have been completely explored. This investigation is now in progress. Whether the decomposition of hydrazine sulfate by ammonia is to be regarded as a simple displacement of hydrazine by ammonia, or as a process involving dissociation of the ammonia molecule, it may, in the opinion of the authors, be looked upon as an instance of *ammonolysis*, *i. e.*, of the breaking up of a salt by the action of ammonia.

The reaction obviously suggests a new method for the preparation of free hydrazine from certain of its salts.

Summary.

In the present investigation it has been shown that hydrazine sulfate is decomposed by the action of liquid ammonia at —33° in accordance with the equation

$$N_2H_4.H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 + N_2H_4.$$

The resulting solution of free hydrazine in liquid ammonia may be separated from the entirely insoluble ammonium sulfate (or its addition product with ammonia) by decantation or by filtration. This suggests a new method for the preparation of free hydrazine from certain of its salts. Even at ordinary temperatures, with relatively small active mass of ammonia, the reaction proceeds to an appreciable extent.

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BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. II. AMMONOLYSIS OF CERTAIN HYDRAZINE SALTS.

BY A. W. BROWNE AND A. E. HOULEHAN.

Received September 1, 1911.

It has already been shown in this laboratory[1] that hydrazine disulfate when treated with liquid ammonia at —33° undergoes decomposition, yielding free hydrazine and ammonium sulfate. In conformity with the system of nomenclature used by Goldschmidt and Salcher[2] and by E. C. Franklin[3] this reaction, whether it involves the splitting of an ammonia molecule, with initial formation of hydrazine amide and sulfuric acid, or, as seems more probable, a simple displacement of hydrazine by ammonia in accordance with the law of mass action, has been considered to furnish a new instance of ammonolysis.

The present investigation has been undertaken with the purpose of ascertaining whether or not certain other hydrazine salts undergo ammonolysis in liquid ammonia. The compounds selected comprize a number of salts containing acids, the ammonium salts of which have previously

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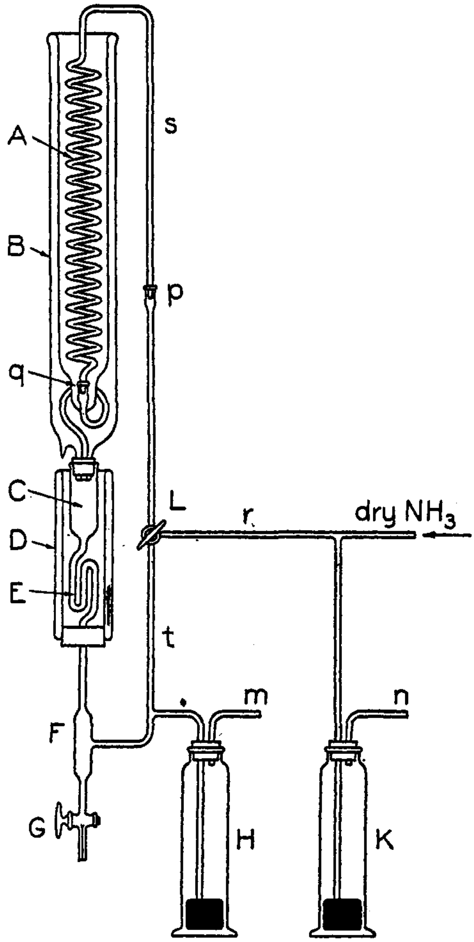
[1] THIS JOURNAL, **33**, 1728 (1911).

[2] *Z. physik. Chem.*, **29**, 89–118 (1899).

[3] THIS JOURNAL, **27**, 82[illegible]1 (1905), page 826.

been shown to be insoluble in liquid ammonia.[1] The behavior of hydrazine monosulfate, hydrazine dioxalate, hydrazine diselenate, hydrazine monophosphate, and hydrazine diphosphate, respectively, in liquid ammonia has been investigated.

Apparatus Employed in the Experiments.—After considerable preliminary experimentation the form of apparatus shown in the subjoined sketch was adopted. This device, which virtually serves as a low temperature extraction apparatus, consists essentially of a spiral condenser tube, *A*, the upper end of which may be connected through the three-way stopcock *L* with a source of pure, dry ammonia, and which is surrounded by the vacuum cylinder *B*. The lower end of the spiral tube is connected through the ground glass joint *q* with an outlet tube which delivers into the cylindrical funnel tube *C*. This tube contains a closely fitted extraction thimble made of heavy filter paper, which is designed to hold the weighed sample of the hydrazine salt under investigation. The loop *E* serves to trap the liquid ammonia and to hold it for a time in contact with the hydrazine salt. The accumulation of liquid upon the salt greatly facilitates the process of ammonolysis and favors the removal of the free hydrazine formed.



