removal of the excess of hydrogen peroxide. The solution was then acidified with 1 : 1 sulfuric acid and was distilled. The distillate gave no tests for hydronitric acid with ferric chloride.

Summary.

The decomposition of hydrazine monochlorate, by heat, in neutral, aqueous solution yielded no hydronitric acid; in (H_2SO_4) acid solution hydronitric acid resulted. The corresponding di-salt yielded hydronitric acid both in the presence and absence of sulfuric acid. The mono- and diperchlorate of hydrazine yielded no hydronitric acid in either acidified or unacidified solution. When the dry crystallized salt was decomposed by heat in a stream of carbon dioxide, hydronitric acid was produced from the latter, but not from the former. Both liberated gaseous chlorine, nitrogen and oxygen, and chloride and hydroxide ions. The mono- and disulfates of hydrazine, under similar conditions, gave off water, hydrogen sulfide, sulfur dioxide and sulfur, but no hydronitric acid. A method is described for the detection of hydronitric acid in the presence of sulfur dioxide.

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ELECTROCHEMICAL OXIDATION OF HYDRAZINE SULFATE AND AMMONIUM HYDROXIDE.[1]

By J. W. Turrentine and J. M. Olin.

Received December 15, 1914.

Szarvasy[2] has shown that hydrazine, on electrolysis, yields nitrogen at the anode and hydrogen at the cathode in the ratio in which these two elements exist in the hydrazine molecule, namely, $N_2 : 2H_2$. These results were obtained from the electrolysis of solutions of hydrazine hydrate, sulfate and chloride at varying concentrations of solution, current densities and temperatures. The hydrazine cations, he explains, are oxidized at the anode by the discharge anions, oxygen, chlorine, with the formation, respectively, of water and hydrochloric acid, evolving nitrogen; and at the cathode "the free base reacts with two molecules of water, the hydrate being re-formed and hydrogen liberated." Under the conditions of his experiments, as his figures indicate, the hydrazine cation was oxidized at the anode quantitatively to nitrogen without any indication of a reduction at the cathode.

These experiments show conclusively that oxygen and chlorine liberated by electrolysis, under the conditions named, do not oxidize hydrazine in the alkaline solution of the hydrate or in the neutral or weakly acid solution

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[1] In part a chapter from the thesis submitted by the author to the Faculty of Cornell University for the degree of Doctor of Philosophy, May, 1908.

[2] "Electrolysis of the Nitrogen Hydrides and of Hydroxylamine, *J. Chem. Soc.*, [1] 11, 603 (1900).

of the sulfate or chloride[1] to an intermediate oxidation product as ammonia or hydronitric acid, but, as stated above, directly to nitrogen.

The investigation here described was undertaken by the present writer to discover if, under more widely varying conditions than those which obtained on the work of the investigation quoted, reactions could not be induced by electrolysis, as the primary agent, which would yield as a product other hydronitrogens such as ammonia, and more particularly, hydronitric acid.

Looking upon the action of the current at the anode as nothing more than that of an agent whose function it is to liberate in that area some oxidizing agent such as oxygen, chlorine, etc., and wishing to simulate as closely as possible a weak oxidizing agent, as one would conclude from the complete oxidation of the hydrazine directly to nitrogen in the experiments of Szarvasy that the conditions there were such as to yield too strong an oxidizing agent, the electrolysis was conducted, in our earlier experiments, between a large anode and small cathode and with a very low current density at the anode. The small cathode was employed to cut down the reduction in its region.

The electrolysis of the hydrazine sulfate was conducted in strongly acid solutions, since, as observed by Browne and Shetterly[2] in their work on the oxidation of hydrazine, the production of hydronitric acid and ammonia is always most noticeable in strongly acid solution. Moreover, to remove readily the hydronitric acid from its aqueous solution, it is quite advantageous to acidify strongly before distillation. It was hoped thus by acidification and heating to drive off the acid, if formed, from the electrolytic bath as rapidly as produced, as it has been shown[3] that hydronitric acid itself is decomposed electrolytically at the anode.

Experimental.

Experiment 1.—A solution of hydrazine disulfate, saturated in the cold, containing 5% by volume of concentrated sulfuric acid, was electrolyzed at its boiling point between platinum electrodes and contained in the apparatus described as follows:

A 250 cc. beaker contained as anode a sheet of platinum foil of 60 cm. square, on a face, curved so as to fit against the walls of the beaker, and a platinum wire cathode extending horizontally to the center of the beaker and then perpendicularly down. The beaker rested on a sand bath and was covered as tightly as possible by an evaporating funnel. From the top of the funnel extended a Reitmeyer bulb to return any acid spray. From this a narrow glass tube extended downward to the bottom of a test

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[1] The author makes no mention in connection with the chloride and sulfate of hydrazine as to whether he dealt with the neutral, monosalt or the acid disalt.

