be expressed by the equation $H_2NCOOC_2H_5 + KNH_2 = KNCO + C_2H_5OH + NH_3$.

A very similar reaction with potassium ethylate in alcohol solution was noted by Arth.[8]

PREPARATION I.—The potassium amide from 0.61 g. of metal was allowed to react with 1.39 g. of ethyl carbamate. When the two solutions were mixed no precipitate was obtained at first. As the solution was evaporated to small volume a crop of large, flaky crystals separated, evidently fairly soluble. In the course of a few minutes, however, these disintegrated forming a microcrystalline powder of only slight solubility. After two or three hours the crystals were washed with fresh solvent and dried in a vacuum at room temperature for analysis; yield, 0.7369 g.

Anal. Subs., 0.7369: K_2SO_4 (1/10), 0.0788; N (1/5, 1/5), 0.0264, 0.0267.

PREPARATION II.—A liquid ammonia solution of the potassium amide from 1.10 g. of the metal was added to a solution of 2.55 g. of ethyl carbamate. The solutions before and after being mixed were maintained at —33° in order to prevent, if possible, the decomposition of the salt of urethan. It was found, however, that the low temperature did not bring about the desired result. The reaction tube was therefore allowed to stand until decomposition was complete, and the samples were prepared for analysis as before.

After the ammonia had been evaporated it was found that about 1 cc. remained of a liquid, the boiling point of which was above room temperature. This was removed by distillation and found to have the properties of ethyl alcohol.

The microcrystalline material remaining after complete removal of the alcohol weighed 1.5672 g. This material was dissolved in pure water instead of, as ordinarily in dilute acid. This was to avoid hydrolysis of the cyanate ion if present. An aliquot part of this solution was tested for cyanate ion by the copper-pyridine method described by Werner[9] and gave strongly positive results.

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[8] Arth, *Bull. soc. chim.*, **41**, 334 (1884).

[9] Werner, *J. Chem. Soc.*, **123**, 2577 (1923).

Anal. K_2SO_4 ($^1/_5$, $^1/_{10}$ of soln. of sample), 0.3232, 0.1631; N ($^1/_5$, $^1/_5$), 0.05392, 0.05522. Calcd. for KOCN: K, 48.2; N, 17.3. Found: K, (I) 48.0, (II) 46.3, 46.7; N, (I) 17.9, 18.0, (II) 17.2, 17.6.

Biuret

Schiff[10] has described the preparation of several metallic salts of biuret which are, however, not of simple character but of two distinct types. These are, first, basic salts such as the mercuric salt of the formula $Hg(NHCONHCONH.HgOH)_2$ and, second, salts which presumably have added water or acids to form bases or salts of the "ammonium" type. Examples of the latter type are the potassium and cupric salts of the formulas $KHNCONHCONH_3OH$ and $Cu(NHCONHCONH_3NO_3)_2$, respectively. In all of the salts prepared by Schiff, biuret behaves as a monobasic acid.

A disilver salt of the formula, $Ag_2H_3C_2O_2N_3$ has also been reported.[11]

Monopotassium Biuret, $KH_4C_2O_2N_3$.—When liquid ammonia solutions of biuret and potassium amide were mixed, the biuret being in molecular excess, it was found that monopotassium biuret was formed in accordance with the equation $H_5C_2O_2N_3 + KNH_2 = KH_4C_2O_2N_3 + NH_3$.

PREPARATION I.—The potassium amide from 0.087 g. of potassium was added to a liquid ammonia solution of 0.25 g. of biuret. Biuret, it may be stated, was found to be fairly soluble in liquid ammonia. The monopotassium salt, formed in this manner, gave a very voluminous, extremely insoluble precipitate. After standing for several hours the precipitate was washed with fresh solvent and dried in a vacuum at room temperature; yield, 0.2762 g.

Anal. Subs., 0.2762: K_2SO_4 ($^1/_5$), 0.0555; N ($^1/_5$, $^1/_5$), 0.01644, 0.01664. Calcd. for $KH_4C_2O_2N_3$: K, 27.7; N, 29.8. Found: K, 27.2; N, 29.8, 30.1.

Tripotassium Biuret, $K_3H_2C_2O_2N_3$.—When a liquid ammonia solution of biuret is added to a solution containing a large excess of potassium amide, tripotassium biuret is formed according to the equation $H_5C_2O_2N_3 + 3KNH_2 = K_3H_2C_2O_2N_3 + 3NH_3$.

PREPARATION I.—A liquid ammonia solution of 0.1 g. of biuret was added to the potassium amide from 0.214 g. or 5.5 equivalents, of the metal. This quantity of potassium amide was used to allow an opportunity for all five of the hydrogen atoms of biuret to be substituted by potassium. Only three potassium atoms were introduced, however, under the conditions of experiment. The tripotassium salt was formed as an abundant, almost gelatinous precipitate which, however, settled well and was well washed and dried in a vacuum for analysis; yield, 0.2182 g.

