

The reverse replacement was accomplished by heating a small piece of gold with an excess of a concentrated solution of potassium silver cyanide. After two hours' heating in a water-bath the gold was covered with a white deposit. This deposit was washed with water, then with ammonia, and again with water. It was then dissolved in nitric acid, and with this solution hydrochloric acid gave a precipitate which was soluble in ammonia and which returned on the addition of nitric acid to the ammoniacal solution.

#### SUMMARY.

An abbreviated electrochemical series of the metals reads as follows: +K, Na, Ba, Sr, Ca, Mg, Al, Zn, Cd, Fe, Co, Ni, Sn, Pb, Cu, Hg, Ag, Pt, Au —.

The author has shown the metals in the following pairs to be reciprocally replaceable in aqueous solution, the metal first named in each pair being under ordinary circumstances more readily replaceable by the second than the second by the first.

K-Na; K-Ba; Na-Ba; Zn-Cu; Cd-Cu; (Fe-Hg); (Fe-Ag); Hg-Ag; Hg-Pt; Hg-Au; Ag-Au.

It is the intention of the author to continue the study of reciprocal replacements, as well in the presence of mercury as in its absence.

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## A NEW SYNTHESIS OF HYDRONITRIC ACID.

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SEVERAL methods for the preparation of hydronitric acid from inorganic hydrazine compounds have been described. Curtius<sup>1</sup> obtained a dilute solution of the acid by passing the gaseous reduction products of nitric acid through a solution of hydrazine hydrate. Angeli<sup>2</sup> prepared silver trinitride by adding a saturated solution of silver nitrite to a solution of hydrazine sulphate. Dennstedt and Göhlich<sup>3</sup> made use of the interaction of hydrazine sulphate and potassium nitrite. Sabanejeff and Dengin<sup>4</sup> heated

<sup>1</sup> *Ber. chem. Ges.*, **26**, 1263 (1893).

<sup>2</sup> *Atti. d. Reale Accad.* (5), **2**, I, 569; *Centrbl.*, II, 559 (1893).

<sup>3</sup> *Chem. Ztg.*, **21**, 876 (1897); *Centrbl.*, II, 1093 (1897).

<sup>4</sup> *Ztschr. anorg. Chem.*, **20**, 21 (1899).

hydrazine sulphate with nitric acid. Tanatar<sup>1</sup> treated hydrazine with nitrogen trichloride, and later<sup>2</sup> oxidized a molecular mixture of hydrazine sulphate and hydroxylamine chloride in acid solution by treating with each of the following: chromic acid, hydrogen peroxide, bromine water, permanganic acid, lead dioxide and read lead.

#### ON THE REACTION BETWEEN HYDROGEN PEROXIDE AND HYDRAZINE SULPHATE IN PRESENCE OF SULPHURIC ACID.

Hydronitric acid may be obtained in considerable quantity by the action of hydrogen peroxide upon hydrazine sulphate in acid solution.<sup>3</sup>

The hydrazine sulphate used in the experiments to be described in the following pages was obtained from Kahlbaum (Berlin, S. O.). The percentage of sulphur was determined in four different samples of the compound by precipitating with excess of barium chloride and weighing the barium sulphate formed. Found: 24.36, 24.62, 24.39 and 24.31 per cent.; theory, 24.63 per cent.

The hydrogen peroxide solution was obtained from the Malinckrodt Chemical Works (New York). The strength of this solution was determined at six different times during the course of the experiments by titration with potassium permanganate in acid solution. Between 3.02 and 3.07 per cent. of anhydrous hydrogen peroxide were found in the different samples taken.

The following procedure was adopted in the experiments. The weighed sample of hydrazine sulphate was in each case dissolved in water, acidified with sulphuric acid and put into a 300 cc. distilling flask. The hydrogen peroxide was then added and the solution was gently heated until the larger part of the water had distilled over into the receiver. In Expts. 6 and 7, 5 cc. of hydrogen peroxide were taken at the outset and 15 more were added through a separatory funnel during the course of the distillation. In each of the eleven experiments an additional 5 cc. of hydrogen peroxide and 5 cc. of water, not recorded in the table, were added toward the close of the experiment, and distillation was continued to insure complete separation of the hydronitric acid. Still

<sup>1</sup> *Ber. chem. Ges.*, **32**, 1399 (1899).

