

THE ELECTROCHEMICAL OXIDATION OF SOME HYDRAZINE SALTS.¹

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The investigation here reported embraces the electrochemical oxidation of hydrazine carbonate, and of the two halogen compounds of hydrazine, the chloride and bromide, as obtained under various conditions of electrolysis. The original plan of the work included also the study of the oxidation of hydrazine iodide. The results obtained with the other two halogen compounds of hydrazine, however, made the proposed electrolysis of the iodide appear of doubtful profit.

In connection with his study of the electrolysis of the hydronitrogens, Szarvasy² observed the behavior of hydrazine hydroxide, sulfate and chloride. He found that under the conditions which were obtained during his experiments there was no evidence of the formation of oxidation or reduction products of hydrazine other than nitrogen and hydrogen, respectively, and that these products were evolved at the anode and cathode, respectively, in the ratio of 1 : 2. This is obviously the proportion theoretically resulting from the quantitative decomposition of that substance into its elements. In explanation of the formation of these electrode products, the authority cited states that the hydrazine cations were discharged at the cathode, there "reacting with two molecules of water, forming hydrazine hydrate, and liberating hydrogen." At the anode, he explained, the hydrazine was oxidized. The presumption is that the hydrogen of the hydrazine molecule was taken up by the liberated oxidizing agent at the anode and that nitrogen was evolved. Where the hydroxide or the sulfate was electrolyzed, the oxidizing agent evolved at the anode was presumably oxygen, and where the chloride was electrolyzed, the oxidizing agent was free chlorine. The products of oxidation were then, in the first two cases, nitrogen and water, and in the third case, nitrogen and hydrochloric acid.

The condition of the solution employed with respect to its acidity or neutrality is not mentioned, nor can one infer, except in the case of the solution of the hydroxide, what that condition was, as either the neutral or mono-acid, or the acidic, or di-acid, salt may have been employed.

In the belief that a wider variation in conditions of electrolysis, the conditions at the anode being made to simulate oxidizing agents of varying activity or intensity, would yield oxidation products other than nitrogen and water, one of us³ electrolyzed hydrazine sulfate in solutions of varying degrees of acidity, with the current density at the anode vary-

¹ From the thesis of Willis A. Gibbons presented to the Faculty of Wesleyan University in partial fulfilment of the requirements for the M.A. degree.

² *J. Chem. Soc.*, 1900, 603.

³ Turrentine, *Am. Chem. Soc., Proc.*, New Haven, July, 1908.

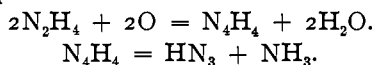
ing between very high and very low values, and the temperature varying between the boiling point of the solution and zero degrees. The anode reactions were followed, not through observing the ratio of the volumes of gas evolved at the anode and cathode, respectively, but rather by examining the solution, and the vapors coming therefrom, for hydronitric acid.

In these experiments no hydronitric acid was obtained at any temperature during the electrolysis with currents giving low current densities at the anode, nor at high temperatures with high current densities at the anode. However, with high current density and low temperature, and with saturated solutions of the sulfate of hydrazine, strongly acidified with sulfuric acid, there was an abundant evolution of hydronitric acid observable on distillation.

The conditions prevailing during these experiments, together with the results obtained, justified the belief that the electrochemical oxidation of hydrazine here obtained was a secondary oxidation, rather than a primary. Under conditions of low temperature and high current density, the electrolysis of solutions of high concentration in the sulfate ion leads to the production of the persulfate ion. The latter is capable of oxidizing hydrazine to hydronitric acid.¹

The oxidation of hydrazine by chemical means has been shown to yield only nitrogen and water,² or in addition to these, ammonia or ammonia and hydronitric acid,³ depending on the nature of the oxidizing agent.

Browne and Shetterly⁴ have made an elaborate study of the chemical oxidation of hydrazine, using a variety of oxidizing agents and determining the nature and amounts of the oxidation products obtainable with each. The results obtained by these investigators have enabled them to effect a classification of the various oxidizing agents studied into three groups: (a) Those "oxidizing agents such as hydrogen peroxide, potassium chlorate, and potassium persulfate [which] decompose hydrazine sulfate in acid solution, yielding varying amounts of some such intermediate condensation product as 'Buzylene,' $\text{HN} : \text{N.NH.NH}_2$, or 'aminotriimide,' which in turn decomposes with formation of hydronitric acid and ammonia." The two stages of this reaction may be represented by the two equations:



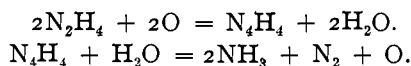
¹ Browne and Shetterly, *THIS JOURNAL*, 31, 221 (1909).

