The conductivity of some very pure toluene was measured, and a solution of iodine prepared in this solvent, but not the slightest increase in conductivity due to the iodine present could be detected.

It seems not unlikely that the feeble conducting power of the alcoholic solutions of iodine, when first prepared, which are brown in color, is due to the dissociation of a compound formed between the alcohol and iodine. This compound is probably dissociated, however, only to a very small extent.

Summary.

(1) The conductivity of solutions of platinum tetraiodide in ethyl alcohol have been measured.

(2) The molecular conductivity of these solutions increases with the dilution and attains a constant value at dilutions of about 600 liters.

(3) The conductivity of solutions of iodine in alcohol increases with the time reaching a maximum value in about 25 hours.

(4) The velocity of the reaction which probably accounts for this increase in conductivity is greatly accelerated by the presence of platinum black.

(5) The initial specific conductivity of 0.1 *N* iodine in ethyl alcohol amounts to 2.4×10^{-6} reciprocal ohms.

(6) It is suggested that the brown color of the alcoholic solutions of iodine is due to the formation of a compound between the solvent and solute which is feebly ionized, giving the low initial conductivity observed.

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CONTRIBUTIONS TO THE ELECTROCHEMISTRY OF HYDRONITRIC ACID AND ITS SALTS. II. THE REDUCTION OF HYDRONITRIC ACID BY CUPROUS OXIDE.

BY J. W. TURRENTINE AND RAYMOND L. MOORE.

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In a previous communication[1] it was shown that corrosion efficiencies exceeding 100% were obtained when the metals magnesium, aluminium and zinc were made anode in a 2% sodium trinitride solution. In some instances the efficiencies approached 200%, the calculations being based on the cathode values obtained from a copper coulometer, and on the electrochemical equivalents of those metals computed from the valence normally displayed by them.

To account for the anomalously large values obtained under the conditions existing in these experiments, it was deemed plausible to hypothesize for those elements electrochemical equivalents twice as large as those ordinarily attributed to them. To do so it was necessary to consider them as dissolving electrochemically as metals of a lower valence. Thus,

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[1] THIS JOURNAL, 33, 803 (1911).

electrochemical equivalents calculated for monovalent magnesium and zinc gave corrosion efficiencies which appeared to conform with Faraday's law, while those obtained for the same metals as divalent elements manifestly could not so conform. Other reactions into which these elements are known to enter make it necessary to hypothesize for them valences lower than that normally manifested by them.

Furthermore, in the experiments referred to, gaseous nitrogen was evolved at the anode in every instance, thus seemingly increasing the electrochemical efficiency.

In the stable compounds of magnesium and zinc, those elements exhibit only divalence, from which it may be concluded that compounds in which they exhibit monovalence are sufficiently unstable to make their isolation difficult, or impossible. So, such compounds, forming at an anode undergoing corrosion, must break down practically instantaneously to the more stable form. The change of the metal from the monovalent to the divalent form is an oxidation and therefore involves a reduction of the oxidizing agent.

In a previous research[1] the same explanation was advanced for a similar anomalous behavior of magnesium and aluminium anodes. In substantiation of the explanation, an evolution of hydrogen at the anode was observed. This was taken to be a product of the reaction between the unstable metallic compounds and water—being a reduction of water.

In the study of the electrochemical corrosion of metals in sodium trinitride solution, the gas evolved at the anode was nitrogen, with, perhaps, in some cases, a small proportion of hydrogen. Nitrogen, normally, would be evolved at the anode in such a solution, resulting from the discharge of the nitride ions, if the corrosion were not quantitative.[2] However, even then, in instances, the equivalent in nitrogen of the corrosion deficiency was exceeded. Clearly, the indication was that some nitrogen was being liberated through a secondary, anode reaction; and, as hydrogen was not evolved, it appeared that the oxidation was being effected by some substance capable of yielding nitrogen as a reduction product. Such a substance was the sodium trinitride, or the nitride ion.