After the ammonia has collected to a sufficient depth it is automatically siphoned from the thimble, and is delivered into the receiver *F*. The vacuum jacket *D* is used as a container for solid carbon dioxide, which serves to prevent evaporation of the liquid in *C* and *E*. The receiver is provided with a stopcock, *G*, through which samples of the product

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[1] Franklin and Kraus, THIS JOURNAL, 20, 820–36 (1898).

may be removed, and with a side-arm, which communicates through *L* with the spiral condenser tube. The mercury traps *H* and *K* serve as safety outlets. For the sake of convenience in setting up or dismantling the apparatus the tube *s* is provided with the ground joint *p*. The spiral tube may, therefore, be removed by simply disconnecting at *p* and *q*. In its latest form the vacuum cylinder *B* has been provided, at its lower end, with a hollow, ground glass stopper that fits into the funnel tube *C*. This eliminates the small cork that was used in the apparatus as shown in the sketch.

General Procedure.--A weighed amount of the hydrazine salt to be investigated was first introduced into the thimble. All air in the apparatus was then displaced by a current of pure ammonia gas that had been dried by passing it through a 60 cm. tube filled with sodium wire. Solid carbon dioxide was introduced into *B* and *D*, and a current of ammonia, sufficiently rapid to supply a steady dropping of liquid upon the salt, was caused to pass into *A*. As soon as an appreciable quantity of the resulting solution of free hydrazine in ammonia had been delivered into *F*, the stopcock *L* was turned so as to connect the receiver with the spiral condenser tube *A*. The liquid soon commenced to evaporate, and the gas returned to *A*, where it was again condensed. By wrapping *F* with the proper thickness of cheese-cloth it was found possible so to regulate the evaporation of the liquid as to permit the cutting off of the supply of ammonia from the steel cylinder. After several successive quantities of liquid had been siphoned from *C* into *F* further condensation of the gas was discontinued, and the liquid in *F* was permitted to evaporate until the ammonia had been expelled as completely as possible at room temperature.

Samples of the residual liquid, which consisted chiefly of free hydrazine, were drawn from *F* through the stopcock *G*, and were weighed in glass stoppered weighing bottles. The samples were then transferred to measuring flasks, were acidified with dilute sulfuric acid, and were diluted with water to exactly 100 cc. The percentage of hydrazine was determined in several portions of this solution by the method of Rimini,[1] and the percentage of ammonia was subsequently determined in the residual solutions, after the titration with standard thiosulfate solution.

The residual solid in the extraction thimble was removed, as nearly as possible quantitatively, and was weighed. The entire sample was then dissolved in water and was diluted to a convenient volume. Hydrazine (if present), ammonia, and the acid of the salt used were determined in different portions of the solution.

Details of Individual Experiments.

Behavior of Hydrazine Monosulfate in Liquid Ammonia.—Since hy-

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[1] THIS JOURNAL, 33, 1353-62 (1911).

drazine disulfate has already been shown to undergo decomposition in liquid ammonia with formation of free hydrazine and ammonium sulfate, it has been considered likely that hydrazine monosulfate, a substance containing a much larger percentage of hydrazine than the disulfate, would undergo ammonolysis under similar conditions with even greater readiness.

The hydrazine monosulfate used in these experiments was prepared by neutralizing 15 grams of hydrazine hydrate (Raschig) with dilute sulfuric acid, using methyl orange as indicator. After the resulting solution had been evaporated on the water bath the monosulfate crystallized as a fine white powder. A small sample of the product was analyzed, with the following results:

N_2H_4, 39.4 per cent.; H_2SO_4, 60.8 per cent. Theory for N_2H_4 in $(N_2H_4)_2.H_2SO_4$, 39.5 per cent.; for H_2SO_4, 60.5 per cent.

A weighed sample of hydrazine monosulfate was placed in the extraction thimble, and a current of dry ammonia was swept through the apparatus in order to displace the air. During this operation the air was allowed to escape through the stopcock *G*. When the stopcock was finally closed, a surprizingly rapid diminution in pressure took place within the apparatus, in spite of the fact that a moderately rapid current of ammonia was still being admitted. This diminution in pressure occurred before any solid carbon dioxide was used, and resulted in the drawing of a considerable quantity of mercury from the trap *H* into the apparatus. On removal of the extraction thimble it was found that the hydrazine compound had become very moist and sticky as a result of the absorption of ammonia. When spread out and exposed to the air the moist substance gave off considerable quantities of ammonia, finally resuming its original appearance.

