

PLATE VI.—Water Containing Bicarbonates and Sulphates of Alkaline Earths Treated With Soda Ash and Lime.

ON THE OXIDATION OF HYDRAZINE. I.

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In 1902 Tanatar<sup>1</sup> showed that hydronitric acid could be obtained by treating a molecular mixture of hydrazine sulphate and hydroxylamine chloride in acid solution with certain oxidizing agents. Three years later it was demonstrated in this laboratory<sup>2</sup> that the acid could be prepared by the action of hydrogen peroxide upon hydrazine sulphate in the presence of free sulphuric acid. Still later it was found<sup>3</sup> that by the action of several other oxidizing agents, respectively, upon hydrazine sulphate in acid solution, varying amounts of hydronitric acid could be produced. In the present article is described a series of experiments performed for the purpose of ascertaining the conditions under which hydronitric acid is formed by the action of ammonium metavanadate in acid solution upon hydrazine sulphate.

*Examination of Materials Employed.*—In order to test the purity of the hydrazine sulphate (obtained from Kahlbaum, Berlin) used in these experiments, the percentage of sulphur was determined in six different samples of the material. Found: 24.57, 24.60, 24.56, 24.59, 24.58 and 24.54 per cent. ; theory, 24.64 per cent.

<sup>1</sup> Ber. 35, 1810-1811.

<sup>2</sup> Browne, This Journal 27, 551-555 (1905).

<sup>3</sup> Browne, Science (N. S.) 22, 81 (1905).

In the ammonium metavanadate (obtained from E. Merck, Darmstadt) the percentage of vanadium was determined by weighing the pentoxide formed by ignition of a weighed quantity of the original material. Found: 43.23, 43.18, 43.19 and 43.17 per cent.; theory, 43.67 per cent. The percentage of nitrogen was determined by distilling the ammonia liberated from a weighed amount of the material in alkaline solution into a measured excess of standard hydrochloric acid. Found: 11.84 and 11.85 per cent.; theory, 11.95 per cent.

*Preparation of Solutions.*—Two solutions of hydrazine sulphate were employed: one containing 15 g. of the salt per liter, and the other 10 g. The solution of ammonium metavanadate was prepared in each case by dissolving the proper amount of the salt in a certain measured amount of pure concentrated sulphuric acid and diluting with a measured amount of water after the solution had been cooled to room temperature.

*General Procedure Followed in the Experiments.*—A measured volume of the hydrazine sulphate solution was placed in a distilling flask of about one liter capacity. Through a separatory funnel was introduced a measured volume of the ammonium metavanadate solution. A slow current of air was drawn through the flask in order to carry the hydronitric acid through the condenser into the absorption apparatus. This absorption apparatus consisted essentially of an Erlenmeyer flask (150 cc.) and a Muencke gas wash bottle. The Erlenmeyer flask was provided with a two-hole stopper through which passed the end of an adapter (connected with the condenser) dipping beneath the surface of the absorbing solution. After passing through the flask the gas was led through a second quantity of the same solution in the Muencke gas wash bottle.

The absorbing solution was prepared by adding 2 cc. of sodium acetate solution (10 g. in 100 cc.) and 5 cc. of silver nitrate solution (10 g. in 100 cc.) to 35 cc. of water. Any hydronitric acid evolved from the reacting mixture was precipitated in the form of silver trinitride. The presence of sodium acetate decreases the solubility of the silver trinitride<sup>1</sup>. In every experiment complete absorption of the acid was effected in the Erlenmeyer flask. The yield of hydronitric acid was determined by the method of Dennis and Isham.<sup>2</sup>

*Results Obtained in the Experiments.*—Four series of experiments were performed in order to ascertain the effect upon the yield of hydronitric acid of varying (1) the temperature at which the reaction is permitted to take place, (2) the amount of metavanadate solution used, (3) the method of introducing the metavanadate solution and (4) the amount of sulphuric acid present. The results of the different series of experiments are given respectively in Tables I to IV.

<sup>1</sup> Dennis and Isham, *This Journal* 29, 18 (1907).

