[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNELL UNIVERSITY.]

ANHYDROUS HYDRAZINE. IV. CHEMICAL REACTIONS IN ANHYDROUS HYDRAZINE.[1]

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Considerable attention has been given to the study of chemical reactions in nonaqueous inorganic solvents by a number of investigators. The most important work as related to the present investigation was that carried out by Franklin and his associates upon liquid ammonia.[2] The behavior of hydrazine sulfate in liquid ammonia has been studied by Browne, Welsh, and Houlehan,[3] and by Friedrichs[4] who showed that ammonolysis took place with formation of free hydrazine and ammonium sulfate.

That sulfur dioxide will act as a solvent and also as a medium in which chemical action may take place has been shown by Walden[5] and his associates, and also by Franklin.[6] Investigations of reactions in organic solvents have been carried on by Naumann,[7] Kahlenberg,[8] Kahlenberg and Schmidt,[9] Matthews,[10] Gates,[11] and Barneby.[12]

Franklin has shown that the acids of the ammonia system are the acid amides and imides, including the amides and imides of the nonmetallic elements. The bases are the metallic amides and imides and the salts the metallic derivatives of the amides and imides. In an analogous man-

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[1] For the previous articles of this series see Hale and Shetterly, THIS JOURNAL, **33**, 1071–6 (1911); Welsh, *Ibid.*, **37**, 497–508 (1915); Welsh and Broderson, *Ibid.*, **37**, 816. The experimental work of this article was completed in June, 1913.

[2] See Franklin and Kraus, *Am. Chem. J.*, **20**, 820, 836 (1898); **21**, 14 (1899); **23**, 277 (1900); THIS JOURNAL, **27**, 191 (1905); *J. Phys. Chem.*, **11**, 553 (1907); Franklin and Stafford, *Am. Chem. J.*, **28**, 83 (1902); Franklin and Cady, THIS JOURNAL, **26**, 499 (1904); Franklin, THIS JOURNAL, **27**, 820–51 (1905); **29**, 35 (1907); *Z. physik. Chem.*, **69**, 272 (1909); *Am. Chem. J.*, **47**, 285, 361 (1912); *Orig. Comm. 8th Intern. Cong. Appl. Chem.*, **2**, 103; **6**, 119–30, 1410 (1912); Franklin and Hine, THIS JOURNAL, **34**, 1497, 1501 (1912). See also Browne and Holmes, THIS JOURNAL, **35**, 672–81 (1913); Kraus and Bray, *Ibid.*, **35**, 1315–1434 (1913); Cady and Lichtenwalter, *Ibid.*, **35**, 1434–40 (1913); Kraus, *Ibid.*, **36**, 864–77 (1914).

[3] THIS JOURNAL, **33**, 1728, 1734 (1911).

[4] *Ibid.*, **35**, 244 (1913); *Z. angew. Chem.*, **26**, 201 (1913).

[5] *Ber.*, **32**, 2865 (1899); *Z. anorg. Chem.*, **25**, 209 (1900); **29**, 371 (1902); Walden and Centnerzwer, *Ibid.*, **30**, 145 (1902); *Z. physik. Chem.*, **39**, 513 (1902); Centnerzwer and Teleton, *Z. Elektrochem.*, **9**, 799–802 (1903); *J. russ. phys. chem. Ges.*, **36**, 62–71 (1904).

[6] *J. Phys. Chem.*, **15**, 675–97 (1912).

[7] *Ber.*, **32**, 999 (1899).

[8] *J. Phys. Chem.*, **6**, 6 (1902); *Z. physik. Chem.*, **46**, 63 (1903).

[9] *J. Phys. Chem.*, **6**, 447 (1902).

[10] *Ibid.*, **9**, 641 (1905).

[11] *Ibid.*, **15**, 97 (1911).

[12] THIS JOURNAL, **34**, 1174–89 (1912).

ner, the acid hydrazides, the metallic hydrazides and the metallic derivatives of the acid hydrazides may be considered, respectively, as acids, bases, and salts in the hydrazine system. The nitrides and tetrahydrazides may be considered as bearing the same relation to the ammonia and the hydrazine system, respectively, that the oxides bear to the aquo system of Lavoisier. Furthermore that the hydrazine salts of aquo acids, soluble in anhydrous hydrazine, will act as acids is indicated by the fact that they will discharge the color of phenolphthalein, and will dissolve certain metals that are insoluble in anhydrous hydrazine itself, with liberation of hydrogen. This is similar to the action of analogous ammonium salts in liquid ammonia.