² Rimini, *Gazz. chim. ital.*, 29, I, 265 (1899); *Atti. accad. Lincei Roma*, [5] 15, II, 320; *Chem. Zentr.*, 1906, II, 1662. Browne and Shetterly, *THIS JOURNAL*, 30, 53 (1908).

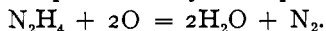
³ Browne and Shetterly, *Loc. cit.*, *et al.*

⁴ *THIS JOURNAL*, 29, 1305 (1907); 30, 53 (1908); 31, 221 (1909).

(b) Those "oxidizing agents, typified by potassium permanganate, manganese dioxide, and ferric oxide [which], decompose hydrazine sulfate in acid solution yielding varying amounts of some such intermediate condensation product as 'tetrazone,' $\text{H}_2\text{N.N}:\text{N.NH}_2$, which breaks up under the conditions of the experiment with the formation of nitrogen and ammonia." The following equations are offered to represent these reactions:



(c) Those "oxidizing agents, as for example potassium iodate, mercuric oxide, and mercuric chloride [which], decompose hydrazine sulfate in acid solution at a temperature of 100° apparently without formation of intermediate condensation products." The reactions of this class of oxidizing agents may be represented by the equation



An additional conclusion resulting from this investigation is quoted: "In general, it may be said that the progress of the reaction in any case is very largely influenced by the temperature, by the concentration of the hydrazine, of the sulfuric acid or the alkali, and of the oxidizing agent, by the potential of the oxidizing agent, and by the methods adopted in bringing the substances together." The interesting observation is made that the production of NH_3 and HN_3 by the oxidation of N_2H_4 by the halogen compounds conforms with the periodic arrangement of the halogens in the particular, that, with the increasing atomic weight of the halogens, the yield of these oxidation products decreases. Thus chlorates yield ammonia and hydrochloric acid, while bromates yield less of them, and iodates, none at all.

In the light of the results obtained in the electrochemical oxidation of the sulfate of hydrazine, and in the chemical oxidation of this compound, it did not appear improbable that an electrochemical oxidation of the halides and of other compounds of hydrazine could be effected in which an oxidation simulating that of the first or second class of oxidizing agents could be produced. In case a direct electrochemical oxidation could not be induced which would simulate the oxidizing agents of the first or second class, it was deemed probable that an indirect electrochemical oxidation could be brought about through the formation of anode products which would act as oxidizing agents of the desired class. This possibility was probably realized in the electrochemical oxidation of hydrazine sulfate. The experiments of Szarvasy would indicate that the oxidizing influences existing at the anode under the conditions of his experiments analogized an oxidizing agent of the third class. These influences, under suitable control, should lead to the formation of oxidizing agents of any one of the three classes which should react subse-

quently, though perhaps practically simultaneously, with the hydrazine ion.

The investigation of the chemical oxidation of hydrazine has shown that while an oxidizing agent applied under one set of conditions acts as a member of one class, when applied under entirely different conditions it may act as a member of a different class. It does not follow, then, from this consideration that because the electrochemical oxidation under one set of conditions may be classified with the third group of oxidizing agents, that obtained under entirely different conditions may not act as a member of one of the other groups of oxidizing agents.

To produce those conditions electrochemically simulating a decrease in the active mass of a chemical oxidizing agent, the current density at the anode should be decreased. The relative active mass of this agent, so to speak, may be still further decreased by increasing the active mass of the reducing agent with which it is to react. This may be accomplished by stirring the solution undergoing electrolysis, best by rotating the anode. While, of course, this procedure does not increase in the solution the actual concentration of the substance undergoing oxidation, it does very greatly increase its concentration within the zone of oxidation in the immediate neighborhood of the anode.

The "potential" of the oxidizing agent at the anode can be influenced probably only by varying the electrolyte, or the relative concentrations of the several electrolytes present—as by increasing or decreasing the relative concentrations of the different anions.

Temperature may be controlled with ease within certain limits. With increasing current densities, however, it is increasingly difficult to prevent a rise in temperature in the immediate proximity of the electrode and in the entire solution. Thus, by electrochemical means we are able to vary the temperature, the concentration of the hydrazine (the substance undergoing oxidation), the acidity or alkalinity of the solution undergoing electrolysis, the intensity of the oxidation influences at the anode simulating the oxidizing agents, and, within limits, also their "potential."

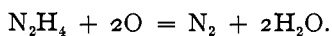
The Electrochemical Oxidation of Hydrazine Carbonate.