<sup>2</sup> *loc. cit.*

TABLE I.

| Number of Experiment | $N_2H_4H_2SO_4$ (100 gr. per L.) |     | $NH_4VO_3$ Solution per 100 cc. |                             | Temperature | AgCl obtained gr. | Yield $HN_3$ per cent. |
|----------------------|----------------------------------|-----|---------------------------------|-----------------------------|-------------|-------------------|------------------------|
|                      | cc.                              | cc. | $NH_4VO_3$ gr.                  | Conc. $H_2SO_4$ per 100 cc. |             |                   |                        |
| 1                    | 30                               | 100 | 1.2709                          | 12.8 cc.                    | 20°         | 0.00345           | 2.09                   |
| 2                    | 30                               | 100 | 1.2709                          | 12.8                        | 60°         | 0.0049            | 2.97                   |
| 3                    | 20 <sup>1</sup>                  | 100 | 1.2709                          | 12.8                        | 60°         | 0.00485           | 2.94                   |
| 4                    | 30                               | 100 | 1.2709                          | 12.8                        | 100°        | 0.0126            | 7.62                   |
| 5                    | 30                               | 100 | 1.2709                          | 12.8                        | 100°        | 0.01215           | 7.35                   |

In the sixth column is given for each experiment the highest temperature to which the reacting mixture was heated. As this temperature was raised larger yields of hydronitric acid were obtained. This is at least partially attributable to the fact that the acid formed by the reaction is not completely distilled over into the absorption apparatus unless the temperature is raised to 100°. In these experiments the metavanadate was added at once, with the result that the yield of acid even at 100° was not so high as when the solution was added drop by drop under similar conditions (see experiment 6).

The most satisfactory procedure was found to be as follows. The reacting mixture was maintained at a temperature of 80° during the addition of the metavanadate solution. The solution was then brought to the boiling point and was held at that temperature for a few minutes in order to effect the complete removal of the hydronitric acid from the mixture. This procedure was followed in all the experiments recorded in tables II, III and IV.

TABLE II.

| Number of Experiment | $N_2H_4H_2SO_4$ (10 gr. per L.) |     | $NH_4VO_3$ Solution per 100 cc. |                             | AgCl obtained gr. | Yield $HN_3$ per cent. |
|----------------------|---------------------------------|-----|---------------------------------|-----------------------------|-------------------|------------------------|
|                      | cc.                             | cc. | $NH_4VO_3$ gr.                  | Conc. $H_2SO_4$ per 100 cc. |                   |                        |
| 6                    | 20 <sup>1</sup>                 | 100 | 1.2709                          | 12.8 cc.                    | 0.0207            | 12.52                  |
| 7                    | 30                              | 100 | 1.0811                          | 12.8                        | 0.01735           | 10.50                  |
| 8                    | 30                              | 100 | 0.9009                          | 12.8                        | 0.01845           | 11.16                  |
| 9                    | 30                              | 100 | 0.7205                          | 12.8                        | 0.0166            | 10.04                  |
| 10                   | 30                              | 100 | 0.5405                          | 12.8                        | 0.0135            | 8.17                   |

In experiments, 7, 8, 9 and 10 the amounts of ammonium metavanadate solution employed correspond to 12, 10, 8 and 6 molecules, respectively of the salt for every 3 molecules of hydrazine sulphate. In all of these experiments the metavanadate solution was added drop by drop after the hydrazine sulphate solution had been heated to 80°. From these experiments it is apparent that as a general rule the formation of hydronitric acid is facilitated, within certain limits, by increasing the amount of ammonium metavanadate.

TABLE III.

| Number of Experiment | $N_2H_4H_2SO_4$ (10 gr. per L.) |     | $NH_4VO_3$ Solution per 100 cc. |                             | Method of adding | AgCl obtained gr. | Yield $HN_3$ per cent. |
|----------------------|---------------------------------|-----|---------------------------------|-----------------------------|------------------|-------------------|------------------------|
|                      | cc.                             | cc. | $NH_4VO_3$ cc. gr.              | Conc. $H_2SO_4$ per 100 cc. |                  |                   |                        |
| 11                   | 30                              | 100 | 1.0811                          | 12.8                        | At once          | 0.0135            | 8.17                   |
| 7                    | 30                              | 100 | 1.0811                          | 12.8                        | Drop by drop     | 0.01735           | 10.50                  |
| 12                   | 30                              | 100 | 0.9009                          | 12.8                        | At once          | 0.01055           | 6.38                   |
| 8                    | 30                              | 100 | 0.9009                          | 12.8                        | Drop by drop     | 0.01845           | 11.16                  |
| 13                   | 30                              | 100 | 0.7207                          | 12.8                        | At once          | 0.0135            | 8.17                   |
| 9                    | 30                              | 100 | 0.7207                          | 12.8                        | Drop by drop     | 0.0166            | 10.04                  |

<sup>1</sup> 15 gr.  $N_2H_4H_2SO_4$  per liter.