[2] "On the Oxidation of Hydrazine, I," THIS JOURNAL, **29**, 1305 (1907); II, *Ibid.*, **30**, 53 (1908); III, *Ibid.*, **31**, 221, 783 (1909).

[3] Szarvasy, *Loc. cit.*; Peratoner and Oddo, *Gazz. chim. ital.*, **25**, II, 13; **30**, II, 95.

tube containing a few cubic centimeters of an aqueous solution of ferric chloride. The test tube was closed by means of a two-hole rubber stopper and was connected in turn through a suction flask, to a Bunsen pump. This complication in the apparatus was introduced to make it possible, by drawing a rapid stream of air into the funnel from the edges of the beaker and on through the test solution of ferric chloride, to catch and detect any hydronitric acid distilled from the solution during the electrolysis. The liquid from the condensed vapors was conducted from the collecting rim of the funnel likewise to a test tube containing a test solution of ferric chloride.

The solution of above composition was poured into the electrolytic cell until it covered the entire anode and submerged 1.5 cm. of the wire cathode; its temperature was then raised to its boiling point and there maintained throughout the electrolysis. Distilled water was added from time to time to prevent too great concentration. The current density at first was regulated so that only the slightest evolution of gas was visible at the anode. Under these conditions no indication of the presence of hydronitric acid could be found in either test solution.

The current density was subsequently raised, but with only negative results.

Experiments 2, 3 and 4.—The concentration of the sulfuric acid in the solution undergoing electrolysis was increased successively to 10%, 15% and 20%, respectively, in these experiments, but only negative results as regards the formation of hydronitric acid were obtained. No tests were made for ammonia.

These negative results made it appear improbable that the direct oxidation of the hydrazine cation by the oxygen set free by the current could be made to yield readily the less highly oxidized products of hydrazine as hydronitric acid and ammonia. Oxygen, in its active condition as evolved from the anode, apparently is too strong an oxidizing agent, carrying the oxidation to the extreme of removing all the hydrogen atoms from the union with nitrogen atoms in the hydrazine molecule. The conditions of the experiments were then so altered as to permit of the formation in the electrolytic bath of oxidation products which would escape from the sphere of action less readily than the oxygen. The oxidation products could then, by secondary reactions, subsequently, or during the electrolysis, oxidize the hydrazine.

The oxidation products formed from the electrolysis of solutions in which SO_4'' ions predominate are ozone (H_2O_2) and persulfuric acid. These are produced in largest amounts at high current densities. Accordingly, a long, thin, platinum wire anode, encircling the cup and exposing an active surface for about 10 cm. of its length, was substituted for the large sheet anode in the electrolytic cell, as described in Experiment 1.

In every other respect the cell was allowed to remain as originally described.

Experiment 5.—A saturated solution of hydrazine sulfate, $N_2H_4.H_2SO_4$, containing 10% by volume of concentrated sulfuric acid, was electrolyzed with a current of 1.5 amperes. As the electrolysis continued, the solution became heated. Ozone was evolved.

Hydronitric acid soon made its appearance both in the gases and distillate from the cell and continued to come over during the electrolysis. Stong tests were obtained with solutions of ferric chloride and silver nitrate.

Experiment 6.—This experiment was a duplicate of Experiment 5, with the modification that the temperature of the solution in the cell was maintained at the boiling point from the beginning of the electrolysis. Both the gases and distillate products contained hydronitric acid, though only in small amounts.

It was feared that under the conditions of this experiment the hydronitric acid might be oxidized in its vaporous form by the ozone evolved with it,[1] thus accounting for the low yield of the acid. It seemed desirable, therefore, to conduct the electrolysis at so low a temperature that the acid would remain in solution. The experiment was designed, also, with a view to determining whether hydronitric acid was produced at low temperatures and, as indicated by Experiment 5, continuously during the electrolysis.

Experiment 7.—A solution of the same composition as that used in the previous experiments was electrolyzed in the cell as described, its temperature being maintained during the electrolysis, by means of an ice bath, at 0° and below. The presence of the acid in the gases drawn from the cell could not be detected. There was a free evolution of ozone.

