[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. VI. ELECTROLYTIC NITRIDATION OF VARIOUS ANODES IN A SOLUTION OF AMMONIUM TRINITRIDE.[1]

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Attention has already been called by investigators in this laboratory to the similarity that exists between the peroxides and the pernitrides, and between the processes of oxidation and nitridation.[2] Turrentine[3] has adduced evidence in support of the view that hydronitric acid is a nitridizing agent, analogous in both structure and behavior to nitric acid. Welsh[4] has shown that sodium hydrazide probably undergoes ammonolysis in liquid ammonia, with formation of sodium amide, ammonia, and nitrogen, just as sodium peroxide undergoes hydrolysis in water, with formation of sodium hydroxide, water, and oxygen.

In the fifth article of the current series were recorded the results of an investigation upon the behavior of a solution of ammonium trinitride in liquid ammonia when electrolyzed between platinum or graphite electrodes. From this work it may be concluded that under suitable conditions either nascent nitrine, N_3, which at once breaks up into molecular nitrogen, or nascent nitrogen, N, can be liberated at the anode. It has been the purpose of the present investigation to ascertain whether or not nitridation of certain metallic anodes will take place, under similar conditions, with formation of the corresponding metallic nitrides or pernitrides. Anodes of copper, silver, cadmium, aluminum, lead, antimony, iron, and nickel were employed in the experiments to be described.

Apparatus and General Procedure.—The H-tube described and figured in Article V[5] of this series was used throughout the greater part of the work. This cell was provided with two electrode tubes, as before, for the collection of gases liberated during electrolysis. Through the anode tube, however, instead of the slender wire attached directly to the platinum electrode, was fused a short piece of heavy platinum wire, terminating on the inside of the tube in a flattened hook into which the bent-over end of an electrode could readily be drawn so as to give a satisfactory contact. The cathode used with this apparatus consisted of a piece of smooth platinum foil 2 cm. long and 0.5 cm. wide.

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[1] For the earlier articles of this series see THIS JOURNAL, **33**, 1728–34, 1734–42, 1742–52 (1911); **35**, 649–58, 672–81 (1913).

[2] See Browne and Welsh, *Ibid.*, **33**, 1728 (1911); Goldberg, *Ibid.*, **34**, 886 (1912).

[3] *Ibid.*, **34**, 385–7 (1912). See also Turrentine and Moore, *Ibid.*, **34**, 375–382, 382–384 (1912).

[4] *Ibid.*, **37**, 497–508 (1915).

[5] THIS JOURNAL, **35**, 663–71 (1913).

At the beginning of an experiment the carefully cleaned, dried, and weighed anode was suspended in the tube. The electrode tubes were then set in position in the cell, into which had been placed 1.000 g. of pure ammonium trinitride. After the air had been displaced with pure, dry ammonia gas, 36 cc. of liquid ammonia was condensed in the apparatus with the aid of solid carbon dioxide and alcohol, and the solution was thoroughly stirred. The gases liberated during electrolysis were collected, transferred, and analyzed in the usual way. Immediately after the completion of the electrolysis, which was conducted at a temperature of about —67°, the anode was quickly detached, was cleansed from adhering deposits, in case any were formed, and was washed, dried, and weighed in the usual manner. The cell was finally allowed to warm up to room temperature, and the residual solid obtained by evaporation of the liquid ammonia was subjected to further tests as outlined below.

Details of the Experiments.—The principal numerical details of the individual experiments are recorded in the table. Additional results are appended in the paragraphs that follow.

Table I.