Anal. Subs., 0.2182: K_2SO_4 ($^1/_5$), 0.0517; N ($^1/_5$, $^1/_5$) 0.00842, 0.00846. Calcd. for $K_3H_2C_2O_2N_3$: K, 54.0; N, 19.4. Found: K, 53.0; N, 19.3, 19.4.

It is quite possible and indeed probable that biuret is capable of forming a dipotassium salt with potassium amide in liquid ammonia solution. Since both the monopotassium salt, which is formed when biuret is in excess, and the tripotassium salt formed when potassium amide is in

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[10] Schiff, *Ber.*, **29**, 299 (1896); *Ann.*, **299**, 236 (1897).

[11] Wislicenus, Bonné and Goldenberg, *Ber.*, **7**, 287 (1874).

excess, are extremely insoluble, no method was at hand for preparing a salt that could be identified with certainty as containing two potassium atoms per molecule. A material having such a composition could indeed be made by using biuret and potassium amide in exactly the proper proportions but it could not be distinguished with certainty from an equimolecular mixture of the mono- and tripotassium salts.

Triuret (Carbonyl-diurea)

Triuret, or carbonyl-diurea, was made by the action of phosgene on urea in the manner described by Schiff.[12] This substance is to be distinguished from cyanuric acid, which has also been called "Triuret"[13] but which certainly does not have as much right to the name as does the substance under discussion.

Monopotassium Triuret $KH_5C_3O_3N_4$.—It was found that triuret, which is readily soluble in liquid ammonia, would react, when in molecular excess, with potassium amide to form a monopotassium salt in accordance with the equation $H_6C_3O_3N_4 + KNH_2 = KH_5C_3O_3N_4 + NH_3$.

PREPARATION I.—The potassium amide from 0.083 g. of metal was added to a liquid ammonia solution of 0.31 g., or a slight molecular excess, of triuret. Immediate precipitation of a microcrystalline salt took place which, however, did not manifest the extreme insolubility in liquid ammonia that seems to be the rule with this class of compounds. After several hours the precipitate was prepared for analysis by thorough washing with fresh solvent and drying in a vacuum; yield, 0.3482 g.

Anal. Subs., 0.3482: K_2SO_4 ($^1/_{10}$, $^1/_5$), 0.0167, 0.0329; N ($^1/_{10}$, $^1/_{10}$), 0.01075, 0.01082. Calcd. for $KH_5C_3O_3N_4$: K, 21.2; N, 30.4. Found: K, 21.5, 21.2; N, 30.8, 31.0.

Dipotassium Triuret, $K_2H_4C_3O_3N_4$.—When a liquid ammonia solution of triuret was added to a solution containing a large excess of potassium amide, dipotassium triuret was formed according to the equation $H_6C_3O_3N_4 + 2KNH_2 = K_2H_4C_3O_3N_4 + 2NH_3$.

PREPARATION I.—A liquid ammonia solution of 0.33 g. of triuret was added to a solution containing the potassium amide from 0.54 g. of the metal. This quantity of potassium is more than six equivalents per molecule of triuret, so that opportunity was afforded for a possible complete replacement by potassium of the hydrogen of the compound. A compound having, however, the composition of a dipotassium salt was formed as an extremely insoluble microcrystalline precipitate. This was thoroughly washed with fresh solvent and dried in a vacuum for analysis; yield, 0.3303 g.

Anal. Subs., 0.3303: K_2SO_4 ($^1/_5$, $^1/_{10}$), 0.0520, 0.0259; N ($^1/_5$, $^1/_5$), 0.01655, 0.01650. Calcd. for $K_2H_4C_3O_3N_4$: K, 35.1; N, 25.2. Found: K, 35.3, 35.1; N, 25.0, 24.9.

What was supposed to be an ammonium salt of triuret has been reported by Dains.[14] A small quantity of triuret was therefore dissolved in anhydrous liquid ammonia and the

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

[13] Beilstein, "Handbuch der organischen Chemie," Leopold Voss, Hamburg, 3rd ed., **1893,** I, p. 1267.

[14] Dains, THIS JOURNAL, **21,** 192 (1899).

solution evaporated to dryness in the expectation that the ammonium salt would be thereby obtained. However, a nitrogen determination on the residue, dried in a vacuum at room temperature, showed that it was unchanged triuret; yield, 0.2669 g.

Anal. Subs., 0.2669: N ($^1/_5$), 0.01297. Calcd. for $H_6C_3O_3N_4$: N, 38.3; calcd. for $NH_4.H_5C_3O_3N_4$: 43.0. Found: 38.9.

