BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. I. AMMONOLYSIS OF HYDRAZINE SULFATE.

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In 1899 Goldschmidt and Salcher[1] studied the distribution of hydrochloric, hydrobromic, nitric, and orthobenzoic acids between certain tertiary bases and aniline, which was used as the solvent. The process by which these bases were to a certain extent liberated from their salts by the action of the solvent was designated by the authors, in recognition of a certain analogy with hydrolysis, as *aminolysis*.

In 1905 Franklin[2] brought to light the remarkable analogy that exists between the reactions involved in ordinary hydrolysis and the reactions in which ammonia effects the decomposition of various substances with formation of amides, imides, nitrides, or ammono-basic salts. In accordance with this analogy the breaking up of certain substances by the action of ammonia was appropriately regarded as a process of *ammonolysis*.

Having felt the impetus given by the work of Franklin and his associates to research in the field of non-aqueous solvents, the authors have planned a series of investigations upon the behavior of the hydronitrogens and their derivatives in liquid ammonia. Hydrazine, or hydrogen dinitride, as it might be called, obviously bears a relation to ammonia empirically similar to that borne by hydrogen peroxide to water,[3] while hydronitric acid, or hydrogen trinitride, may in a sense be regarded as analogous with the hypothetical higher oxides of hydrogen[4] concerning which there has been some recent discussion. In case the hydrogen pernitrides in liquid ammonia possess properties similar to those of hydrogen peroxide in aqueous solution it is to be expected that under proper conditions they should act in a sense as oxidizing agents, or more strictly as *nitridizing* agents. One ultimate purpose of the research has therefore been to study the phenomena of ammono-oxidation, or *nitridation*. Another purpose has been to investigate the phase rule relations, especially the pressure-concentration curves, in the two component systems (1) ammonia, hydrazine, (2) ammonia, hydronitric acid, (3) hydrazine, hydronitric acid, and in the three-component system ammonia, hydrazine, hydronitric

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[1] *Z. physik. Chem.*, 29, 89–118 (1899); see also Goldschmidt, *Ann.*, 351, 108–33 (1907).

[2] This Journal, 27, 820–51 (1905), page 826.

[3] See Remsen, *Inorganic Chemistry*, 1899, 276. Brühl, *Ber.*, 30, 162–72 (1897). Angeli, *Atti accad. Lincei*, [5] 19, II, 29–36 or 94–101 (1910).

[4] Thénard, *Compt. rend.*, 75, 177 (1872). Berthelot, *Ibid.*, 90, 656–60 (1880). Bach, *Ber.*, 33, 1506–17, 3111–8 (1900); 34, 3851–5 (1901); 35, 158–60 (1902). Armstrong, *Proc. Chem. Soc.*, 16, 134 (1900). Baeyer and Villiger, *Ber.*, 33, 2488–97 (1900). Ramsay, *J. Chem. Soc.*, 79, 1324–6 (1901). Bach, *Ber.*, 35, 3424–5 (1902). Clover, *Am. Chem. J.*, 29, 463–74 (1903).

acid. The first few articles of the series will be of an introductory character.

It seemed advizable at the outset to study the behavior of hydrazine sulfate, the compound of hydrazine most readily obtainable in a pure condition, in liquid ammonia. A vacuum beaker was provided with a tightly fitting cork, through which passed a large test tube, an inlet tube for liquid ammonia, and an outlet for ammonia gas. The test tube was closed with a cork provided with inlet and outlet tubes for ammonia, with a tube through which portions of the liquid could be siphoned off at will into sample tubes, and with platinized platinum electrodes for use in determining the conductivity of the solution obtained. The beaker, which served merely as a jacket for the test tube, was filled with crude liquid ammonia drawn directly from the steel container, and the test tube was partly filled with liquid ammonia obtained by condensing a current of the gas which had been dried over metallic sodium. A sample of recrystallized hydrazine sulfate (Raschig) weighing 0.73 gram was introduced into the test tube. The solid was soon observed to increase considerably in bulk, undergoing a sort of slaking process similar to that noted by Gore[1] and by Franklin[2] when the chlorides of magnesium, calcium, strontium, barium, zinc, cadmium, manganese, cobalt, nickel, and lead were treated with liquid ammonia. That considerable heat was evolved during this slaking process was evidenced by the rapid boiling, not only of the ammonia in the test tube, but also of that in the jacket.