No. of expt.	Anode used.	Anode loss. G.	Coulometer cath. gain. G.	Electrochem. effic. corrosion. Per cent.	Nitrogen evolved at anode (corrected). Cc.	Nitrogen evolved at anode (corrected). G.	Hydrogen evolved at cathode (corrected). Cc.	Hydrogen evolved at cathode (corrected). G.	Calc. wt. hydrogen. G.	Av. current. Milliamps.
1....	Copper	0.0925	0.0645	143.4	none		...	......	.....	100
2....	Copper	0.0489	0.0347	140.9	none		...	......	.....	..
3....	Copper	0.0990	0.0688	143.9	none		23.44	0.00211	0.00218	110
4....	Copper	0.1274	0.0916	139.1	none		22.50	0.00202	0.00290	75
5....	Silver	0.2664	0.0775	101.3	none		30.30	0.00272	0.00246	100
6....	Silver	0.1549	0.0452	101.0	none		...	.....	.....	150
7....	Cadmium	0.1369	0.0768	100.8	none		25.44	0.00229	0.00244	100
8....	Cadmium	0.1451	0.0810	101.3	none		...	.....	.....	70
9....	Aluminum	0.0274	0.1143	84.3	3.80	0.00502	39.70	0.00357	0.00363	45
10....	Aluminum	0.0288	0.1168	86.8	4.73	0.00626	34.28	0.00308	0.00370	35
11....	Aluminum	0.1712	0.7846	76.8	...	.....	...	.....	.....	390
12....	Aluminum	0.4378	1.9126	80.5	...	.....	...	.....	.....	400
13....	Aluminum	0.4339	1.9301	79.1	...	.....	...	.....	.....	1000
14....	Aluminum	0.5082	2.4902	71.8	...	.....	...	.....	.....	1000
15....	Lead	0.3068	0.0922	102.1	none		29.49	0.00265	0.00292	110
16....	Lead	0.1661	0.0490	104.1	none		...	.....	.....	100
17....	Antimony	0.1264	0.0962	104.2	none		34.59	0.00311	0.00305	180
18....	Antimony	0.1882	0.1457	102.5	none		51.53	0.00463	0.00462	135
19....	Iron	0.0332	0.1340	42.3	15.60	0.0206	45.33	0.00408	0.00425	80
20....	Iron	0.0364	0.1309	47.5	16.87	0.0223	37.95	0.00341	0.00415	50
21....	Nickel	0.0547	0.1073	55.2	9.48	0.0125	34.67	0.00312	0.00340	95
22....	Nickel	0.0653	0.1078	65.6	5.44	0.0072	34.19	0.00307	0.00342	73

Expt. 1.—The anode consisted of a strip of sheet copper 2 cm. long and 0.5 cm. wide. Before the circuit was closed the cell was allowed to stand for 3 hours, in order to ascertain whether or not the anode would

suffer chemical corrosion when allowed to rest in contact with the electrolyte. No such corrosion was found to take place. As soon as the circuit was closed, however, a distinct blue coloration was observed in the neighborhood of the anode, and before long a layer of deep blue solution had accumulated in the bottom of the anode compartment. The anode was partly coated with a black deposit.

Expt. 2.—The deep blue solution remaining after the completion of the electrolysis, which was carried out under conditions similar to those prevailing in Expt. 1, was allowed to warm up until the liquid ammonia had completely vaporized. The solid residue was treated with water, and the light green precipitate resulting from hydrolysis of the copper salt was removed by filtration. No indication of the presence of hydrazine, the formation of which during the electrolysis had been regarded as at least remotely possible, was obtained when the filtrate was treated with Fehling's solution. The light green precipitate was thoroughly washed with water to remove the ammonium trinitride, and was then treated with a solution of ferric chloride. The deep red coloration indicated the presence of the N_3 group in the solid, which was undoubtedly a basic copper trinitride.

Expt. 3.—A copper anode having a surface (on one side) of 3.25 sq. cm. was used in this experiment. After an exposure of 3 hours to the action of the electrolyte before the current was passed through the cell, the anode seemed to have undergone a very slight chemical corrosion, as indicated by the appearance of a faint blue coloration in the anode compartment.

Expt. 4.—The same electrolyte was used in this as in the preceding experiment. The anode was removed and weighed, and then returned to the cell with suitable precautions to avoid the introduction of moisture. After completion of the electrolysis, which was continued for about an hour, the cell was allowed to warm up to room temperature. The solid residue, which contained ammonium trinitride and the copper salt formed as the corrosion product, was treated with water, which readily dissolved the former, but only slightly dissolved the latter constituent. The solution was decanted from the dark green crystals, which were then dried on filter paper without further washing, and were preserved for subsequent examination. Treatment with water was found to result in immediate hydrolysis, with formation of the light green basic trinitride[1] to which reference was made in connection with Expt. 3. On the other hand, treatment of the basic trinitride with ammonium trinitride caused a reversal of the hydrolytic action, with formation of the dark green crystalline product, which ultimately went into solution completely. For example, 0.06 g. of the dark green salt was treated with 3.7 cc. of