The electrolysis was then discontinued, and to test the cold solution for the presence of hydronitric acid the solution was transferred to a 500 cc. distilling flask. Through the mouth of the flask to the bottom extended a glass tube. The side arm of the flask was connected to a condenser, the lower end of which was joined, by means of an adapter, to a suction flask which in turn was connected with a Chapman pump. In the suction flask was held a small test tube containing the test solution of ferric chloride into which dipped the elongated tube of the adapter. Air was then drawn through the cold solution and was caused to bubble through the ferric chloride solution in the test tube, thus sweeping the hydronitric acid from the acid solution through the test solution.

While a distinct test was obtained, only a small amount of hydronitric acid was thus detected. The solution was then heated to boiling, the dis-

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[1] It may be questioned and remain undetermined whether the ozone could escape from the solution at the temperature at which the electrolysis was conducted without undergoing instantaneous decomposition.

tillate was caught in 5 cc. fractions and each tested with 6 drops of ferric chloride. A series of strong tests for hydronitric acid was thus procured.

The foregoing experiments tended to show that hydronitric acid was produced in the electrolytic bath during the electrolysis either directly, *i. e.*, by the direct oxidation of the hydrazine cation by oxygen, which seemed impossible in the light of previous experiments, or by secondary reactions with other anode products.

So far only qualitative determination had been made of the yield of acid. To obtain quantitative measurement Experiment 8 was performed.

Experiment 8.—In the apparatus and under the same conditions of temperature as described under Experiment 7 a solution of the disulfate containing exactly 1.00 g. of the salt in 150 cc. H_2O and 50 cc. concentrated H_2SO_4 was electrolyzed for six hours with a current which varied from 0.5 to 1.5 amperes.

For the ferric chloride solution, formerly placed in the test tube to catch and detect vapors of hydronitric acid in the gaseous products of the electrolysis, was substituted a few cubic centimeters of a solution of silver nitrate containing sodium acetate, prepared by adding to 2 cc. of a 10% solution of $AgNO_3$, 2 cc. of a 10% solution of sodium acetate, and sufficient water to completely dissolve the silver acetate formed. During the course of the experiment a slight precipitate of silver trinitride appeared in this tube. At the end of the electrolysis the solution was transferred to the distilling apparatus mentioned under Experiment 7. The tube of the adapter dipped beneath the surface of a solution of $AgNO_3$, prepared as above, so that both liquid and vapor products of the distillation could be recovered. A copious, white precipitate of AgN_3 was formed in the receiver. When the distillate no longer showed the presence of hydronitric acid, when subjected in small amounts to the ferric chloride test, the solution was again made up to 200 cc. with distilled water, and two 2 cc. portions, each equal to 0.01% of the total sample, were withdrawn for analysis. The average of the two analyses gave 0.00729 g. of $N_2H_4.H_2SO_4$ in 2 cc., making the value of the total solution 0.729 g. $N_2H_4.H_2SO_4$. This value, subtracted from the total amount (1.00 g.) started with, gave the weight of the salt oxidized as 0.271 g. of $N_2H_4.H_2SO_4$. The silver trinitride was filtered on a Gooch filter, quickly washed with small amounts of disilled water, dried at 110° and weighed. Weight of AgN_3 = 0.0464 g. = 0.0130 g. HN_3.

Experiments 9 and 10.—The solution that remained from Experiment 8 was subjected to two successive treatments as described under Experiment 8, the electrolysis in each case being prolonged for a period of three hours, with a current of 1.0 to 1.5 amperes. After each distillation the solution was made up again carefully to its original volume and samples were withdrawn for analysis. The silver trinitride also was determined in both cases as above. The results of these two experiments, with those of two others, are given in Table I.

TABLE I.

No.	Amount $N_2H_4.H_2SO_4$. Before electrolysis.	Amount $N_2H_4.H_2SO_4$. After electrolysis.	Oxidized.	Weight AgN_3.	Weight HN_3.	Per cent. HN_3.
8	1.00	0.729	0.271	0.0464	0.013	29.0
9	0.714	0.432	0.282	0.0470	0.0132	28.3
10	0.423	0.000	0.423	0.0576	0.0161	23.0
11	0.50	0.000	0.50	0.0838	0.0235	28.4

For the sake of comparing these results with those obtained in the purely chemical oxidation, the yields of hydronitric acid have been calculated on the basis of the equation:

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O$$

During the oxidation of hydrazine by purely chemical means ammonia seems invariably to be formed under the conditions favorable to the production of hydronitric acid. In order to ascertain whether this same general principle is applicable to the electrolytic oxidation of hydrazine, a portion of the residual solution from which all the hydrazine and hydronitric acid had previously been eliminated, as described above, was made alkaline with potassium hydroxide and distilled in the usual way, the ammonia being caught in a measured excess of standard hydrochloric acid. By titrating back with standard alkali, it was found that about 0.05 g. of NH_3 had been formed during the decomposition of about 1.5 g. $N_2H_4.H_2SO_4$, corresponding to a yield of about 51% of NH_3 on the basis of the above equation.

The electrolysis of the hydrazine salt in the latter experiments was conducted under conditions chosen with a view to the production of more permanent oxidizing agents than the oxygen evolved from the anode. The fulfilment of our prediction and the success of our efforts indicate from the start that the oxidizing agent which one knows to be formed as anode products under these conditions are the agents which yield HN_3 and NH_3. Only three oxidizing agents are possible, namely, the oxygen evolved from the anode, the ozone evolved from the anode and dissolving in the solution, and the persulfuric acid also dissolved in solution, both of the latter two being inevitable products of electrolysis under the conditions maintained. The early experiments in this work as well as those of Szarvasy are sufficient to lead one to dismiss oxygen, though no direct proof has been adduced to show that under the conditions of very high current density the hydrazine cation might not be oxidized to other hydronitrogens.

Chattaway[1] observes that phenylhydrazine in a liquid film on filter

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[1] "Oxidation of Hydrazines by Oxygen," *J. Chem. Soc.*, **91**, 1323 (1907).

paper, when exposed to the action of oxygen confined in stoppered bottles, rapidly absorbs oxygen with the production of heat and evolves a volume of nitrogen greater than that of the oxygen absorbed.

The chemical action of ozone on hydrazine has not been studied as yet, but the slight tests for HN_3 obtained from the cold solutions through which ozone, as well as oxygen, had been passing would indicate that neither of these two acted as the oxidizing agent to any great extent.

Browne and Shetterly[1] have shown that persulfates in hot, acid solutions oxidize hydrazine salts, yielding N_2, HN_3 and NH_3. The present writer, in his attempts to prepare hydrazine persulfates, has found that persulfates do not oxidize hydrazine readily in the cold. It was only necessary, therefore, to analyze the cold solution before and after the distillation to show whether the major portion of the oxidation had occurred during the electrolysis or during the distillation. That some oxidation occurred during the electrolysis in both hot and cold solution has already been shown. The following experiment was designed to reveal to what extent oxidation occurred during the distillation.

Experiment 11.—A solution which contained 0.50 g. $N_2H_4.H_2SO_4$, to 50 cc. of concentrated H_2SO_4 and 150 cc. H_2O, was electrolyzed under the same conditions of time, current, etc., as those which obtained in Experiments 9 and 10. After the electrolysis aliquot portions were analyzed for hydrazine; the results of the analysis showed that 0.1976 g. had been decomposed during the electrolysis, leaving in the solution 0.3024 g. unoxidized. The solution was then distilled until all HN_3 had been removed, was diluted again to a known volume and aliquot portions again analyzed. The results showed that all the remaining hydrazine had been consumed during the distillation.

These facts point conclusively to the persulfuric acid as the oxidizing agent, and explain why a stronger test for HN_3 can be obtained from a warm solution during the electrolysis than from the refrigerated one.

These conclusions fail to take into consideration the possible action of ozone and persulfuric acid on HN_3. Until such a time when we shall understand the chemistry involved in a possible interaction of these substances, we can not say that HN_3 is not a product of the electrolytic oxidation of hydrazine in much greater amounts than indicated in our experiments, and that it is not destroyed almost as fast as formed by ozone or even by the persulfates.

It has been shown[2] in this laboratory that the oxygen evolved by the decomposition of persulfuric acid, theoretically and experimentally is both analogous and similar to that evolved against an insoluble anode in the electrolysis of a sulfate. Why the oxygen from the anode oxidizes hy-

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[1] *Loc. cit.*

[2] Turrentine, *J. Phys. Chem.*, 11, 623 (1907).

drazine to N_2 and that from the decomposition of persulfates oxidizes it only to hydronitrogens may be explained on the basic of the principles of mass action. The oxygen evolved against an anode is necessarily in contact with only the merest film of solution containing the oxidizable cations. The migration of the cations away from the anode would tend further to decrease their concentrations in this film. The conditions resulting are those of relatively high concentration of the oxidizing agent and low concentration of the substance oxidized, conditions suitable for complete oxidation. On the other hand, with persulfates in solution in low concentration and more slowly evolving oxygen and hydrazine in high concentration and with its concentration uninfluenced by migratory tendencies incited by the current, the conditions are the reverse of those existing at the anode—the oxidizing agent is present in low concentration and the reducing agent in relatively high concentration, thus affording conditions suitable for mild or incomplete oxidation.