<sup>2</sup> *Ibid.*, **35**, 1810 (1902).

<sup>3</sup> This contradicts the statement made by Tanatar (*Loc. cit.*, **35**, 1810), after referring to the method of Sabanejeff and to his own earlier method for the preparation of hydronitric acid: "Sonst entsteht diese Säure nicht bei der Einwirkung von Oxydationsmitteln, weder auf Hyrazin noch auf Hydroxylamin allein."

Further addition of both hydrogen peroxide and water after the second distillation had been completed was found to yield no hydronic acid, except in the one case of Expt. 4, in which case the yield was accordingly not determined.

The results of the experiments were as follows:

No.	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> SO <sub>4</sub> . Gram.	H <sub>2</sub> O. cc.	H <sub>2</sub> O <sub>2</sub> . cc.	H <sub>2</sub> SO <sub>4</sub> . cc.	AgN <sub>3</sub> obtained. Gram.	Yield. Per cent.
1.	0.3497	10	30	5 2N	0.0518	19.28
2.	0.4625	25	50	10 2N	0.0404	11.37
3.	0.4618	25	50	10 2N	0.0426	12.01
4.	0.4993	25	10	10 2N	.....	.....
5.	0.5000	25	10	10 2N	0.0616	16.04
6.	0.5008	25	20	10 2N	0.0710	18.45
7.	0.5014	25	20	10 2N	0.0710	18.43
8.	0.5012	25	25	10 conc.	0.0958	24.88
9.	0.5004	25	25	10 conc.	0.1044	27.15
10.	0.5000	40	10	10 conc.	0.1090	28.37
11.	0.5008	25	10	25 conc.	0.1092	28.38

From Expts. 2 and 3 it is apparent that when a considerable excess of hydrogen peroxide was taken, the yield of hydronic acid became smaller. From Expts. 8, 9 and 10 it is apparent that when the amount of sulphuric acid was increased the yield of hydronic acid became larger. From a comparison of Expts. 10 and 11 it is seen that still further increase in the acidity of the solution was not accompanied by appreciable increase in the yield of hydronic acid.

In order to prove that the acid obtained was identical with hydronic acid a comparatively large amount was prepared by using ten times the quantity of materials taken in Expt. 10. The acid was concentrated by redistillation. Even in very dilute solution it possessed the unbearable, headache-producing odor characteristic of hydronic acid. The white precipitate obtained by treating the redistilled acid with silver nitrate solution was completely soluble in dilute nitric acid.<sup>1</sup> When the washed precipitate, suspended in distilled water, was exposed to bright sunlight (in January) for ten minutes it was but very slightly darkened. Exposed in this way for a much longer time it gradually became gray in color. The dried precipitate exploded with violence when thrown upon a hot iron plate, or when touched with a glowing platinum wire. Particles weighing even less than 1 mg. exploded under these conditions with a sharp little snap. A few

<sup>1</sup> Dennis: This Journal, 18, 947 (1896).

particles of the silver salt suspended in a little water sufficed to give the characteristic ferric chloride test,<sup>1</sup> which was also readily given by the acid itself. The red solution was in either case quickly decolorized by a few drops of 2 N hydrochloric acid, but was not decolorized by a few drops of 2 per cent. mercuric chloride solution.<sup>2</sup>