The present paper is a preliminary report on the hydrazine system of acids, bases and salts, and contains a study of the action in anhydrous hydrazine solutions of: (*a*) hydrazine sulfide upon cadmium iodide; (*b*) hydrazine sulfide upon zinc chloride; (*c*) sodium hydrazide upon zinc chloride; (*d*) metallic sodium upon certain salts; (*e*) certain metals upon hydrazine sulfate; (*f*) metallic sodium and sodium hydrazide upon hydrazine chloride.

Action of Hydrazine Sulfide upon Cadmium Iodide in Anhydrous Hydrazine.—Since cadmium iodide is appreciably soluble and cadmium sulfide insoluble in anhydrous hydrazine, it could be reasonably supposed that hydrazine sulfide would precipitate cadmium sulfide from a solution of cadmium iodide in anhydrous hydrazine in accordance with either of the following equations:

$$CdI_2 + (N_2H_4)_2.H_2S = CdS + 2N_2H_4.HI$$

or

$$CdI_2 + N_2H_4.H_2S = CdS + N_2H_4.2HI$$

Ephraim and Peiotrowski[1] state that either $(N_2H_4)_2.H_2S$ or $N_2H_4.H_2S$ is formed when sulfur is dissolved in anhydrous hydrazine. The solution of hydrazine sulfide used in this experiment was prepared, therefore, by dissolving sufficient sulfur in anhydrous hydrazine to form a deep reddish yellow solution. A solution of cadmium iodide was prepared in the form of apparatus used in studying solubilities in anhydrous hydrazine.[2] The hydrazine sulfide solution was added to this, and a yellow precipitate of cadmium sulfide was formed, which on analysis was found to contain cadmium 74.6%, sulfur 22.8%. Theory for CdS, cadmium, 77.79%; sulphur, 22.21%.

In view of the fact that solutions of hydrazine sulfide are highly colored it was considered possible to titrate unknown solutions of such salts as zinc chloride and cadmium iodide, with standard solutions of the sulfide, using the disappearance of the color to indicate the end point of the

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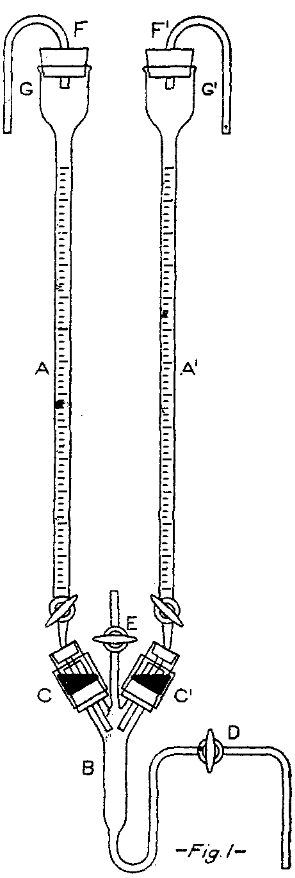
[1] *Ber.*, 44, 386 (1911); see also de Bruyn, *Rec. trav. chim.*, 13, 433 (1894).

[2] See the preceding article.

reaction. In order to test the method in a preliminary way, the apparatus shown in Fig. 1 was devised. It consists of the two ten cubic centimeter burets *A* and *A'* with long curved tips reaching into the vessel *B*. The joints *C* and *C'* are made tight by means of mercury seals. The vessel *B* is connected with a source of pure, dry nitrogen which could be bubbled through the liquid contained in *B* at any desired speed by regulating the stopcock *D*, and then be allowed to escape into the atmosphere through stopcock, *E*. Oxidation of the solutions contained in the burets *A* and *A'* was prevented by keeping them in an atmosphere of nitrogen introduced through the tubes *F* and *F'*, held in place by the corks *G* and *G'*, which were completely encased in tin foil.

Solutions of hydrazine sulfide and cadmium iodide were prepared by dissolving weighed amounts of sulfur and cadmium iodide, respectively, in a known volume of anhydrous hydrazine. The hydrazine sulfide contained 0.039 g. of sulfur per cc. and the cadmium iodide solution 0.27 g. cadmium iodide per cc. A measured amount of the hydrazine sulfide solution was introduced into *B*, nitrogen was slowly bubbled through this in order to provide stirring, and cadmium iodide solution was slowly run in until the yellow color of the sulfur solution disappeared. It was found that 3.3 cc. of cadmium iodide solution completely discharged the yellow color from 2 cc. of the hydrazine sulfide solution. The calculated amount of cadmium iodide solution for 2 cc. of hydrazine solution was 3.2 cc.