A second sample of the monosulfate weighing 6.8768 grams was placed in the thimble. The air in the apparatus was displaced as before, but the precaution was taken to introduce the ammonia with sufficient rapidity to prevent diminution in pressure as the ammonia was absorbed by the hydrazine compound. After the substance had been treated with liquid ammonia as described in a preceding paragraph, a sample of free hydrazine was obtained which, after the ammonia had evaporated as completely as possible at room temperature, was found by analysis to contain 93.2 per cent. of hydrazine. Tests were made for sulfuric acid, with negative results.

The residue in the extraction thimble continued to give off ammonia for some time after it had been removed from the apparatus. When this process had finally come to an end the residual substance was shown, by analysis of its three components, to contain 10.5 per cent. N_2H_4, 70.6 per cent. H_2SO_4, and 18.8 per cent. NH_3. From these facts it is apparent that hydrazine monosulfate very readily undergoes decomposition in liquid ammonia with formation of free hydrazine and ammonium sulfate. Under the conditions of this particular experiment, however, the process was not complete, since a portion of the hydrazine compound apparently escaped the action of the ammonia, probably owing to its enclosure within a protective coating of ammonated ammonium sulfate. The moist, sticky condition of the substance during the early stages of its ammonolysis was in all probability due to the liberation of hydrazine. The gradual drying of the mass on exposure to the atmosphere was presumably attributable to the displacement of ammonia from ammonium sulfate by the free hydrazine.[1]

Behavior of Hydrazine Monosulfate toward Ammonia Gas at Room Temperature.—From the peculiar behavior of the salt when first brought into an atmosphere of ammonia gas in the preceding experiment, it was considered probable that ammonolysis would take place to some extent even at ordinary temperatures. Preliminary experiments were first performed in which weighed samples of hydrazine monosulfate were treated in glass-stoppered U-tubes with dry ammonia gas for definit periods of time. It was found that the salt in every case absorbed very appreciable amounts of ammonia, becoming moist and sticky. Comparative tests with weighed samples of hydrazine disulfate showed that this substance also, under similar conditions, has a tendency to absorb ammonia, but rather more slowly than the monosulfate. A sample of hydrazine monosulfate that weighed 1.0189 grams increased in weight, after one hour's treatment, to 1.0819 grams. At the end of the second, third, and fourth hours, respectively, the sample weighed 1.0771, 1.0764 and 1.0767 grams. The loss in weight after the end of the first hour was undoubtedly due to the escape of hydrazine vapor with the current of ammonia. The presence of hydrazine in an absorbing solution located at the end of the chain of U-tubes was demonstrated at the conclusion of the experiment.

In order to separate the liquid formed by the action of dry ammonia upon hydrazine monosulfate, samples of the salt weighing respectively 3.9315 and 4.3704 grams were first treated with ammonia for an hour and a half, and were then centrifugalized for several minutes at an average rate of about one thousand revolutions per minute. This operation was carried on in special glass tubes made for the purpose, and mounted in a Bausch and Lomb centrifugal apparatus. In each case a clear, colorless, viscous liquid possessing the odor of anhydrous hydrazine was obtained which in the first experiment weighed 0.3474 and in the second 0.3573 gram. The results obtained on analysis of these products are as follows:

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[1] Lobry de Bruyn, *Rec. trav. chim.*, 15, 174–84 (1896), page 179.

(1) N_2H_4 48.4 per cent., NH_3 3.36 per cent., H_2SO_4 46.0 per cent.; (2) N_2H_4 51.3 per cent., NH_3 2.67 per cent., H_2SO_4 48.6 per cent.

From these data it would appear that the liquid in all probability consists essentially of a solution of hydrazine monosulfate in anhydrous hydrazine. The presence of the ammonia may perhaps be explained as a result of the solubility of the gas in the hydrazine. In order to test the first of these statements a number of qualitative experiments upon the behavior of hydrazine monosulfate and hydrazine disulfate toward anhydrous hydrazine were performed. Hydrazine monosulfate was found to be very soluble, and hydrazine disulfate was found to react immediately with the hydrazine, with liberation of considerable heat, and undoubtedly with formation of the monosulfate, which then went into solution. For example, when 5 grams of the disulfate were added to 2 cc. of anhydrous hydrazine, the temperature of the mass quickly rose to 95°, and very nearly all of the solid ultimately went into solution.