Constan and Hansen¹ prepared percarbonate by electrolyzing a saturated solution of potassium carbonate at low temperatures and with a current yielding a high current density at the anode. The electrochemical oxidation is probably analogous to that whereby persulfate is prepared from sulfate. Percarbonates have been shown to decompose in water solution with the formation of hydrogen peroxide and the primary carbonate. It was deemed possible that by the electrolysis of a saturated solution of hydrazine carbonate at low temperatures and high current

¹ *Z. Elektrochem.*, 3, 137 (1896); 3, 445 (1897).

densities, hydrazine percarbonate, a substance hitherto unprepared, might be formed. While it was not expected that the compound would be sufficiently stable to permit of its being recovered in the form of a solid, its formation in solution, it was thought, might be accomplished in a manner similar to that in which hydrazine persulfate was prepared by electrochemical oxidation.

The existence of conditions at the anode favorable to the formation of percarbonate of hydrazine would have been evidenced by an evolution of oxygen there, as such an evolution would have shown that the hydrazine was not undergoing quantitative oxidation. Or the evolution of gas there in amounts less than that called for by the theoretical, quantitative oxidation of the hydrazine to nitrogen and water, should have indicated the possible formation of percarbonate. This volume of nitrogen arising from the oxidation of hydrazine to nitrogen and water should equal the volume of oxygen consumed in that oxidation, as is evident from the equation



The volume of anode gases, then, should have equaled one-half of the cathode gases. Furthermore, the presence of percarbonate should have led to the formation of hydrogen peroxide, which, being an oxidizing agent of the first order, should have produced ammonia and hydronitric acid from its action on the hydrazine. Evidence of the oxidation of hydrazine carbonate to percarbonate could have been gotten, then, both from the ratio of the anode to the cathode gases, and from the products obtained on distillation of the hydrazine carbonate under the proper conditions. Doubtless the N_2H_5^+ (or $\text{N}_2\text{H}_6^{++}$) cation is more easily oxidized than is the CO_3^{--} anion. However, one might rely on the migratory tendencies of the cation cathode-ward to remove it from the region of primary oxidation immediately surrounding the anode.

Experimental.

A solution of hydrazine carbonate was prepared by treating hydrazine sulfate, in saturated solution, with more than the equivalent amount of barium hydroxide, also in saturated solution. Carbon dioxide was then passed to saturation and the precipitate of barium sulfate and carbonate was filtered off. The resulting solution was evaporated over a low flame to a thick syrup. Curtius¹ prepared the carbonate of hydrazine by evaporating the aqueous solution of the carbonate *in vacuo* and likewise obtained a syrup, which he described as caustic. One of us, by carrying the evaporation still further, obtained a solid which was resinous or varnish-like.

The electrolytic cell consisted in a cylindrical glass vessel 2.5 cm. in diameter and 6.5 cm. deep. This was provided with a tightly fitting

¹ Curtius and Jay, *J. prakt. Chem.*, [2] 39, 27.

two-holed stopper, through which capillary tubes were inserted. The platinum wires which were to constitute the electrodes were sealed through the walls of the capillary tubes and entered the cell through them. To one capillary tube was sealed a section of glass tubing, 2.5 cm. long and 0.5 cm. in diameter, which constituted the cathode compartment. The end of the other capillary tube was flush with the lower surface of the stopper. The platinum wire which entered through it encircled the cathode compartment and constituted the anode. The capillary tubes were joined to Hempel gas burettes. The cell was connected in series with an oxy-hydrogen gas coulometer and an ammeter.

The cell was filled to a suitable depth with the syrupy hydrazine carbonate and under it was then placed a Dewar beaker containing a mixture of solid carbon dioxide and alcohol. The temperature of the bath was maintained at -25° - 30° . The electrolysis, effected by a current of 1-1.5 amp. in strength, was conducted for several minutes in order that the evolved gases might displace the air in the cell and tubes. A stronger current was deemed prohibitive because of the difficulties of perfect refrigeration. The electrode gases were collected and analyzed and their volumes compared with one another and with those obtained from the coulometer.

Numerous experimental difficulties were encountered, among which were those incidental to the frothing of the viscous electrolyte and the difficulty of equalizing the gas pressures in the two electrode compartments. The results obtained from the comparison of gas volumes alone showed conclusively that the oxidation at the anode was of the hydrazine, exclusively, and not of the carbonate, ions, unless, indeed, the percarbonate was formed but then reacted quantitatively with the hydrazine. Only nitrogen, with perhaps a trace of oxygen, was evolved there.