In experiments 11, 12 and 13 the entire quantity of ammonium metavanadate solution was added at the outset. It is obvious that when the solution is added drop by drop the yield of hydronitric acid is materially increased.

| Number of Experiment | $N_2H_4H_2SO_4$ (10 gr. per L.) cc. | cc. | $NH_4VO_3$ per 100 gr. | Conc. $H_2SO_4$ per 100 cc. | AgCl obtained gr. | Yield $HN_3$ per cent. |
|----------------------|-------------------------------------|-----|------------------------|-----------------------------|-------------------|------------------------|
| 14                   | 30                                  | 100 | 0.9009                 | 6.4                         | 0.0181            | 10.95                  |
| 8                    | 30                                  | 100 | 0.9009                 | 12.8                        | 0.01845           | 11.16                  |
| 15                   | 30                                  | 100 | 0.9009                 | 19.2                        | 0.0224            | 13.55                  |
| 16                   | 30                                  | 100 | 0.9009                 | 19.2                        | 0.0169            | 10.23                  |
| 17                   | 30                                  | 100 | 0.9009                 | 25.6                        | 0.0200            | 12.10                  |
| 18                   | 30                                  | 100 | 0.9009                 | 38.4                        | 0.01285           | 7.78                   |
| 19                   | 30                                  | 100 | 0.9009                 | 76.8                        | .....             | .....                  |

From these experiments it appears that when the concentration of sulphuric acid is chosen as indicated for experiment 15, the maximum yield of hydronitric acid is obtained. In experiment 16 the metavanadate solution was added more rapidly than in the preceding case, with the result that the yield of the acid was considerably reduced. In all other experiments the solution was added slowly drop by drop.

*Identification of the Hydronitric Acid Formed.*—The properties of the acid and of its silver salt were studied almost exactly in the manner recommended in a previous article.<sup>1</sup> The percentage of silver in the silver salt was determined with the following results: (1) 0.21635 gram of the salt gave 0.20605 gram of silver chloride; (2) 0.21735 gram of the salt gave 0.20680 gram of silver chloride. This corresponds to 71.69 and 71.62 per cent. silver (theory, 71.97 per cent.), or to 3.04 and 3.05 atoms of nitrogen per atom of silver. For all calculations in the present article the atomic weights recommended by the International Committee for 1907 have been employed.

In order to ascertain whether the amount of ammonia present undergoes increase or decrease during the course of the reaction the series of experiments recorded in Table V was performed. In experiments 1, 2, 3 and 4, 50 cc. of ammonium metavanadate solution (containing 12.85 grams of the salt and 128 cc. of pure concentrated sulphuric acid per liter) were added slowly to 10 cc. of hydrazine sulphate solution (containing 15 grams per liter) at a temperature of about 80°. The solution was then made alkaline by the addition of a certain excess of sodium hydroxide solution, and the ammonia was distilled, with the usual precautions, into a measured excess of fifth normal hydrochloric acid. The amount of ammonia was determined by titrating back with fifth normal sodium hydroxide solution. In the two blank experiments 5 and 6, 50 cc. of ammonium metavanadate solution were employed, but no hydrazine sulphate solution.

<sup>1</sup> Browne, This Journal 27, 551-555 (1905).

TABLE V.

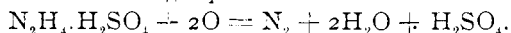
| Number of Experiment | Total wt. $\text{NH}_3$ gr. | $\text{NH}_3$ formed during reaction gr. | Per cent. $\text{NH}_3$ formed |
|----------------------|-----------------------------|--|--------------------------------|
| 1                    | 0.09353                     | 0.00174                                  | 17.7                           |
| 2                    | 0.09327                     | 0.00148                                  | 15.1                           |
| 3                    | 0.09370                     | 0.00191                                  | 19.5                           |
| 4                    | 0.09388                     | 0.00209                                  | 21.3                           |
| 5                    | 0.09179                     | .....                                    | ....                           |
| 6                    | 0.09179                     | .....                                    | ....                           |

The amount of ammonia formed in the course of the first four experiments was ascertained in each case by subtracting the total weight of ammonia obtained in experiment 5 (or 6) from the total weight of ammonia obtained in each of the first four experiments. The percentages of ammonia formed were calculated on the basis of the equation suggested in a subsequent paragraph, and used by the authors in calculating the percentage yields of hydronitric acid.