Allophanic Acid

The sodium, potassium, calcium and barium salts of allophanic acid were prepared by Liebig and Wöhler[15] by the action of the corresponding metallic hydroxides on ethyl allophanate. A disodium salt was prepared in benzene solution, by Ephraim.[16] A disilver salt of ethyl allophanate has been prepared in water solution.[17]

In the present work it was found possible to prepare the monopotassium salt of ethyl allophanate in liquid ammonia solution according to the equation $H_2NCONHCOOC_2H_5 + KNH_2 = KNHCONHCOOC_2H_5 + NH_3$. It is interesting to note that although aqueous ammonia readily ammonolyzes ethyl allophanate to biuret, anhydrous liquid ammonia apparently does not exhibit this behavior. This was also observed by Dains and Wertheim.[18]

PREPARATION I.—The potassium amide from 0.34 g. of the metal was added to a liquid ammonia solution of 1.14 g. of ethyl allophanate. These quantities represent equimolecular proportions. The precipitate which was formed was at first very bulky but on standing for some time a beautifully crystallized product was obtained. This was thoroughly washed with fresh solvent and dried in a vacuum for analysis; yield, 0.7502 g. It was found, on treating the sample with dilute acid as usual, that a product was formed which resembled ethyl allophanate in that it was insoluble in water. This corroborates the analytical evidence that ethyl allophanate does not undergo decomposition, such as that encountered in the case of ethyl carbamate, but simply forms a salt. The entire mixture was therefore transferred to a Kjeldahl flask and digested with concd. sulfuric acid so as to hydrolyze the product and render it soluble. Potassium and nitrogen were then determined in aliquot parts of this solution of potassium and ammonium sulfates.

Anal. Subs., 0.7502: K_2SO_4 ($^1/_5$, $^1/_5$), 0.0759, 0.0750; N ($^1/_5$), 0.0249. Calcd. for $KHNCONHCOOC_2H_5$: K, 22.9; N, 16.5. Found: K, 22.1, 22.4; N, 16.6.

Decomposition of Monopotassium Ethyl Allophanate.—That ethyl allophanate should be stable enough in liquid ammonia solution, when treated with potassium amide, to yield a monopotassium salt, while ethyl carbamate was found to decompose as stated above, forming potassium cyanate and alcohol, was an interesting contrast. Further work was therefore done to ascertain whether the monopotassium ethyl allophanate would also decompose, if at a higher temperature. It was found that, at 215°, decomposition of the monopotassium ethyl allophanate did take place, form-

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[15] Liebig and Wöhler, *Ann.*, **58**, 291 (1846).

[16] Ephraim, *Ber.*, **35**, 779 (1902).

[17] Dains, Greider and Kidwell, THIS JOURNAL, **41**, 1004 (1919).

[18] Dains and Wertheim, *ibid.*, **42**, 2303 (1920).

ing potassium cyanate and ethyl carbamate. $KHNCONHCOOC_2H_5 = KNCO + H_2NCOOC_2H_5$.

In the experiment described just above there was, in the bottom of that leg of the reaction tube which is discarded in the usual procedure, a crystalline material that consisted largely of monopotassium ethyl allophanate slightly contaminated with unchanged ethyl allophanate. This material instead of being discarded was carefully heated in an apparatus in which any volatile products of decomposition could be condensed and collected. No change was noticed until the temperature reached 215°, at which temperature the material decomposed forming two products. One product was a distillate which was identified as urethan by its solubility, its melting point of 48–50°, and the iodoform test. The other product was a white, microcrystalline residue, infusible and non-volatile at 215°, and this was identified as potassium cyanate by the Werner test.[9]

Action of Potassium Amide in Excess on Ethyl Allophanate.—There are three hydrogen atoms in ethyl allophanate which should be replaceable by a metal. Two experiments were carried out, therefore, to ascertain the action of potassium amide in excess on ethyl allophanate in liquid ammonia solution.

Considerable difficulty was encountered in identifying the precipitates which were obtained. These precipitates were extremely insoluble, and as first precipitated were highly flocculent and required days to settle out so that they could be washed for analysis.

Concordant analytical results were not obtained, but two facts were ascertained which can be stated with certainty. In the first place, ethyl allophanate was not obtained when the specimens were treated with water. This shows that the ethyl group had been eliminated during the reaction, presumably by ammonolysis. In the second place, the material gave, in all cases, the Werner test for cyanates.

In view of the inconclusive character of the results, their presentation will be reserved until further work can be done on the reaction of potassium amide on this and other esters in liquid ammonia solution.

In conclusion, the writer wishes to express his indebtedness to Dr. E. C. Franklin for his kindly advice and assistance in the carrying out of the work which is here presented.

Summary

The acidic character of the mixed aquo-ammonocarbonic acids, as defined in the first paper of this series, has been demonstrated by the preparation, in liquid ammonia solution, of the potassium salts of a representative number of this class of compounds.

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