By repeated or continuous treatment of hydrazine monosulfate with ammonia gas it is very probable that yields of free hydrazine much larger than those recorded in the two preliminary experiments could be obtained. Further work on the ammonolysis of hydrazine salts by the action of ammonia at ordinary temperatures and at various pressures is projected, and will be made the subject of a future communication.

Behavior of Hydrazine Dioxalate in Liquid Ammonia.—The hydrazine dioxalate used in these experiments was prepared and analyzed in this laboratory by Dr. J. W. Turrentine.[1] A sample of this substance weighing 6.6634 grams was placed in the extraction thimble and was subjected to the action of liquid ammonia in accordance with the general procedure outlined in an earlier paragraph. After the ammonia had been expelled from the liquid extract as completely as possible at room temperature, the residual liquid was found by analysis to contain 86.8 per cent. N_2H_4, and 0.15 per cent. ammonia. It was not found possible to detect the presence of any oxalic acid in an aqueous solution of the extract.

The solid residue in the extraction thimble was tested for hydrazine by means of Fehling's solution, with negative results. The percentages of oxalic acid and ammonia were found by analysis to be 73.3 and 27.4 per cent. respectively (theory, $H_2C_2O_4$ in $(NH_4)_2C_2O_4$, 72.5 per cent.; NH_3, 27.5 per cent.).

From these results it is apparent that hydrazine dioxalate undergoes ammonolysis when treated with liquid ammonia, with formation of free hydrazine and ammonium oxalate.

Behavior of Hydrazine Diselenate in Liquid Ammonia.—The hydrazine diselenate was prepared by the method of Rimini and Malagnini.[2] A

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[1] THIS JOURNAL, 32, 579–88 (1910).

[2] *Gazz. chim. ital.*, 37, I, 261–6 (1907).

sample of 93.6 per cent. hydrazine hydrate was diluted with water until a 50 per cent. solution of the hydrate was obtained, to which four volumes of alcohol were then added. Two volumes of alcohol were added to a sample of pure selenic acid weighing 10.31 grams. The two solutions were cooled to 0° and were then mixed. A white precipitate of hydrazine diselenate was formed, which was removed by filtration, was thoroughly washed with absolute alcohol and ether and was finally placed in a desiccator over metallic sodium. This product, however, almost immediately assumed a pink color which became very conspicuous after the material had stood overnight, owing to its partial decomposition with the formation of free selenium. A fresh sample was consequently prepared by the same method with the added precaution of cooling the two solutions with the aid of a freezing mixture.

A sample of the perfectly white product weighing 2.6094 grams was immediately transferred to the extraction thimble and was subjected to the action of liquid ammonia. The liquid extract was found to contain 66.5 per cent. of hydrazine and no appreciable amount of ammonia. The white solid residue in the extraction thimble was analyzed with results as follows: NH_3, 20.87 per cent.; H_2SeO_4, 80.9 per cent.; theory for NH_3 in $(NH_4)_2SeO_4$, 19.0 per cent.; for H_2SeO_4,[1] 81.0 per cent. These results show that hydrazine diselenate when treated with liquid ammonia is ammonolyzed with formation of free hydrazine and ammonium selenate.

Behavior of Hydrazine Monophosphate in Liquid Ammonia.—The hydrazine monophosphate was prepared according to the method of Sabanyeev[2] by neutralizing an aqueous solution of hydrazine hydrate containing 10 grams with a solution of phosphoric acid, using methyl orange as indicator. The resulting solution was evaporated over the water bath to a syrupy consistency, and was then cooled and stirred until crystallization took place. After the crystals had stood for a short time in the desiccator over metallic sodium, they were found by analysis to contain 25.2 per cent. N_2H_4 and 73.0 per cent. H_3PO_4. Theory for N_2H_4 in $N_2H_4.H_3PO_4$, 24.6 per cent.; for H_3PO_4, 75.4 per cent. After the substance had remained in the desiccator for four days analysis showed 25.3 per cent. N_2H_4 and 73.7 per cent. H_3PO_4.

A sample of hydrazine monophosphate weighing 9.1287 grams was subjected to the action of liquid ammonia in the usual way. No indication of the liberation of hydrazine was obtained. The receiver was thoroughly rinsed with water at the conclusion of the experiment but the liquid gave no test for hydrazine when treated with Fehling's solution.

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[1] In determining the selenic acid, the method outlined in Olsen's "Quantitative Chemical Analysis," 1908, page 105, was employed.

[2] *Z. anorg. Chem.*, 17, 480–93 (1898), page 488.