The Electrochemical Oxidation of the Neutral Hydrazine Chloride.

Hydrazine dihydrochloride was prepared in solution by treating a known amount of hydrazine sulfate in hot, saturated solution, with an equivalent amount of barium chloride, also in hot, saturated solution. The barium sulfate formed was removed by filtration. The filtrate, after having been tested to show its freedom from both barium and sulfate ions, was neutralized with sodium hydroxide. A portion of this solution was diluted to an approximately two per cent. concentration, calculated on the basis of the neutral, or monohydrochloride of hydrazine. The value of this solution in hydrazine was then determined accurately by analysis of portions of it by the method of Rimini.¹

The apparatus employed was simple and consisted of an electrolytic cell, constructed of a tall, narrow beaker, of 200 cc. capacity. The cathode consisted of a short section of platinum wire. This was immersed

¹ Rimini, *Loc. cit.*

to a depth of something over a centimeter, thus affording a very small active surface, in order that the reduction there might be reduced to a minimum. In those experiments where the anode was held stationary, a piece of platinum foil constituted that electrode. This was suspended in the solution and was supported on the edge of the beaker. Its proximity to the cell wall made it probable that only one face of it was sufficiently active to be considered in computing current density. Where the anode was rotated, a circular disc of platinum gauze was employed. This was 4 cm. in diameter and was supported by a thick wire of the same material fastened perpendicularly to its center. By means of this stem the anode was suspended in the solution from the vertical axis of a small electric motor.

The procedure in general consisted in the electrolysis of a known volume of the analyzed solution of hydrazine hydrochloride for such a length of time as would afford an oxidation of a suitable proportion of the hydrazine present. The length of time required then depended on the current density. The course of the oxidation at the anode was followed, as in the case of the sulfate, by observing the ammonia and the hydronitric acid formed, rather than by determining the nature and the ratio of the gases evolved at the respective poles. Justification for this procedure lay in the fact that it was less laborious and required much less complication of apparatus, and that the only stable oxidation products of hydrazine, with the exception of nitrogen and water, the more common products, are ammonia and hydronitric acid. The formation of these, we have seen, may be accounted for on the supposition that other hypothetical oxidation products are formed which, because of their lack of stability, break down into these products. Thus, both fact and hypothesis may be construed to support this procedure.

At the completion of the electrolysis, the solution was removed from the cell and, in cases where its volume had been changed by evaporation, it was diluted to its original volume. It was then analyzed in aliquot portions and the decrease in value in hydrazine was noted.

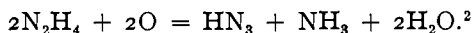
A measured volume of the electrolyzed solution was transferred to a distilling flask, 10 cc. of concentrated sulfuric acid were added through a dropping funnel, and the solution was distilled to a volume of about 10 cc. The distillate and the uncondensed gases were led by means of an adapter into a solution of silver nitrate containing sodium acetate to decrease the formation of free nitric acid.

The precipitate found in the receiver (AgCl and AgN_3) was filtered on a tared Gooch filter, was washed, dried at 105° , weighed and its weight noted. It was then washed with hot nitric acid, containing one part of concentrated nitric acid to four parts of water, to dissolve out any

¹ Dennis and Isham, *THIS JOURNAL*, 29, 18 (1907).

silver trinitride present.¹ After again washing and drying, the precipitate was reweighed and any loss in weight, representing AgN_3 , was noted. As a further check on this observation, the nitric acid solution which had passed through the precipitate was tested with hydrochloric acid for the presence of the Ag^+ ion.

Other portions of the solution were acidified with sulfuric acid and treated with potassium iodate in sufficient amount to oxidize completely any hydrazine remaining therein. This oxidizing agent has been shown to yield no ammonia when employed in this way. The solution was then distilled for ammonia in the usual way and the evolved ammonia was caught in a known volume of standard acid. The theoretical yield of ammonia was based on the equation, proposed by Browne and Shetterly to represent the oxidation of hydrazine to ammonia and hydro-nitric acid,



In calculating the yield, only that hydrazine was considered which the analysis subsequent to the electrolysis showed had been oxidized. In the following paragraphs are given briefly the more important experimental details. The condition of electrolysis designated by "low temperature" may be taken to mean 0° – 10° , and by "high temperature," 50° – 60° . Current density at the anode (a. c. d.) is expressed in amperes per square centimeter.

Experimental Details.

Experiment 1.—Conditions: Low temp., low c. d., stationary anode. Vol. of soln., 175 cc.; time, $6\frac{1}{2}$ hours; current, 0.05–0.075 amp.; a. c. d., 0.003; oxidation, 22.1 per cent.; no NH_3 or HN_3 present.