The phenomena noted by Franklin in connection with the metallic chlorides were explained by him on the ground that in all probability the already known addition products of the respective salts with ammonia were obtained. In the case of calcium chloride this was demonstrated to be correct. It was at first supposed by the authors that this explanation would also hold true in the case of hydrazine sulfate. This idea seemed to be borne out by the fact that the specific conductivity of the ammonia as determined by the method of Kohlrausch[3] underwent but comparatively little increase during the progress of the experiment. After the reaction had gone to completion and the finely divided solid product had settled, several samples of from 3 to 5 cc. of the supernatant liquid were finally siphoned off into weighed test tubes, each of which was provided with a tightly fitting cork and a long glass tube with a crook at the end, to prevent diffusion of atmospheric air into the test tube during the evaporation of the liquid. After the liquid ammonia had completely evaporated,

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[1] *Proc. Roy. Soc.*, **21**, 140 (1873).

[2] *Am. Chem. J.*, **20**, 820–36 (1898), page 822.

[3] *Wied. Ann.*, **64**, 417 (1898). See also *Das Leitvermögen der Electrolyte*, page 1 (1898).

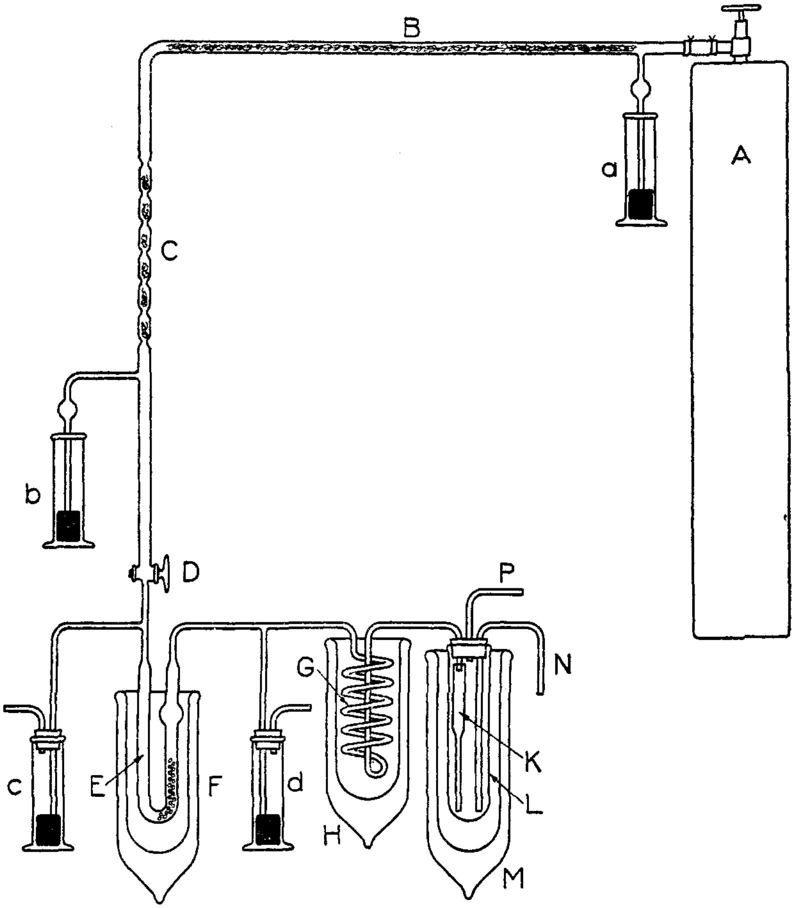
and the test tubes had warmed up to room temperature, small volumes of a residual liquid were found in each case. In blank experiments, previously carried out under similar conditions with liquid ammonia to which no hydrazine sulfate had been added, no ponderable residues were obtained.

