iodide[1] and that the compound thus formed loses two molecules of ammonia on being heated to 160°. In view of the amorphous character of the precipitate, however, the existence of a definite compound of the composition given cannot be certain. At all events it is an insoluble ammonobasic product.

Summary.—A soluble ammonobasic iodide of aluminium is formed in accordance with the reaction represented by the equation $2AlI_3 + 3KNH_2 = Al(NH_2)_3.AlI_3 + 3KI$, when potassium amide in limited amount is added to a liquid ammonia solution of aluminium iodide. At ordinary temperature the salt separates from solution with six molecules of ammonia of crystallization as represented by the formula $Al(NH_2)_3.AlI_3.6NH_3$, at low temperatures a highly ammonated salt containing from 18 to 20 molecules of ammonia separates from the solution.

An insoluble ammonobasic iodide of aluminium, the composition of which is represented by the formula $Al(NH_2)_3.Al(NH_2)_2I.NH_3$ is precipitated when potassium amide is added to a solution of the above soluble basic salt. When heated this compound loses two molecules of ammonia to form a product to which the formula $Al(NH_2)_3.AlNHI$ has been given.

STANFORD UNIVERSITY, CALIFORNIA.

POTASSIUM AMMONOARGENTATE.

BY EDWARD C. FRANKLIN.

Received January 15, 1915.

Some years ago while studying the action of potassium amide on liquid ammonia solutions of silver salts, the observation was made that silver amide dissolves readily in excess of potassium amide solution.[2] Since this is a behavior which recalls the similar action of water solutions of potassium hydroxide on certain metallic hydroxides it was surmised that the observed action of potassium amide solution on silver amide probably results in the formation of an ammonoargentate of potassium.

It was for the purpose of attempting the isolation of such a compound that this investigation was undertaken.

When, in one of the two-legged reaction tubes which have been elsewhere described,[3] a liquid ammonia solution of potassium amide is run into a similar solution of a silver salt a precipitate of silver amide is formed which, as the addition of potassium amide is continued, increases in amount until all the silver is precipitated. With further addition of the precipitant the precipitate dissolves to a clear, colorless solution. When, after a proper adjustment of the concentration, the solution thus obtained is cooled in a bath of liquid ammonia a crop of beautiful crystals separates from the

---

[1] Cf. analytical results given in THIS JOURNAL, **27**, 849 (1905).

[2] THIS JOURNAL, **27**, 835 (1905).

[3] *Ibid., loc. cit.*

solution. The salt is purified by recrystallizing several times from solvent distilled over from the second arm of the reaction tube. After separating the two legs of the reaction tube containing, respectively, the mother liquor and the solution of the pure salt, the excess of ammonia is removed from the latter and the pure, dry salt, together with its container, is weighed. In order to hydrolyze the specimen and get the hydrolytic products into aqueous solution preparatory to analysis, the dried salt is allowed to lie over night in contact with water vapor. The hydrolytic products were then treated successively with liquid water and dilute sulfuric acid. It was expected that the salt, which has been shown to have the composition represented by the formula $AgNHK.NH_3$ would hydrolyze in accordance with the equation $2AgNHK + 3H_2O = Ag_2O + 2KOH + 2NH_3$. Contrary, however, to expectations it was found that considerable quantities of metallic silver and nitrogen gas are always liberated during this treatment of the compound. Furthermore, when the salt was prepared directly from iodide of silver in the manner described above, small quantities of the latter salt were always found mixed with the metallic silver. This contamination was not a portion of the original iodide of silver used in the experiment, but resulted from the action of potassium iodide, which had not completely removed from the salt by the process of purification to which it was submitted, on the silver sulfate formed by the action of the dilute sulfuric acid on the products of hydrolysis. The metallic silver was recovered from the mixture of silver and silver iodide by dissolving in dilute nitric acid and precipitating it as silver chloride. The silver chloride thus obtained is marked (*a*) in the analytical data below. The silver iodide, which was filtered off, washed, weighed and is marked (*b*) below, gives a measure of the amount of potassium iodide with which the specimen was contaminated. The silver contained in the sulfuric acid solution was precipitated as the chloride and is given under (*c*) in the analytical data. The total nitrogen was made up of two parts, that present in the sulfuric acid solution as ammonium sulfate and that set free during the hydrolysis of the ammono salt. The free nitrogen and metallic silver were found to be formed in equivalent quantities.

Preparation I.—In this experiment somewhat more than two equivalents of potassium amide were added to a solution of 2.35 g. of silver iodide in liquid ammonia and the resulting solution, after proper concentration, was cooled to —40°. The crop of beautiful crystals which separated from the solution was dissolved and recrystallized once for analysis.

The specimen dried in vacuum at 20° weighed 0.8880 g. The specimen contained 0.4636 g. Ag, calculated from (*a*) 0.4506 g. AgCl, (*b*) 0.1268 g. AgI and (*c*) 0.0525 g. AgCl from three-fifths of the sulfuric acid solution. The other two-fifths of this solution gave 0.0429 g. N. The free nitrogen collected amounted to 0.0142 g. One-fifth of the filtrate from (*c*) gave 0.0557 g. K_2SO_4.

Preparation II.—The same quantities of silver iodide and potassium amide were used as in the preceding experiment.