Experiment 2.—Conditions: Low temp., low c. d., rotating anode. Vol. of soln., 100 cc.; time, 3 hours; current, 0.1 amp.; oxidation, 21 per cent; no NH_3 or HN_3 present.

Experiments 3–5, Inclusive.—Conditions: Low temp., high c. d., stationary anode. Vol. of soln., 170 cc.; time, 58 minutes, 40 minutes, 30 minutes, respectively; current, 1 amp.; a. c. d., 0.05; oxidation, 75 per cent., 66 per cent., 65.5 per cent., respectively; no NH_3 or HN_3 present.

*Experiment 6.—*A solution made up from the residues from the three preceding experiments was electrolyzed to the point of complete oxidation of the hydrazine, as evidenced by the evolution of Cl_2 at the anode, and by subsequent tests with KIO_3 in acid solution. Analysis showed the absence of HN_3 and the presence of traces of NH_3 .

Experiment 7.—Conditions: Low temp., high c. d., rotating anode. Vol. of soln., 164 cc.; time, $3\frac{3}{4}$ hours; current, 1–1.5 amp. Cl_2 was being evolved at the end of the electrolysis; however, the analysis of the soln. for N_2H_4 showed that the oxidation had amounted to only 95 per cent. This observation is of interest as indicating that it is possible for N_2H_4 and Cl_2 (or hypochlorous acid?) to exist together in soln., provided the concentration of the former be sufficiently low. No HN_3 or NH_3 was present.

¹ Dennis and Isham, *Loc. cit.*

² THIS JOURNAL, 29, 1305 (1907), see p. 1310.

Experiment 8.—Conditions: High temp., low c. d., stationary anode. Vol. of soln., 150 cc.; time, 3 hours; current, 0.076 amp.; oxidation, 7.1 per cent.; no NH_3 or HN_3 present.

Experiment 9.—Conditions: High temp., low c. d., rotating anode. Vol. of soln., 160 cc.; time, 2 hours; current, 0.1 amp.; oxidation, 11.1 per cent.; no NH_3 or HN_3 present.

Experiments 10-12, Inclusive.—Conditions: High temp., high c. d., stationary anode. Vol. of soln., 150 cc. in Experiment 10, 200 cc. in Experiments 11 and 12; time, 2 hours, $2\frac{3}{4}$ hours, $1\frac{1}{4}$ hours, respectively; current, 1-1.5 amp.; a. c. d., 0.05-0.075; oxidation, 49 per cent., 85.88 per cent., 34.36 per cent., respectively; no HN_3 present. Analysis for NH_3 (25 cc. portions): *Experiment 10*, vol. of stand. acid taken, (a) 25 cc., (b) 25 cc.; stand. alkali, to neutralization point, (a) 18.29 cc., (b) 18.26 cc.; vol. of acid neutralized by NH_3 (1 cc. stand. acid = 1 cc. stand. alkali), (a) 6.71 cc., (b) 6.74 cc.; NH_3 present, per cc., (a) 0.000457 g., (b) 0.000458 g.; yield in NH_3 , (a) 71.7 per cent., (b) 71.9 per cent. *Experiment 11*, vol. of stand. acid, (a) 26.0 cc., (b) 26.0 cc.; vol. of alkali to neutralization point, (a) 19.26 cc., (b) 19.2 cc.; vol. of acid neutralized by NH_3 , (a) 6.75 cc., (b) 6.8 cc.; NH_3 present, per cc., (a) 0.0004595 gr., (b) 0.000462 g.; yield in NH_3 , (a) 36.6 per cent., (b) 36.9 per cent. *Experiment 12*, vol. of standard acid, each (a and b), 25 cc.; vol. stand. alkali (average of two), 20.81 cc.; acid neutralized by NH_3 , 4.19 cc.; NH_3 present, per cc., 0.000284 g.; yield in NH_3 , 60.55 per cent.

Experiment 13.—Conditions: High temp., high c. d., rotating anode. Vol. of soln., 150 cc.; time, $1\frac{1}{2}$ hours; current, 1.5 amp.; a. c. d., 0.05. An evolution of Cl_2 was noticeable at the end of the electrolysis. Oxidation, 95.75 per cent.; no HN_3 present. Analysis for NH_3 (25 cc. portions): vol. of stand. acid (a) 25 cc., (b) 25 cc.; vol. of standard alkali, to neutralization point, (a) 18.4 cc., (b) 18.9 cc.; vol. of acid neutralized by NH_3 , (a) 6.6 cc., (b) 6.7 cc.; NH_3 present, per cc., (a) 0.000449 g., (b) 0.000456 g.; yield in NH_3 (aver. of two), 30.67 per cent.