-Fig. 1-

Action of Hydrazine Sulfide upon Zinc Chloride in Anhydrous Hydrazine.—The apparatus employed and the procedure were the same as were described in the preceding experiments. When a solution of zinc chloride was added to a solution of hydrazine sulfide a white precipitate of ZnS was obtained, probably in accordance with either of the following equations:

$$ZnCl_2 + (N_2H_4)_2H_2S = ZnS + 2N_2H_4.HCl \quad \text{or}$$

$$ZnCl_2 + (N_2H_4).H_2S = ZnS + N_2H_4.2HCl$$

The precipitate was analyzed and was found to contain zinc 60.7%, and sulphur 28.3%. Theory for ZnS, zinc 67.1%, sulphur 32.9%.

A solution of hydrazine sulfide containing 0.039 g. sulfur per cc. was titrated against a solution of zinc chloride containing 0.098 g. per cc. It was found that 3.3 cc. of the zinc chloride solution would discharge the color from 1.9 cc. of the sulfide solution. The calculated amount of zinc chloride solution for 1.9 cc. sulfide solution is 3.26 cc.

Action of Sodium Hydrazide on Zinc Chloride in Anhydrous Hydrazine.—Ebler and Krause[1] prepared zinc hydrazide by the action of zinc ethyl or zinc diamide on a suspension of hydrazine in anhydrous ether, and suggest these methods as generally applicable for the preparation of metallic hydrazides. It was thought that zinc hydrazide might be precipitated in hydrazine by the action of sodium hydrazide on zinc chloride in accordance with the following equation:

$$ZnCl_2 + 2NaN_2H_3 = Zn(N_2H_3)_2 + 2NaCl$$

which would be analogous to the precipitation of zinc hydroxide by sodium hydroxide in aqueous solution. A preliminary study of this reaction was made in the apparatus described in Fig. 1. Approximately equivalent solutions of sodium hydrazide and zinc chloride were employed. The yellow color of sodium hydrazide solution was immediately destroyed on coming into contact with zinc chloride solution and a white flocculent precipitate, probably zinc hydrazide, was immediately formed. This precipitate seemed to be insoluble in an excess of sodium hydrazide but was dissolved in an excess of zinc chloride solution. Satisfactory analyses of the product could not be obtained both because of the small amount of the product and because of the difficulty in removing the last trace of hydrazine without decomposition. This solubility of zinc hydrazide in a hydrazine solution of zinc chloride is analogous to the solubility of zinc hydroxide in a water solution of zinc chloride.

Action of Metallic Sodium on Solutions of Certain Salts in Anhydrous Hydrazine.—A preliminary study was made of the action of metallic sodium upon solutions of cadmium iodide, zinc chloride, magnesium chloride, calcium chloride, barium chloride, and ferric sulfate in anhydrous hydrazine.

About 10 cc. of a saturated solution of cadmium iodide in a solubility tube was treated successively with small amounts of metallic sodium. The action proceeded fairly rapidly with the formation of a finely divided black precipitate, undoubtedly metallic cadmium. In contact with water the precipitate became superficially coated with a white material, probably cadmium hydroxide, which, when treated with a small amount of dilute hydrochloric acid, was dissolved, leaving at first the black finely divided cadmium which finally reacted with the acid with evolution of gas. The black precipitate oxidized very readily in the air, and even during the process of drying the moist product at 150° in an atmosphere of hydrogen,

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[1] *Ber.*, 43, 1690–5 (1910).

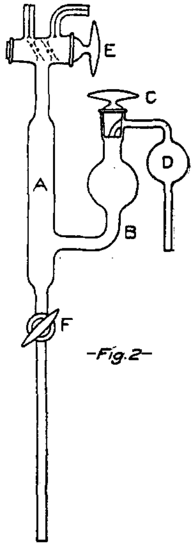
oxidation took place with formation of small amounts of yellow and green oxides.

When a solution of zinc chloride was treated with metallic sodium a finely divided black precipitate was produced which was very easily oxidized in the presence of air or moisture. The material, after being dried in hydrogen at 200°, was decidedly metallic and showed traces of zinc oxide. No satisfactory analyses could be made because of the small amount of precipitate obtained, but the substance was undoubtedly metallic zinc in finely divided form.

When a solution of ferric sulfate was treated with metallic sodium, a black precipitate was formed which, after being washed with alcohol and water, was found to be soluble in hydrochloric acid with evolution of gas. Qualitative tests of this solution showed the presence of iron and the absence of hydrazine and sulfuric acid, showing that the precipitate was in all probability metallic iron.