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[1] Wöhler and Krupko, *Ber.*, **46**, 2045–57 (1913).

water. The light green precipitate thus formed was changed back by 0.3 g. of solid ammonium trinitride. When treated under similar conditions with ammonium chloride the precipitate did not redissolve. The presence of bivalent copper, of N_3, and of ammonia, in samples of the original dark green crystals was established by the usual tests. The crystals were insoluble in water, but were soluble in dilute acids. They were found to explode with a loud report when heated. The amount of material obtainable was not sufficient to permit more accurate determination of its decomposition. From qualitative tests, however, it would seem to be either an ammonated cupric trinitride,[1] such as $CuN_6.2NH_3$, or possibly a cupric ammonium trinitride.

It will be noted from the data given in Column 5 of the table that in Expts. 1 to 4 the anode corrosion efficiency is considerably above 100%, as calculated on the basis of the ratio $Cu: 2N_3$. In the absence of appreciable chemical corrosion this indicates that formation of cuprous trinitride, CuN_3, must have taken pace to some extent.[2]

Expt. 5.—The silver anode used in this and in the following experiment was 0.75 cm. wide, and was immersed to a depth of 8 cm. The electrolysis was continued for 30 minutes. As was usual in these experiments, the corrosion took place chiefly at the lower end of the electrode owing to the special construction of the cell, which was designed so as to permit the collection of the gases liberated at the electrodes. After completion of the electrolysis the anode was removed and reweighed, and was again inserted in the cell, in preparation for the next experiment. No evolution of gas, change of color, or formation of a solid deposit occurred at the anode. A heavy deposit of metallic silver gradually accumulated upon the cathode.

Expt. 6.—The electrolysis was allowed to proceed for 30 minutes under conditions the same as those prevailing in the preceding experiment. The deposit of metallic silver on the cathode extended outside of the electrode tube, making it impossible to collect the gas quantitatively. No gas was evolved at the anode, which could be seen to undergo rapid electrolytic corrosion. The solid residue obtained after evaporation of the solvent and removal of the soluble ammonium trinitride by treatment with water, was found to consist of silver trinitride. The electrochemical efficiency has been calculated on the theory that AgN_3 was the sole product of corrosion in this case.

Expt. 7.—The cadmium wire which served as the anode in Expts. 7 and 8 extended to a depth of 8 cm. below the surface of the electrolyte. No corrosion was observed to take place before the circuit was closed. The electrolysis was carried on through a period of 40 minutes, during

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[1] Dennis and Isham, THIS JOURNAL, 29, 19 (1907).

[2] Wöhler, *Chem. Ztg.*, 35, 1096 (1911); Wöhler and Krupko, *Loc. cit.*

which no evolution of gas took place at the anode. A heavy, white deposit was formed at this electrode, however, and a slight deposit of black material, probably finely-divided metallic cadmium, appeared at the cathode.

Expt. 8.—In continuation of Expt. 7 the electrolysis was conducted until the cathode deposit extended beyond the cathode tube, making impossible the quantitative collection of the gas liberated at the cathode. The white anode product was found to be stable in the air at ordinary temperatures, but was found to explode when heated. Treated with a solution of ferric chloride it showed the usual red coloration indicative of the presence of the trinitride ion. After it had been washed with water until the filtrate no longer gave evidence of this ion, a residue was obtained which contained N_3 and which exploded on heating. This was soluble in hydrochloric acid, in hydronitric acid, and in ammonium trinitride solutions, and the resulting solutions yielded cadmium sulfide when treated with hydrogen sulfide. The anode product was probably either an ammonated cadmium trinitride, or an ammono-basic cadmium trinitride formed by ammonolysis of the original CdN_6 quantitatively produced by the action of N_3 upon the metallic anode.