The Electrochemical Oxidation of the Neutral Hydrazine Bromide.

A solution of hydrazine carbonate was prepared in the manner already described. A water solution of hydrobromic acid was then added in the requisite amount. The solution was analyzed for hydrazine, by the method of Rimini, and was then diluted to a 2 per cent. concentration.

The method of Rimini obviously cannot be applied to the analysis of hydrazine as hydrobromide, or in the presence of bromide, unless a suitable correction be made for the reduction of the iodate by the bromide ion. The value of the standard iodate solution was determined in terms of the bromide ion by analyzing a solution of potassium bromide of known content. This standardization was conducted in an exactly similar manner to that prescribed by the method of Rimini for the determination of hydrazine by iodate. The solution of hydrazine bromide was then analyzed for the bromide ion by precipitation, under suitable conditions, with silver nitrate. From the weight of the resulting silver bromide was calculated the bromide content of the hydrazine solution, and, from that, the correction which would have to be introduced in the results obtained from the analysis of portions of the same solution for hydrazine.

The apparatus employed and the procedure observed in the electrochemical oxidation of hydrazine monohydrobromide were the same as those which have been described under the account of the parallel experiments with hydrazine hydrochloride. In each of the experiments, details of which follow, the volume of solution subjected to electrolysis was 200 cc.

In every experiment the analysis for hydronitric acid gave negative results.

Experimental Details.

Experiment 14.—Conditions: Low temp., low c. d., stationary anode. Time, 11½ hours; current, 0.11 amp.; a. c. d., 0.005; oxidation, 27.1 per cent; no NH₃ present.

Experiment 15.—Conditions: Low temp., low c. d., rotating anode. Time, 5 hours; current, 0.05 amp. The percentage oxidation in the experiment was so slight that NH₃ and HN₃ were not tested for.

Experiment 16.—Conditions: Low temp., high c. d., stationary anode. Time, 2 hours; current, 1-1.5 amp.; a. c. d., 0.05-0.075; oxidation, 47.2 per cent; no NH₃ or HN₃ present.

A second analysis for HN₃ was made in which the modification was introduced of adding solid Ag₂SO₄ to the solution about to undergo distillation for HN₃. The silver salt was added in sufficient amount to combine with all the bromide ions present and thus prevent the distillation of HBr. This modification was introduced in order that NH₃, by the formation of AgN₃ in the receiver of the condenser, might be detected in smaller amounts. When Ag₂SO₄ was employed, no precipitate at all appeared in the receiving solution, indicating the absence of HN₃.

Experiment 17.—Conditions: Low temp., high c. d., rotating anode. Time, 3½ hours; current, 1.25 amp.; oxidation, 57.7 per cent.; yield in NH₃, 10.4 per cent.

Experiment 18.—Conditions: High temp., low c. d., stationary anode. Current, 0.11 amp.; a. c. d., 0.005; oxidation, 41.9 per cent.; yield in NH₃, 39.8 per cent.

Experiment 19.—Conditions: High temp., high c. d., stationary anode. Current, 1-1.5 amp.; a. c. d. 0.05-0.075; oxidation, 66.6 per cent.; no NH₃ present.

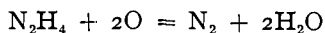
Experiment 20.—Conditions: High temp., high c. d., rotating anode. Time, 2½ hours; current, 1-1.5 amp.; oxidation, 68 per cent.; yield in NH₃, 9.1 per cent.

Discussion of Results.

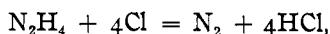
A survey of the results obtained from the electrochemical oxidation of hydrazine hydrochloride shows (a) that no hydronitric acid is obtained from any solution, whatever the conditions may have been under which the oxidation was effected; (b) that only nitrogen and water (or hydrochloric acid) are obtained at low temperatures, and at low current densities, whatever the other conditions may have been; and (c) that only the combination of high temperature and high current density lead to the formation of ammonia; under these conditions a very satisfactory yield is obtained. The rotation of the electrode, under the conditions of current density observed in these experiments, appeared to have but little, if any, effect. It may be remarked that the evolution of gas from the electrode itself effects pretty efficient stirring.