The contents of the extraction thimble were found to have undergone an appreciable increase in weight during the experiment. On analysis this residue was found to contain 23.15 per cent. N_2H_4, 67.2 per cent. H_3PO_4 and 7.23 per cent. NH_3.

Behavior of Hydrazine Diphosphate in Liquid Ammonia.—The hydrazine diphosphate was prepared by the method of Sabanyeev.[1] Fifty cc. of a solution of phosphoric acid containing 0.1494 gram per cc. were diluted with a solution of hydrazine hydrate, using methyl orange as indicator. After the end-point had been reached, 50 cc. more of the acid were added and the resulting solution was evaporated over the water bath. The syrupy liquid thus obtained was cooled by means of a freezing mixture and was stirred until crystallization took place. The crystallin substance was pulverized and was dried in a vacuum desiccator over metallic sodium. On analysis the following results were obtained: N_2H_4, 14.09 per cent.; H_3PO_4, 86.2 per cent. Theory for N_2H_4 in $N_2H_4.2H_3PO_4$, 14.05 per cent.; for H_3PO_4, 85.95 per cent.

A sample of hydrazine diphosphate weighing 7.9588 grams was treated with liquid ammonia as in the preceding experiments. The solution obtained by rinsing out the receiver with water at the close of the experiment gave no test for hydrazine. From this fact it is apparent that hydrazine diphosphate does not undergo ammonolysis under the conditions of the present experiment.

The solid residue in the extraction thimble was found to have undergone an appreciable increase in weight during the experiment. On analysis the substance was found to have the following composition: N_2H_4 13.96 per cent., H_3PO_4 84.7 per cent., NH_3 1.41 per cent.

In a duplicate experiment 13.3311 grams of hydrazine diphosphate were treated with liquid ammonia with results entirely similar to those just described.

The failure of hydrazine monophosphate and hydrazine diphosphate to decompose when treated with liquid ammonia with formation of ammonium phosphate and free hydrazine seems to point towards the supposition that these salts may be less soluble in liquid ammonia than is ammonium phosphate.

Summary.

In the present investigation it has been shown:

1. That hydrazine monosulfate, hydrazine dioxalate, and hydrazine diselenate, like hydrazine disulfate, decompose in liquid ammonia with formation of free hydrazine and the ammonium salt of the acid previously combined with the hydrazine.

2. That hydrazine monophosphate and hydrazine diphosphate do not decompose when treated with liquid ammonia.

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[1] *Loc. cit.*, p. 489.

3. That hydrazine monosulfate when treated with ammonia gas at room temperature undergoes ammonolysis to some extent, and that a liquid consisting essentially of a solution of hydrazine monosulfate in free hydrazine may be separated from the mixture by centrifugal action.

These facts may serve as the basis for a new method for the preparation of free hydrazine from its salts. Further work upon this phase of the investigation is projected.

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BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. III. ACTION OF AMMONIUM TRINITRIDE UPON CERTAIN METALS.

BY A. W. BROWNE AND A. E. HOULEHAN.

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In his epoch-making work upon reactions in liquid ammonia, E. C. Franklin[1] makes the statement that "many acids, both oxygen acids and halogen acids, as a matter of course in the form of their ammonium salts, dissolve freely in ammonia to form solutions which exhibit certain truly acid properties, as follows: First, they discharge the color of an ammonia solution of phenolphthalein, which has been rendered alkaline by the addition of a small quantity of a base. Second, solutions of ammonium salts in ammonia dissolve sodium, potassium, calcium and magnesium with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation,

$$M + NH_4X = MX + NH_3 + H.$$

Third, many metallic oxides and certain basic salts, all members of both classes of compounds being insoluble in ammonia, dissolve in solutions of ammonium salts."

The present investigation has been undertaken with a view to ascertaining whether or not ammonium trinitride behaves in liquid ammonia solution toward metals in accordance with the generalization made by Franklin. In the prosecution of this work an incidental study of the following topics has been found necessary: (1) Methods of preparing pure ammonium trinitride, (2) method for conveniently carrying out at —33° the reaction between weighed amounts of a metal and of ammonium trinitride in liquid ammonia, and under such conditions that the gas evolved may be collected, measured, and analyzed without difficulty, and that the solid reaction product may be readily weighed and analyzed.

Preparation of Ammonium Trinitride.—Ammonium trinitride was first prepared by Curtius,[2] who saturated an alcoholic solution of diazohippuramide with gaseous ammonia, and precipitated the pure ammonium

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[1] THIS JOURNAL, 27, 820–51 (1905), page 822.

[2] *Ber.*, 23, 3023–33 (1890), page 3033.