*On the Use of Ammonium Metavanadate in the Determination of Hydrazine.*—Hofmann and Küssert<sup>1</sup> have recommended the use of ammonium meta vanadate in the determination of hydrazine. The procedure followed by these investigators consisted in the slow addition of an excess of ammonium metavanadate solution strongly acidified with sulphuric acid to the hydrazine sulphate solution. When the evolution of nitrogen (which lasts for about 20 minutes) had ceased, the solution was warmed for several minutes to about 65°. The amount of metavanadate that had been reduced was then determined by titration with permanganate solution. In addition to this volumetric method Hofmann and Küssert also suggested the simultaneous measurement of the nitrogen evolved from the mixture. In effecting this operation the reaction was conducted in a current of carbon dioxide by means of which the evolved nitrogen was carried into the measuring apparatus.

In 1899 Rimini<sup>2</sup> after reviewing several different methods for the determination of hydrazine made the statement that the above method was undoubtedly the best of those considered.

The reaction was considered by Hofmann and Küssert to proceed in accordance with the following equation:—



In experiments 1 to 6 (Tables I and II) the authors of the present article have used hydrazine sulphate, ammonium metavanadate and sulphuric acid in the proportions employed in the experiments of Hofmann and Küssert. In each case appreciable amounts of hydronitric acid were obtained. In experiment 3 the conditions recommended by Hofmann and Küssert have been exactly duplicated; the reacting mixture was allowed to stand at room temperature until the effervescence had ceased,

<sup>1</sup> Ber. 31, 64-67 (1897).

<sup>2</sup> Gazz. chim. ital. 29, (1) 265-69 (1899).

when it was heated to 60° for a few minutes. Even under these conditions, unfavorable as they were to the quantitative removal and absorption of the hydronitric acid formed, a yield of nearly three per cent. was obtained. In experiment 2 the conditions were the same as in experiment 3 except that the hydrazine sulphate solution was more dilute. No very appreciable variation in the yield of acid, however, was observed. In experiments 4 and 5 the yields of hydronitric acid were considerably higher. In experiment 6 the method of adding the metavanadate solution was modified and the most favorable temperature conditions were chosen. In this case 12.52 per cent. of hydronitric acid were produced.

For the sake of simplicity the percentage yields of hydronitric acid and ammonia have both been calculated on the basis of the equation



From the fact, however, that the yields of ammonia under the most favorable conditions were found to be higher than the yields of hydronitric acid, it is apparent that the secondary reaction does not proceed quantitatively in accordance with this equation.

The magnitude of the error introduced as a result of the secondary reaction indicated by the above equation obviously depends upon the character of the analytical method chosen. If the oxidimetric method is employed, the percentage error will be numerically smaller than the percentage yield of hydronitric acid, while if the gasometric method is employed the percentage loss of nitrogen due to the formation of hydronitric acid should be numerically equal to the percentage yield of the acid.

In the four experiments performed by Hofmann and Küspert it was found that one molecule of hydrazine sulphate required 1.996, 1.964, 1.959 and 1.939 atoms of oxygen (theory, 2 atoms). The mean deficit in consumed oxygen (0.0355 atom oxygen per molecule of hydrazine sulphate or 1.78 per cent. deficit in oxygen), corresponds to a yield of 3.55 per cent. of hydronitric acid, provided that the absence of possible errors arising from other sources be assumed.

In order to ascertain experimentally the ratio existing between the errors to which the two methods are respectively subject, a series of determinations has been made of the volume of nitrogen liberated and of the amount of oxygen consumed by the oxidation of a measured amount of hydrazine sulphate. In these experiments a Lunge nitrometer was employed, but the ordinary gas evolution bottle was replaced by a 125 cc. Erlenmeyer flask provided with a small test tube placed in a slanting position. This flask was immersed in a beaker filled with water for the purpose of avoiding errors due to changes in temperature. The hydrazine sulphate and ammonium metavanadate solutions were identical in composition with those employed by Hofmann and Küspert, and the

amount of each solution used was also the same as that employed by these investigators (i.e., 10 cc. of hydrazine sulphate solution containing 15 gr. per liter, and 50 cc. of ammonium metavanadate solution containing 12.85 gr. of the salt and 128 cc. of concentrated sulphuric acid per liter were used). After the flask had been brought to room temperature by immersing it in the beaker of water for some time, the two solutions were mixed in the flask, and with frequent shaking were allowed to remain at room temperature until the greater part of the gas had been evolved. The temperature was then raised to 60° for a few minutes, in order to effect the complete evolution of the gas. After the apparatus had been again brought to room temperature, the volume of gas was carefully measured. Since water was used as the confining liquid, corrections for the tension of aqueous vapor were introduced. The amount of oxygen consumed was in each case determined by titration of the residual solution (after diluting to 250 cc.) with a solution of potassium permanganate containing 7.0274 gr. of the salt per liter. Owing to the difficulty in observing the exact end-point of the reaction a slight excess of permanganate was in each case unavoidably introduced, for which no correction could be satisfactorily made. For this reason the error inherent in the oxidimetric method is to some extent reduced by the compensating error due to the presence of a slight excess of permanganate. The results obtained are appended in Table VI.