There is no circumstance in Expts. 1-8 which would encourage the be-

lief that the oxidation of hydrazine electrochemically to ammonia is a matter of "potential" of the oxidizing agent, or of the rate at which the oxidizing agent, or influence, is administered to the hydrazine. Whether the potential of the oxidizing influence at the anode changes or not is a matter of conjecture. While the solution undergoes a change from neutrality to acidity, it is probable that the solution in immediate contact with the anode is always acid. A state of acidity would result there whether the reaction be an oxidation of the nature represented by the equation



or a "chloridation" of that, represented by the equation



as both reactions remove the base. And it is doubtful if the most efficient stirring obtainable experimentally would reduce this condition to zero. These considerations would rather discount the idea of a change of potential. If the change in temperature effected a change in potential, this should have been evidenced in Expts. 9 and 10, unless the oxidizing agent at this potential requires in addition a certain active mass, produced at high current density, to oxidize hydrazine to ammonia and hydro-nitric acid, realized in Expts. 11-14.

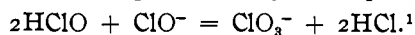
An accumulation of hypochlorite ions in the neighborhood of the anode would lead to the evolution of oxygen there with a lowering of anode potential. A high current density and a low temperature would be favorable to this condition. Such a change, if occurring, produced no result different from that realized in other experiments where such a condition was less probable.

The high current density in Expts. 9 and 10 is only relatively high, being limited by the increasing difficulty of refrigeration by ordinary refrigerants, and a much higher current density might have resulted in producing other oxidation products. Expts. 1-10, inclusive, would indicate that a rise in temperature is not able to change the order of the oxidation under the set of conditions observed. Why a still higher temperature was not maintained will become apparent later. There is, then, but little evidence to support the supposition that the change in oxidation products is effected through a change in potential of, or in the rate of production of the oxidizing agents at the anode, or in the temperature at which they are produced. An explanation is obtainable, however, from the consideration of the secondary reactions which occur in general at the anode when chlorides are electrolyzed.¹ Hypochlorite, stable at

¹ A supposition that the N_2H_6^+ ion undergoes a further dissociation yielding an anion in which nitrogen exists alone is not here advanced, although it is strongly suggested by the extreme readiness with which nitrogen is evolved from solutions containing this ion. Such a dissociation would be analogous to that attributed to the

low temperatures, results when neutral or slightly acid solutions of chlorides are electrolyzed. Its formation may result through the interaction of water and discharged chlorine, or of the OH^- ion and discharged chlorine. The production of free OH^- ion within the solution, through the discharge of H^+ ions at the cathode, and their possible participation in the anode reactions, need hardly be considered in view of the rapidly increasing acidity within the solution during the electrolysis. When the concentration of the ClO^- ions becomes sufficiently high, oxygen may be liberated at the anode, which then oxidizes hypochlorite to chlorate. Thus, at low temperature, a high concentration of hypochlorite is essential to the formation of other oxy-chloride compounds. Free chlorine evolved at the anode could react with hydrazine or, in case that were not immediately available, with water, to form in the former case, hydrochloric acid, with liberation of nitrogen, and in the latter case hypochlorous acid. Hypochlorite would undoubtedly react with hydrazine in a manner approximating that of nascent chlorine. So, as long as the hydrazine is present in any considerable amount, the concentration of the ClO^- ion will be kept low and the electrochemical formation of chlorates prohibited. The chemical oxidation of hydrazine by chlorine has been shown to yield little or no ammonia and hydronitric acid, when allowed to react under the most favorable conditions. It is therefore readily understood why no ammonia and hydronitric acid should be formed under the conditions obtaining in Expts. 1-8, inclusive.

At higher temperatures the anode products may be quite different as the result of secondary reactions. In slightly acid solutions of hypochlorite at a temperature of 50° , hypochlorous acid oxidizes the hypochlorite ion to chlorate, as represented by the equation



This is a reaction of low velocity.

In Expts. 9 and 10 the temperature is favorable to the formation of chlorates. On account of a low current density the formation of hypochlorite is slow and the chances for a high concentration in hypochlorite ions correspondingly poor, both on account of the slow formation of the hypochlorite and the speed of the reduction of it by the hydrazine present. The yield in chlorate, then, and in ammonia and hydronitric acid should be practically *nil*. The conclusions conform with the results.

However, in Expts. 11-14, inclusive, where both a high current density and a high temperature are maintained, it is conceivable that there OH^- ion whereby O^{2-} ions are produced and the evolution of oxygen at the anode during the electrolysis of certain solutions is so satisfactorily explained.