Expt. 9.—A thin sheet of aluminum 0.75 cm. wide was employed as the anode. This was immersed to a depth of 8 cm. in the electrolyte. The electrolysis was allowed to proceed for two hours, during which a bulky, yellowish brown deposit accumulated at the lower end of the anode. On the upper part of the anode a very firm and coherent black coating of somewhat iridescent appearance was formed. This was presumably of identical composition with the yellowish deposit, but of very different physical form and compactness. The deposit was found to be non-explosive, and to contain no N_3. It was insoluble in water, but dissolved readily in a solution of sodium hydroxide. The resulting solution yielded flocculent aluminum hydroxide when boiled with ammonium chloride.

Expt. 10.—The electrolysis was effected under conditions similar to those prevailing in the preceding experiment. The residue obtained after vaporization of the liquid ammonia from the electrolyte was washed on the filter with successive 10 cc. portions of water, and the filtrate was in each case treated with ferric chloride. The ammonium trinitride was completely removed by the first 3 washings and in subsequent portions of the wash water no indications of N_3 in appreciable amount was obtained. The residue was found to be non-explosive, and to contain no N_3. It was found by the usual tests to be aluminum hydroxide.

Expts. 11 to 14.—For use in these 4 experiments a larger electrolytic cell was constructed, in which no provision was made for collection of the gases liberated at the electrodes, but in which the anode product could be prepared in larger quantity, and under conditions of lower and more nearly uniform anode current density. The product was obtained in the form of a fairly compact, though brittle, scale usually of an iridescent steel blue or black appearance. On the back of the electrode, where the current density was very low, a thin, coherent black coating identical with that described under Expt. 9 was deposited. This coating could be removed from the metal only with considerable difficulty.

A curious phenomenon was observed in two cases during the removal of the loosely adherent scale from the front side of the anode. Almost immediately after the material was first exposed to the air, a spontaneous evolution of heat took place, accompanied by the appearance of a small quantity of smoke-like fumes. For the reason that this product is unstable in the air, no definite conclusion can be reached concerning its composition on the basis of the work herein described. Further work upon this problem has been carried out by other investigators in this laboratory, whose results will be published in the next article of the current series.

After the electrolysis had been in progess for some time, a deposit began to form upon the cathode in each of these experiments. This was originally of a dark appearance, but it faded to a dull gray color after the ammonia had been allowed to vaporize from the cell.

Expt. 15.—The anode consisted of a strip of sheet lead 1.5 cm. wide. This was as usual immersed in the electrolyte to a depth of 8 cm. The duration of the electrolysis was for 30 minutes. No gas was evolved at the anode. A dark, loosely-adhering solid was formed at the anode, and a deposit, presumably of metallic lead, accumulated upon the cathode.

Expt. 16.—The material deposited upon the anode during this experiment, in which the conditions prevailing in Expt. 15 were duplicated, was found to explode on heating. It dissolved slightly in cold, and quite readily in hot water. The solution showed the characteristic reactions of lead salts and of trinitrides. The conclusion that the deposit consisted of lead trinitride, PbN_6, was substantiated by the calculated corrosion efficiency, and by the absence of any evolution of gas at the anode.

Expt. 17.—An antimony rod 0.5 cm. in diameter extending 8 cm. into the solution was used as the anode in this and the following experiment. The electrolysis covered a period of 30 minutes. No gas was evolved at the anode. A yellow solid was deposited upon the anode, and dropped from it at intervals.

Expt. 18.—The electrolysis was in this case continued for one hour. The yellow product that accumulated upon the anode was found to explode on heating. A portion of this solid was washed upon the filter with successive 10 cc. portions of water. Hydrolysis took place, with the result that hydronitric acid was found in the filtrates, while the color of the solid faded from yellow to white. The white residue was found to be non-explosive, and to contain no N_3. When dissolved in hydrochloric acid this material showed the characteristic reaction of antimony compounds toward hydrogen sulfide. The anode corrosion efficiency was calculated on the assumption that antimony trinitride, $Sb(N_3)_3$, was formed at the anode.

Expt. 19.—An iron anode made of 20 strands of piano wire woven together was employed in Expts. 19 and 20. It was immersed to a depth of 7 cm. in the electrolyte, and was allowed to stand for two hours before the circuit was closed. No evidence of chemical action was observed. As soon as the current was turned on, however, the deep red color of ferric trinitride appeared in the neighborhood of the anode. Gas was evolved at the anode, but not so rapidly as at the cathode. The electrolysis was continued for 80 minutes.