The Electrochemical Oxidation of Ammonia to Hydrazine.[1]

Raschig[2] obtained hydrazine as a product of the chemical oxidation of ammonia when he treated ammonium hydroxide, in 20% solution, with sodium hypochlorite, in normal solution, in the presence of glue. The proportions taken in a typical experiment were, 200 cc. of ammonium hydroxide, 100 cc. (normal) sodium hypochlorite, with 5 cc. of 1% glue solution.

Attempts were made to induce analogous reactions electrochemically by electrolyzing under various conditions solutions of ammonium hydroxide with ammonium or sodium chloride, and glue. The proportions taken were 200 cc. 25% ammonium hydroxide, 100 cc. normal ammonium chloride or sodium chloride, with 5 cc. 2% glue, a solution not widely differing from that employed by Raschig. The strength of the electrolyzing current was varied between 4.5 amperes and 0.3 ampere, the temperature between that of ice and of the boiling point of the solution, and the concentrations of the ammonium hydroxide and glue from zero to that indicated by the above statement of concentrations. These conditions, with either ammonium or sodium chloride, yielded no hydrazine detectable by Fehling's solution. Finally, with sodium chloride, when that solution was added slowly during the electrolysis, the formation of hydrazine took place. The conditions obtaining were as follows: Current strength, 0.3–0.4 ampere; temperature, 100°; strength of solution, that cited above. The sodium chloride solution was added gradually until it totaled 310 cc. To replace the ammonia lost through volatilization, additional volumes of the solution, likewise, were poured in from time to time, until its volume

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[1] Experimentation by J. M. Olin.

[2] *Ber.*, 40, 4580–8 (1907); D. R. P. 198,307.

also totaled 310 cc. The experiments were repeated and the above observations duplicated.

Summary.

Hydrazine, in saturated solution of the sulfate, containing 10% by volume of concentrated sulfuric acid, is oxidized electrochemically to hydronitric acid when a high current density is maintained at the anode. The yield in hydronitric acid is greater when the solution undergoing electrolysis is held at a low temperature (0°). Since these are the conditions favoring the formation of persulfates, it is believed that the oxidation is the product of a secondary anode reaction, the action of the persulfate ion, a product of a primary anode reaction, on the hydrazine ion. The degree of oxidation has been determined.

Ammonium hydroxide, in the presence of sodium chloride and glue and with low current density, is oxidized electrochemically to hydrazine, provided the solution of sodium chloride is added in small amounts at intervals during the electrolysis.

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A DESCRIPTION OF THE NEW COMPOUND, HYDRAZINE DIPERCHLORATE.[1]

BY J. W. TURRENTINE (with crystallographic notes by A. C. GILL).

Received November 14, 1914.

While perchloric acid is perhaps the most stable of the oxyacids of chlorine, yet it is a sufficiently strong oxidizing agent, especially in concentrated solution, to lend especial interest to a compound which it can form by union with so instable and easily oxidizable a base as hydrazine. In even greater degree is this true of the salt formed from chloric acid and the base, hydrazine.

Actuated by such considerations, a research was undertaken in this laboratory, which was originally intended to embrace an investigation of the methods of preparation and the properties of the series of hydrazine salts, the mono-, and dichlorates, and the mono-, and diperchlorates. The work had progressed to a satisfactory stage, all four substances having been prepared and studied in varying degree and the two more stable ones, the perchlorates, having been purified and analyzed, when Salvadori[2] announced his complete research in an article replete with data on the more stable of both of the chlorates and perchlorates, the mono-salts. No further work has been done in this laboratory, therefore, on either of the compounds studied by him, though our probably more casual observations in some minor details do not coincide with those of the author referred to.

[1] A chapter from the thesis of the author submitted to the Faculty of Cornell University, May 1908, for the degree of Doctor of Philosophy.

[2] *Gazz. chim. ital.*, **37**, 32 (1907).