¹ Foerster, *J. prakt. Chem.*, 59, 53 (1899); 63, 141 (1901). *Z. Elektrochem.*, 9, 6 (1903). Thomsen, *J. prakt. Chem.*, 59, 244 (1899). Kretzschmar, *Z. Elektrochem.* 10, 789 (1904).

hypochlorite forms at a sufficiently great rate to acquire a concentration high enough to react with the formation of chlorate, a reaction favored by the temperature. By a tertiary reaction, then, hydrazine is oxidized to ammonia and hydronitric acid.

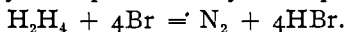
At low temperatures and in slightly acid or neutral solution the chlorate and the hydrazine ion may exist simultaneously, as both the mono- and the dichlorate have been formed and crystallized from aqueous solution.¹ In hot solution, however, it is doubtful if they can so exist without mutual interaction.

If the foregoing explanation of the result obtained in these experiments is the correct one, low concentration in hydrazine is favorable to those reactions which are proposed in explanation of the formation of ammonia and hydronitric acid. More interesting results could not be looked for, then, for the electrolysis of solutions more concentrated in hydrazine.

The supposed action of chlorate on the hydrazine has been spoken of as yielding both ammonia and hydronitric acid, or as belonging to the first class of oxidizing agents. However, no hydronitric acid was found. This fact is explainable by either of two suppositions: the chlorate under the conditions of these experiments acted as an oxidizing agent of the second class and produced only ammonia; or, more probably, hydronitric acid was formed but was subsequently decomposed electrochemically through the discharge of the N_3^- ion at the anode.

In Expts. 14-20, where the bromide is electrolyzed, the results obtained do not conform so well with theory based on the known behavior of discharged bromide ions.

As the bromide ion may be discharged at a low potential, it is probable that no oxygen is evolved at all. The reaction whereby the hydrazine is bromidized may be represented by the equation



In the electrolysis of bromides the formation of bromates from hypobromites takes place with much greater readiness than the analogous reactions which occur when chlorides are electrolyzed. Therefore, the formation of bromates is not so readily controlled or retarded by conditions and it is less easy to say that they would or would not form under this or that set of conditions—the conditions being those which were obtained in the experiments under discussion. There is reason to believe that the oxidation occurring in those experiments where ammonia was formed was effected by bromate and not by hypobromite. Furthermore, while bromate is more readily formed in solution under various conditions of electrolysis than is chlorate, and for that reason should have been found in larger amounts, it is more reactive with hydrazine at all temperatures

¹ Salvadori, *Gazz. chim. ital.*, 37, 32 (1907).

and in its oxidation of that substance yields smaller amounts of ammonia and hydronitric acid than the chlorate.

The reasons for not subjecting the iodides of hydrazine to the same study are now apparent; both iodine¹ and iodate,² under all conditions tested, are oxidizing agents of the third class and therefore can be expected to yield no interesting products.

Summary.

1. The electrochemical oxidation of hydrazine carbonate, under conditions which favor the formation of percarbonates, results in the quantitative oxidation of the hydrazine.

2. That of hydrazine hydrochloride and hydrobromide yields only nitrogen and water or, in addition to these, also ammonia, depending on the conditions of the electrolysis.

3. The reactivity of hypochlorites with hydrazine appears to preclude the possibility of the formation in the presence of hydrazine in large amounts of the more highly oxidized oxy-chlorine ions.

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NOTES.

A Jointless Stock-Bottle-Support Buret.—It is believed that with the apparatus herein described and figured, titration will be made easier, more economical of solutions, and (especially with caustic alkalies) more accurate, than with other apparatus, for the reasons that (1) exposure to the air and (2) the difficulties of transferring the solution back and forth between container and buret are reduced to a minimum.

Since the first draft of this article was made, the apparatus of Burkhardt³ has appeared, which, however, though similar in principle, is believed to be not so good as the one herein described; because of (1) the *joint* wet by the solution, (2) the closed-in top to the buret, (3) the metal brace below, and (4) the arrangement of the opening above, which would seem to make it difficult to empty the buret back into the container.

As the diagram shows, our apparatus consists essentially of a *container-limb* (made experimentally from a tall open-mouthed cylinder), joined above by a short, wide, unobstructed, nearly horizontal tube, to a *buret-limb* (made experimentally from a 50 cc. buret shortened to a net (measuring) capacity of 15 or 20 cc.).

In transferring the solution from container to buret, or *vice versa*, the apparatus is tipped to an almost horizontal position, with the limb from which the liquid is to flow, uppermost. To facilitate this transfer, the

¹ Browne and Shetterly, *THIS JOURNAL*, 30, 53 (1908).

² Rimini, *Loc. cit.*

³ *Chem. Ztg.*, 35, 656; *C. A.*, 5, 20, 3359.