The salt, recrystallized four times and dried in vacuum at 20°, weighed 0.5479 g. The specimen contained a total of 0.3211 g. Ag, calculated from (*a*) 0.3755 g. AgCl, (*b*) 0.0078 g. AgI and (*c*) 0.0465 g. AgCl from the whole of the sulfuric acid solution, and a total of 0.0867 g. N, calculated from the nitrogen equivalent of metallic silver (*a*) and 0.0186 g. N obtained from one-fourth of the filtrate from AgCl (*c*). Another fourth of this filtrate gave 0.0688 g. K_2SO_4.

Preparation III.—In this experiment slightly more than three equivalents of potassium amide were added to a solution of 2.5 g. of silver iodide with the object in view of ascertaining whether possibly a salt containing two atoms of potassium may be obtained.

The specimen, which was recrystallized four times, weighed 0.4603 g. when dried in vacuum at 20°. It was found to contain a total of 0.2732 g. Ag, calculated from (*a*) 0.3075 g. AgCl, (*b*) 0.0065 g. AgI and (*c*) 0.0386 g. AgCl from three-fourths of the sulfuric acid solution. One-fourth of this solution gave 0.0158 g. N, which, together with the nitrogen equivalent of (*a*), gives a total of 0.0732 g. N. One-half of the filtrate from AgCl (*c*) gave 0.0826 g. K_2SO_4.

Preparation IV.—Finding the silver persistently low in the above preparations, as the result of contamination with potassium iodide, it was determined to prepare pure silver amide and dissolve this in a solution of potassium amide with the expectation that a pure specimen of potassium ammonoargentate would result. Accordingly a three-legged reaction tube was prepared and into one leg was introduced 1 g. of silver nitrate and into each of the other two one equivalent of metallic potassium together with a minute quantity of platinum black.[1] Ammonia was distilled into the apparatus and after all the potassium had been converted into potassium amide the solvent from one of the legs containing potassium amide was evaporated away, leaving the ammono base clinging to the walls and bottom of the tube. This potassium amide was reserved for dissolving the pure silver amide. The preparation and purification of silver amide was then carried on in the other two legs of the reaction tube after the manner previously described.[2] After thoroughly washing the silver amide, liquid ammonia was distilled from the washings and distributed between the two legs containing the precipitate and the reserve potassium amide, respectively. The leg containing the washings was then sealed off leaving a two-legged tube in which the operations of dissolving the silver amide and purifying the resulting salt were carried on in the usual manner. The crop of crystals obtained was recrystallized once preparatory to analysis.

Dried in vacuum at 100° the specimen weighed 0.4852 g. The metallic silver formed during the hydrolysis of the salt was dissolved in dilute nitric acid and added to the sulfuric acid solution. From the combined solutions 0.3877 g. AgCl

---

[1] Platinum black accelerates the reaction between the ammonia and potassium.

[2] *Loc. cit.*

was obtained. One-half of the filtrate from the silver chloride gave 0.0310 g. N, which, together with 12.7 cc. N measured over water at 20° and 760 mm., gives a total of 0.0765 g. N. The other half of the filtrate gave 0.1169 g. K_2SO_4.

The following results have been calculated from the above data:

	Calculated for $AgNHK.NH_3$.	Found.			
		I.	II.	III.	IV.
Ag	60.3	52.3	58.6	59.3	60.2
N	15.6	13.7	15.8	15.9	15.7
K	21.8	23.4	22.5	21.4	21.6
I	0.0	7.7	0.9	0.7	....

A compound of the composition represented by the formula $AgNHK.NH_3$ or $AgNH_2.KNH_2$ is therefore formed by the action of a solution of potassium amide on the amide of silver in accordance with a reaction represented by the equation

$$AgNH_2 + KNH_2 = AgNHK + NH_3.$$

The salt separates from concentrated solutions in the form of beautiful crystals which are unaffected at a temperature of 100°. It is gradually discolored and decomposed by contact with the air. When heated over the open flame it decomposes vigorously but without explosive violence. In contact with water it decomposes but does not explode. This behavior is in marked contrast with that of silver amide which, it will be remembered, explodes with great violence on the slightest provocation, frequently without any assignable cause whatever. Liquid ammonia solutions of acids decompose potassium ammonoargentate, precipitating first silver amide which dissolves on further addition of the acid to form a silver salt of the acid used.

Summary.—It is shown in this paper that silver amide dissolves in a liquid ammonia solution of the ammono base, potassium amide, to form potassium ammonoargentate, an ammono salt of the composition represented by the formula $AgNHK.NH_3$ or $AgNH_2.KNH_2$.

STANFORD UNIVERSITY, CALIFORNIA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

INTERPRETATIONS OF SOME STEREOCHEMICAL PROBLEMS IN TERMS OF THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.[1]

PART III: A CONTINUATION OF THE INTERPRETATION OF THE BROWN AND GIBSON RULE. PART IV: THE SIMULTANEOUS FORMATION OF ORTHO-, META- AND PARA-SUBSTITUTED DERIVATIVES OF BENZENE. PART V: A REPLY TO A. F. HOLLEMAN.

BY HARRY SHIPLEY FRY.

Received January 21, 1915.

Introduction.

In the first paper (I)[2] of this series, the electronic conception of positive

---

[1] Read before the Cincinnati Section, Am. Chem. Soc., Dec. 9, 1914.

[2] Fry, THIS JOURNAL, 36, 248 and 262 (1914).