The liquid residues were found by analysis to consist chiefly of free hydrazine. Small amounts of sulfuric acid were also found, no doubt because of the carrying over of small amounts of the finely divided white solid during the process of siphoning the liquid. The solid residue in the large test tube in which the reaction had taken place continued to give off ammonia for some time after the liquid ammonia had disappeared. After the evolution of ammonia had ceased the shrunken mass of solid was by analysis shown to be ammonium sulfate containing a negligible amount of hydrazine. The solid as it appeared at first after the evaporation of the supernatant liquid was in all probability an ammonated ammonium sulfate, which underwent gradual deammonation as it warmed up to room temperature.

In order to subject the reaction to further investigation the apparatus shown in the accompanying sketch was constructed. The steel cylinder *A* served as the source of ammonia, which was led first through the tube *B*, about one meter long, filled with sodium wire. It then passed through *C*, which contained ignited asbestos, and through the stopcock *D* into the U-tube *E*, which was partly filled with glass beads. After the air had been displaced from the entire apparatus at the beginning of an experiment, the vacuum beaker *F*, filled with solid carbon dioxide and alcohol, was cautiously brought up around *E*, and sufficient ammonia to cover the beads with liquid was condensed. During the progress of the experiment the height of *F* was so adjusted as to keep the amount of liquid in *E* as nearly as possible constant.

After bubbling through the liquid ammonia in *E* the gas passed over into the condenser *G*, which was refrigerated by means of solid carbon dioxide and alcohol in the vacuum beaker *H*, where it was entirely liquefied. By suitable adjustment of the stopcock *D* it was found possible to deliver a steady drip or stream of liquid ammonia into the funnel tube *K*. Into this tube was placed, at the beginning of each experiment, a closely fitting extraction thimble containing a weighed amount of hydrazine sulfate. The delivery tube from the condenser passed through one of the three openings in a cork which was fitted into the top of a large reaction tube *L*. Through the other openings in the cork passed *P*, the outlet for gaseous ammonia, and *N*, the delivery tube for the liquid extract. Until ready for use the end of this tube was kept covered in order to prevent the introduction of air or of moisture into the apparatus. The reaction tube *L* was kept at the proper temperature by means of the vacuum beaker *M*, which was filled with solid carbon dioxide and alcohol.

The mercury traps *a*, *b*, *c* and *d*, served as safety outlets. Various accessory devices have been omitted from the sketch for the sake of clearness.



Three experiments were performed in this apparatus, using weighed amounts of pure hydrazine sulfate. The sample was in each case introduced into the extraction thimble in the funnel tube *K*, and ammonia was allowed to drip upon it until the reaction, so far as could be seen, had proceeded to completion. By this time a considerable quantity of the liquid ammonia had accumulated in the lower part of *L*. No difficulty whatever was experienced in effecting a perfect separation of the finely divided white solid from the liquid. No sulfuric acid whatever was found in the extract. It was not found possible to effect so nearly quantitative a decomposition of the hydrazine sulfate in this apparatus as in the device in which the preliminary work was carried out, for the simple reason that in the preliminary work the "wet" method was employed and in the subsequent experiments the "dry" method. When the wet method was used, that is, when the hydrazine sulfate was directly introduced into a relatively large amount of liquid ammonia, stirring could be readily effected, and there was but little chance that any portion of the salt could escape the action of the ammonia. On the other hand, when the ammonia was slowly dropped upon a relatively large amount of hydrazine sulfate, occlusion of the unchanged salt within a protective coating of ammonated ammonium sulfate took place to some extent.

When a sufficient quantity of the liquid ammonia extract had been collected, samples were forced out into weighed tubes, as in the preliminary experiment. After the liquid ammonia had evaporated and the tubes had come to room temperature they were again weighed, and the residues, which possessed an odor similar to that of anhydrous hydrazine, were subjected to analysis. In the first experiment, a sample of the liquid residue weighing 0.1632 gram was found to contain 0.1364 gram, or 83.6 per cent. of hydrazine, and 0.0032 gram, or 1.96 per cent. of ammonia. In the second, a sample weighing 0.2411 gram contained 0.1599 gram, or 66.3 per cent. of hydrazine, and 0.00374 gram, or 1.55 per cent. of ammonia. In the third, a sample weighing 0.4042 gram contained 0.3341 gram, or 82.7 per cent. of hydrazine, and 0.00837 gram, or 2.07 per cent. of ammonia.