When saturated solutions of the chlorides of magnesium, calcium or barium were treated with metallic sodium, chemical action took place and ceased when the sodium became coated with a white material. When this was removed by scraping with a glass rod, the action again commenced and continued until the metal was again coated. Since metallic magnesium calcium and barium in the finely divided state react with anhydrous hydrazine in the presence of hydrazine salts, these metals would not be expected to precipitate as do cadmium, zinc and iron. The white coating on the sodium was probably sodium chloride.

Action of Certain Metals upon a Solution of Hydrazine Sulfate in Anhydrous Hydrazine.—The behavior of zinc, copper, tin, aluminum, magnesium, calcium, and lithium toward anhydrous hydrazine and toward solutions of hydrazine sulfate in anhydrous hydrazine was studied with the apparatus shown in Fig. 2. This consisted of the tube *A* of about 10 cc. capacity with the side arm *B*, which was formed with a bulb of slightly greater capacity than tube *A*. The glass stopper *C* could be removed for the purpose of introducing solid material or of connecting the tube *B* with the tube *D*, which was connected with a mercury trap, not shown in the sketch. Communication could be established between *A* and either a Hempel buret or a suction apparatus by means of a two-way stopcock *E*. The stopcock *F* served for the introduction of hydrazine by means of suction or for the withdrawal of a sample during the course of the experiments.



-Fig. 2-

The behavior of zinc upon anhydrous hydrazine was studied in the following manner: the apparatus was evacuated, tube *A* was filled with anhydrous hydrazine drawn in through the stopcock *F*, stopcock *C* was then withdrawn and about 0.02 g. of zinc was introduced through the side arm *B*. Stopcock *C* was then turned to make connection with *D*. No measurable amount of gas was evolved. About 0.06 g. of hydrazine sulfate was introduced through *C* but no action was observed to take place. Even in contact with small pieces of platinum foil the zinc showed no tendency to dissolve. Metallic copper, tin, and aluminum, respectively, were similarly introduced, but were found to be without action upon either the hydrazine or the solution of hydrazine sulfate in hydrazine. Magnesium and calcium showed no tendency to dissolve in hydrazine or to react with it, while lithium slowly went into solution with evolution of gas. On the addition of hydrazine sulfate, however, gas was rapidly evolved in each case until the metal became coated with a white deposit which in all probability consisted of the sulfate. This coating could be partially removed by shaking, whereupon gas was again evolved until the metal became recoated. Shaking was continued from time to time until no further evolution of gas could be induced. The gases were analyzed in each case and were found to consist solely of hydrogen and nitrogen, the former in rather larger amounts than the latter. The presence of nitrogen in the gases evolved from hydrazine, when acted upon by certain metals, recalls the work of Turrentine and Moore[1] who have found that by the action of metallic copper upon hydronitric acid in aqueous solution nitrogen and ammonia were formed. Hydrazine under these conditions may therefore be considered to act virtually as an oxidizing or more strictly a nitridizing[2] agent. The reduction of hydrazine (hydrogen dinitride) with formation of ammonia and nitrogen would obviously be analogous to the reduction of hydrogen dioxide with the formation of water and oxygen. Magnesium was used both in the form of ribbon and powder. The action of the powder was much more rapid and complete than that of the ribbon. From the above results hydrazine sulfate can be regarded as acting as an acid in anhydrous hydrazine solution. This action is analogous to that of an ammonium salt in liquid ammonia.[3]

Action of Metallic Sodium and a Solution of Sodium Hydrazide upon Solutions of Hydrazine Chloride in Anhydrous Hydrazine.—Hydrazine monochloride was prepared according to the method described by Curtius and Schulz.[4]

The action of sodium upon a solution of hydrazine chloride was studied in one of the solubility tubes described in the preceding article. A strong

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[1] This Journal, 33, 382–4 (1912).

[2] See Browne and Welsh, This Journal, 33, 1728 (1911).