The percentage of silver in the silver salt was determined as an additional check upon the foregoing qualitative tests. A quantity of the substance was prepared by treating the acid with an excess of silver nitrate solution, and was washed by decantation until the wash-water gave no test for silver. The precipitate, suspended in a little water, was then transferred to two weighed platinum crucibles, was dried to constant weight over concentrated sulphuric acid in a vacuum desiccator and was weighed. Ten cc. of distilled water and 10 cc. of concentrated hydrochloric acid were then poured into each crucible, the solutions were evaporated to dryness at 100° and the silver chloride was dried to constant weight at a somewhat higher temperature. The amount of residue left on evaporating to dryness samples of the hydrochloric acid and water used in the analyses was next determined. The residue left after the evaporation of 10 cc. of hydrochloric acid and 10 cc. of water weighed 0.00025 gram. This amount was subtracted from the gross weight in order to obtain the true weight of silver chloride. (1) 0.1135 gram of the silver salt gave 0.10845 gram silver chloride. (2) 0.1306 gram of the silver salt gave 0.1248 gram silver chloride. This corresponds to 71.9 and 71.9 per cent. silver; theory, 71.9 per cent.<sup>3</sup>

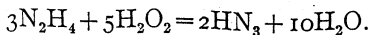
The percentage yields of hydronitric acid obtained by the action of hydrogen peroxide upon hydrazine sulphate have been cal-

<sup>1</sup> Dennis and Browne: This Journal, 26, 577 (1904).

<sup>2</sup> Dennis and Browne: *Loc. cit.*

<sup>3</sup> It may be of interest to state that the atomic weight of nitrogen calculated from these analyses, assuming that the atomic weight of silver ( $O = 16$ ) is 107.93 and that the atomic weight of chlorine is 35.45, is in each case 14.04. This result is identical with the value given in the last report of the International Committee on Atomic Weights (this Journal, 27, 5 (1905)), and is higher than the results (mean, 13.903) recently obtained by Miss Aston in the laboratory of Professor Ramsay (*Verhandlungen der Versammlung deutscher Naturforscher und Aerzte*, 1903, 1, 62-74; *Chem. Centralbl.*, 1904, 1, 977). The authors's analyses were not made with any idea of obtaining accurate data concerning the atomic weight of nitrogen, nor are they to be considered as final in any sense, since the amounts of silver trinitride employed in the analyses were rather too small to insure accuracy in the second decimal. The author plans, in coöperation with Professor Dennis, to make in the near future a thorough study of the atomic weight of nitrogen in different salts of hydronitric acid. Professor Ramsay has kindly expressed to us his willingness that we should continue the investigation commenced in his laboratory.

culated (see table, last column) on the basis of the equation



This seems to be the simplest and, on the whole, most plausible equation to express the reaction. It may be possible, however, that there are first formed unstable intermediate products that are subsequently decomposed so as to form hydronitric acid. If for example, the hypothetical "buzylene,"  $\text{NH}_2\text{.NH.N:NH}$  (of which the phenyl hippuryl derivative has been prepared by Curtius<sup>1</sup>), should be formed by the partial oxidation of two hydrazine molecules it is probable that it would readily decompose in presence of additional hydrogen peroxide, yielding hydronitric acid as the principal product of its decomposition.

#### SUMMARY.

Hydrazine sulphate and hydrogen peroxide react in presence of sulphuric acid, yielding hydronitric acid. Under certain conditions (see table, Expts. 10 and 11) the yield of hydronitric acid amounts to over 28 per cent. of theory.

All previous methods for obtaining hydronitric acid from hydrazine compounds have been based upon the reaction, under proper conditions, of these compounds with such substances as nitrous acid, potassium nitrite, silver nitrite, nitrogen trichloride, nitric acid and hydroxylamine chloride, all of which contain nitrogen.

The method described in the preceding pages is of theoretical interest, because it is the first method that has been suggested for the formation of hydronitric acid by the action, upon hydrazine, of a compound containing no nitrogen.

Further experiments in this laboratory have shown that hydronitric acid may be obtained in small quantities by the action upon hydrazine sulphate of certain oxidizing agents other than hydrogen peroxide, some of which have been previously used by other investigators in the quantitative determination of hydrazine. In a future communication a detailed account of these experiments will be given.

In concluding, the author wishes to express his gratitude to Prof. L. M. Dennis for the interest he has shown in this work, and for the suggestions he has offered during its prosecution.

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<sup>1</sup> *Ber. chem. Ges.*, 26, 1263 (1893).