The rather bulky solid residues in the extraction thimbles were found to shrink in a curious way upon exposure to air, even after the liquid ammonia had completely evaporated from them, and they had warmed up nearly to room temperature. This shrinking process was always accompanied by an evolution of ammonia, and seems to indicate that ammonium sulfate under the conditions of the experiments undergoes ammonation, with formation of one or more addition products which are unstable at ordinary temperature and pressure.

Action of Ammonia Gas upon Hydrazine Sulfate.—Samples of hydrazine sulfate weighing 0.2616, 0.2427 and 0.1848 gram were exposed in glass stoppered U-tubes to a current of ammonia gas for several hours at a temperature of about 22°. After two hours the samples had gained respectively 0.0131, 0.0106 and 0.0116 gram; after five and one-half hours, 0.0291, 0.0187 and 0.0140 gram; after twelve hours, 0.0329, 0.0450 and 0.0170 gram. Small drops of a colorless, viscous liquid, probably a solution of hydrazine monosulfate in free hydrazine, appeared on the salt and on the walls of the tubes, but the reaction did not progress to an end, owing no doubt to the relative smallness of the active mass of ammonia. At higher pressures the equilibrium would undoubtedly be displaced in the direction of a higher concentration of free hydrazine.

Action of Liquid Ammonia upon Ammonium Sulfate.—In order to as-certain in a preliminary way whether ammonium sulfate unites with liquid ammonia under the conditions of these experiments, weighed samples of the salt were treated with liquid ammonia in glass stoppered U-tubes. These tubes were cooled with solid carbon dioxide to about —72°, and the liquid ammonia was permitted to stand in contact with the solid for some time. A slight swelling of the salt was noted, and a tendency for it to cake in the bottom of the tubes. Dry air was now caused to pass slowly through the tubes, which were still immersed beneath the refrigerant, until the escaping current was shown, with the aid of Nessler's solution, to be free from ammonia. The tubes were then closed, permitted to warm to room temperature, and were weighed. In the first tube the sample, which weighed 0.3375 gram at the outset, was found to have gained 0.0407 gram. In the second, the sample, which originally weighed 0.2853 gram, was found to have gained 0.0505 gram. The presence of an excess of ammonia in the samples was also directly shown by subsequent analysis. It is very probable therefore that the ammonium sulfate formed by the action of ammonia upon hydrazine sulfate forms an addition product with ammonia under the conditions of the experiments. No attempt will be made, however, to describe the composition of this product until certain pressure-concentration isotherms in the system ammonia, ammonium sulfate have been investigated. At ordinary temperatures and under a pressure of one atmosphere of ammonia gas the salt does not absorb appreciable amounts of the gas.

Discussion of Results.—The decomposition of hydrazine sulfate by the action of liquid ammonia may be explained with the aid of the equation

$$N_2H_4.H_2SO_4 + 2NH_3 \rightleftarrows (NH_4)_2SO_4 + N_2H_4.$$

With ammonia as solvent, the active mass of that component is, of course, very large, and this in conjunction with the insolubility of ammonium sulfate in liquid ammonia[1] insures, under favorable mechanical conditions, the quantitative decomposition of the hydrazine salt. Lobry de Bruyn[2] has shown, on the other hand, that free hydrazine can displace ammonia from ammonium salts.

It is, of course, conceivable that the decomposition of hydrazine sulfate by the action of ammonia might involve a dissociation of the ammonia molecule, with initial formation of hydrazine amide, or some other compound of hydrazine with ammonia, and of sulfuric acid. Certain preliminary experiments performed in connection with the present research indicate that at —33° free hydrazine does hold a certain amount of ammonia rather tenaciously, but whether this is held in physical solution or in chemical combination cannot be stated until certain isotherms in the pressure-concentration diagram of the system ammonia, hydrazine

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[1] Franklin and Kraus, *Am. Chem. J.*, **20**, 820–36 (1898), page 823.

[2] *Rec. trav. chim.*, **15**, 174–84 (1896), page 179.

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.

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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, 820–[illegible]1 (1905), page 826.