Table VI.

| Number of Experiment | Nitrogen evolved (0°, 760 mm.) cc. | Deficit in Nitrogen per cent. | Permanganate Solution cc. | Oxygen Consumed gram. | Atoms of Oxygen per molecule hydrazine | Deficit in Oxygen per cent. |
|----------------------|------------------------------------|-------------------------------|---------------------------|-----------------------|--|-----------------------------|
| 1                    | 24.65                              | 4.57                          | 20.4                      | 0.03626               | 1.966                                  | 1.70                        |
| 2                    | 24.17                              | 6.43                          | 20.45                     | 0.03635               | 1.971                                  | 1.45                        |
| 3                    | 24.61                              | 4.72                          | 20.5                      | 0.03644               | 1.976                                  | 1.20                        |
| 4                    | 24.86                              | 3.76                          | 20.7                      | 0.03679               | 1.995                                  | 0.25                        |
| 5                    | 24.78                              | 4.07                          | 20.6                      | 0.03661               | 1.985                                  | 0.75                        |
| 6                    | 25.02                              | 3.14                          | 20.65                     | 0.03670               | 1.990                                  | 0.50                        |
| Average              | .....                              | 4.45                          | .....                     | .....                 | .....                                  | 0.975                       |

From the above experiments it is apparent that when the reaction between hydrazine sulphate and ammonium metavanadate in sulphuric acid solution takes place in a Lunge nitrometer the error due to the formation of hydronitric acid averages about 4.5 per cent. in case the gasometric method is employed, or about one per cent. when the oxidimetric method is used.

*Summary.*—When hydrazine sulphate and ammonium metavanadate are brought together under favorable conditions in the presence of sulphuric acid a secondary reaction takes place (to an extent depending on the conditions chosen) which results in the formation of hydronitric acid and ammonia. Under the most favorable conditions studied by the authors the yield of hydronitric acid, as calculated from the equation

$2\text{N}_2\text{H}_4 + 2\text{O} \rightarrow \text{HN}_3 + \text{NH}_3 + 2\text{H}_2\text{O}$ , amounted to 13.55 per cent. of the theory. The highest yield of ammonia amounted to 21.3 per cent. on the basis of the same equation. The use of ammonium metavanadate in the determination of hydrazine, as recommended by Hofmann and Küspert, is theoretically subject to a percentage error numerically equivalent to the percentage yield of hydronitric acid when the nitrometric method is employed, and to a smaller error when the oxidimetric method is chosen. By the use of a Lunge nitrometer the error was found to be about 4.5 per cent. for the nitrometric method and about one per cent. for the oxidimetric method.

CORNELL UNIVERSITY,  
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## UNIFICATION OF TERMS USED IN REPORTING ANALYTICAL RESULTS.<sup>1</sup>

BY CYRIL G. HOPKINS, Chairman of Committee from the Association of American Agricultural Colleges and Experiment Stations.

Received July 5, 1907.

In 1904 at the St. Louis meeting of the Association of Official Agricultural Chemists, a committee was appointed on unification of terms used in reporting analysis; and at the Des Moines meeting a similar committee was appointed by the Association of American Agricultural Colleges and Experiment Stations.

These two committees have cooperated in the work assigned and at the last annual meetings made substantially the same report to their respective associations.

Final action on the report was postponed for one year by the Association of Official Agricultural Chemists at Washington last November, in part, because at that time no action had been taken by the broader association of Agricultural Colleges and Experiment Stations, whose annual convention was held a week later at Baton Rouge, at which meeting, however, the report which follows was adopted with the conditions stated:

### Report of Committee on Unification of Terms Used in Chemical Analysis.

"Your committee has been working in cooperation with a similar committee from the Association of Official Agricultural Chemists, and the following report is in harmony with a report already made to that association by its own committee, on which action was postponed for one year.

The subject-matter referred to your committee naturally divides itself into two classes, one of which includes soils, fertilizers, ash and other materials whose analysis may be expressed in terms of chemical elements or in simple compounds; while the other class includes foodstuffs, condiments, and other materials whose analysis may best be expressed in terms

<sup>1</sup> Read at the Toronto Meeting of the American Chemical Society, June 28th, 1907.