Expt. 20.—The electrolysis was in this case allowed to proceed for 105 minutes. The solution assumed a deep red color, and a small amount of a dark colored substance was deposited upon the cathode. This was soluble in nitric acid, and the solution obtained showed the characteristic tests for iron. Vaporization of the liquid ammonia from the deep red electrolyte resulted in the formation of a brownish red residue. This was found by test to be in all probability an ammono-basic ferric trinitride, the exact composition of which was not determined.

Expt. 21.—A thin strip of nickel 0.25 cm. wide constituted the anode used in this and in the following experiment. This anode extended into the liquid to a depth of 8 cm. The electrolysis covered a period of one hour. Gas was evolved at the anode. A pink deposit gradually formed at this electrode, dropping off from time to time, and in part redissolving in the liquid, to which it imparted a decided brownish red coloration. The solid was found to explode on heating. On treatment with water the substance turned green, and gradually dissolved, forming a green solution, from which later a heavy green precipitate settled out. This precipitate was found to be explosive, and to contain nickel and N_3. It was undoubtedly a basic nickel trinitride formed by hydrolysis of the nickel trinitride, or possibly ammono-basic nickel trinitride formed in the cell. The washed residue differed from the original deposit in that it was insoluble in water and in ammonium trinitride solutions.

Expt. 22.—The electrolysis was continued over a period of 74 minutes. The observations made were corroborative of those described in the preceding paragraph. A very faint deposit was formed on the cathode in both of these experiments.

Summary.

In the present article are recorded the results of a series of experiments upon the behavior of various metallic anodes in a liquid ammonia solution of ammonium trinitride.

It has been shown that copper anodes undergo electrolytic corrosion to an extent indicating the formation of some cuprous trinitride, CuN_3, with the cupric trinitride CuN_6 formed as the main product. No gas was liberated at the anode.

With silver, cadmium, lead, and antimony anodes, the corrosion resulted in the formation of the normal trinitrides AgN_3, CdN_6, PbN_6, and SbN_9, without liberation of gas at the anode. The corrosion efficiency as calculated on the basis of the quantitative formation of these compounds was found to be slightly in excess of 100%. This is probably not attributable to ordinary experimental error, but either to a slight mechanical or chemical corrosion, or else to a tendency toward the formation of unstable compounds containing the metals in a lower state of valence.

The aluminum, iron, and nickel anodes were found to undergo corrosion accompanied by liberation of nitrogen gas, as the result of which the efficiency fell far below 100%. The aluminum anode became coated with a bulky, pyrophoric scale of varying color and texture. Deep red ferric trinitride, FeN_9, was obtained in solution when the iron anode was employed, but this product was ammonolyzed, yielding an ammono-basic ferric trinitride. Upon the nickel anode a pink deposit, presumably an amono-basic nickel trinitride, was formed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE MIDVALE STEEL AND ORDNANCE COMPANY.]

AN ELECTROMETRIC METHOD FOR THE DETERMINATION OF FERROCYANIDES DEPENDING ON A CHANGE IN OXIDATION POTENTIAL.

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In connection with some work in this laboratory, it became necessary to analyze potassium ferrocyanide solutions accurately. The oxidation of hydroferrocyanic acid by excess of iodine followed by titration with thiosulfate in the presence of alkali bicarbonate as proposed by Rupp and Scheidt[1] has been shown to be inaccurate.[2] Knublauch[3] titrates a sulfuric acid solution of the salt with copper of zinc sulfate, using a ferric salt as indicator. Smith's electrolytic method[4] would not distinguish between ferro- and ferricyanide ion if such were necessary. DeHaen[5] titrated a sulfuric acid solution with permanganate, but the difficulty of determining the end-point in a yellow solution of ferricyanide is mani-

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[1] *J. Soc. Chem. Ind.*, 21, 1099 (1902).

[2] Sutton, *Volumetric Anal.*, 10th Ed., p. 217.

[3] *Ibid.*, p. 219.

[4] *Electro-Analysis*, 5th Ed., 1912, p. 302.

[5] *Ann. Chem. Pharm.*, 90, 160 (1854).