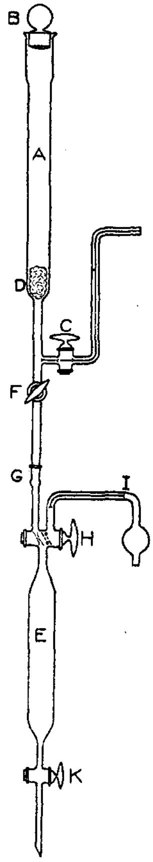
[3] Franklin, *loc. cit.*; see also Browne and Houlehan, This Journal, 33, 1734 (1911)

[4] *J. prakt. Chem.*, [2] 42, 520 (1890)

solution of hydrazine chloride was placed in the tube and metallic sodium was added in successive small quantities. The sodium floated on the surface of the solution and reacted slowly. A white crystalline precipitate was formed which, after it had accumulated in sufficient quantity, was filtered in a Gooch crucible, washed with 95% alcohol, dried, and heated to dull redness on platinum foil to remove any hydrazine chloride. This material was dissolved in a measured volume of water and aliquot portions were analyzed for sodium and chlorine. The sodium was determined as sodium sulfate and the chlorine was titrated with ammonium thiocyanate. The results of the analyses of the two samples were: Na (1) 39.12%, (2) 39.03%; Cl (1) 60.41%, (2) 60.03%. Theory for NaCl: Na 39.34%, Cl 60.66%.

The action of sodium hydrazide upon hydrazine chloride was next studied. In order to prepare and keep a sufficient amount of sodium hydrazide solution, the apparatus shown in Fig. 3 was devised. It consisted of a mixing tube, *A*, closed by the glass stopper *B*, and connected with a supply of pure dry nitrogen through the capillary tube and stopcock *C*. The glass wool shown at *D* served to filter out any solid material when the solution was passed into the storage tube *E* which was connected with *A* through the stopcock *F* and the ground joint *G*. *H* is a two-way stopcock connecting either with *G* or with the capillary tube and bulb *I*. Stopcock *K* served for the withdrawal of portions of sodium hydrazide solution.

Sodium hydrazide was prepared in the following manner: a quantity of hydrazine was introduced into *A*, after air had been displaced from the entire apparatus by means of nitrogen introduced through *C*. While nitrogen was allowed to bubble through the liquid in *A*, successive portions of metallic sodium were introduced by removing stopper *B* which was prevented from fitting tightly by means of a piece of fine platinum wire hung over the lip. After the sodium had completely dissolved, the storage tube *E* was evacuated and the sodium hydrazide solution was introduced by proper manipulation of stopcocks *F* and *H*. The storage tube was then separated from the rest of the apparatus, the end of tube *I* was allowed to dip below the surface of mercury contained in a vessel not shown in the sketch, and the stopcock *H* adjusted so as to permit the escape of any gas that might be formed in *E* through *I* without danger of introduction of air.



-Fig.3-

When solutions of sodium hydrazide and hydrazine chloride are mixed the yellow color of the sodium hydrazide is immediately discharged, provided that the hydrazine chloride is in excess. In order to obtain the sodium chloride, which did not precipitate from the rather dilute solutions employed, the resulting liquid was evaporated to dryness, and the residue was heated to drive off the excess of hydrazine chloride. Analysis of two samples of the solid residue gave the following results: Na (1) 39.53%, (2) 39.59%; Cl (1) 59.61%, (2) 60.15%. Theory for NaCl: Na 39.34%, Cl 60.66%.

The action of sodium and of sodium hydrazide upon hydrazine chloride in hydrazine solution may be expressed by means of the following equations:

$$Na + N_2H_4.HCl = NaCl + N_2H_4 + H$$

and

$$NaN_2H_3 + N_2H_4.HCl = NaCl + 2N_2H_4.$$

Summary.

In the present investigation it has been shown :

1. That cadmium and zinc may be precipitated as sulfides (or hydrazinated sulfides) by the action of hydrazine sulfide on salts of these metals soluble in anhydrous hydrazine. It was also shown that the yellow color of the hydrazine sulfide could be made to serve as indicator in the titration of cadmium and zinc salts.

2. That a hydrazide of zinc is probably precipitated when sodium hydrazide acts upon zinc chloride in anhydrous hydrazine.

3. That metallic sodium will precipitate the metals cadmium, zinc, and iron from solutions of these salts in anhydrous hydrazine and that magnesium, calcium, and barium are not precipitated.

4. That zinc, copper, tin, and aluminum do not react with anhydrous hydrazine; but that magnesium, calcium, and lithium show a slight action.

5. That sodium chloride is formed by the action of either metallic sodium or a solution of sodium hydrazide on a solution of hydrazine chloride in anhydrous hydrazine.

6. That reactions may take place in anhydrous hydrazine similar to those that occur in water, in liquid ammonia and in certain other dissociating solvents.

A further study of reactions in anhydrous hydrazine solution with the special object in view of gaining information regarding the hydrazine system of acids, bases, and salts is now in progress in this laboratory and will be made the subject of a future communication.

This investigation was undertaken at the suggestion of Professor A. W. Browne and was carried out in coöperation with him.

ITHACA, N. Y.