The reduction of hydronitric acid has been shown to yield ammonia under certain conditions.[3] A reaction was proposed, therefore, which considered the formation of ammonia as well as the evolution of nitrogen. This reaction may be represented by the equation:

$$(1)\quad 4M^{(I)}N_3 + 6H_2O = M^{(II)}N_6[+ 3M^{(II)}(OH)_2] + 2NH_3 + 2N_2$$

In substantiation of the proposed reaction, the evolution of nitrogen having been determined, the solution which had been undergoing elec-

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[1] "Reversed Electrolysis," *J. physic. Chem.*, 12, 448 (1908).

[2] Szarvasy, *J. Chem. Soc.*, 77, 603 (1900).

[3] Cf. reference to literature, THIS JOURNAL, *loc. cit.*

trolysis (with zinc anode) was analyzed for ammonia, with affirmative results. Furthermore, in the solution in which magnesium anodes were corroded, hydrazine also appeared to be present, in addition to ammonia. To account for the additional reduction product, the following equation was proposed:

(2) $8M^{(I)}N_3 + 10H_2O = 3M^{(II)}N_6[+ 5M^{(II)}(OH)_2] + 2NH_3 + N_2H_4 + N_2$

Such reactions as these should lend themselves to experimental verification. While it may not be possible to prepare at will magnesious, aluminous, or zincous compounds, and to permit them to react with hydronitric acid, it should be possible to induce reactions, in a general way similar to those proposed, with metallic compounds, more stable than the hypothetical magnesium and zinc compounds, but still easily oxidized.

It was deemed possible that cuprous compounds might be induced to react with hydronitric acid in a manner analogous, if not similar, to that hypothesized for magnesious, zincous and aluminous compounds. However, it was recognized that the former should be a weaker reducing agent than the latter, judging by their relative positions in the electrochemical series; and that, if the liberation of the so-called nascent hydrogen functioned in the reduction by the latter, the cuprous compound could not effect the desired reduction of the hydronitrogen.

The reactions, then, between a cuprous compound and hydronitric acid, or the trinitride ion, should result in either the precipitation of a mixture of metallic copper and cupric trinitride,[1] a reaction analogous to that of sulfuric acid with cuprous oxide in the cold, or in the oxidation of the copper to the cupric condition with the formation of ammonia, or of ammonia and hydrazine, within the solution, and with the evolution of gaseous nitrogen. The demonstration of the occurrence of such a reaction with cuprous compounds and hydronitric acid, it was believed, would be acceptable as a sort of proof of the correctness of the proposition that reactions of the same type occur at magnesium and zinc anodes in trinitride solutions.

To reproduce chemically, then, or to analogize, the hypothetical reactions induced electrochemically, the experiments to be described in the following paragraphs were performed:

Historical.—Curtius and Rissom[2] prepared compounds of copper with hydronitric acid by treating (1) copper sulfate with sodium trinitride, in aqueous solution, and (2) by allowing an aqueous hydronitric acid solution to react with metallic copper. In both cases, brown-yellow, crystallin salts were obtained, difficultly soluble in water, the one prepared

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[1] Cupric trinitride is a sparingly soluble body. Cf. Curtius and Rissom, *J. prakt. Chem.*, **58**, 261 (1898).

[2] *Loc. cit.*

from copper sulfate showing the composition corresponding to the formula CuN_6. While, superficially, both substances were identical, the authors having in mind the analogy which appeared to exist between hydronitric acid and the halogen hydracids, expected to obtain a cuprous compound from the interaction of metallic copper and hydronitric acid, corresponding to cuprous chloride, obtainable from the interaction of metallic copper and hydrochloric acid. In a later communication,[1] Curtius mentions the existence of cuprous trinitride, obtainable by treating cuprous oxide with hydronitric acid. This compound was described as deep red in color.

Dennis and Isham[2] prepared cupric-ammonium trinitride ($CuN_6.2NH_3$) and cupric-pyridine trinitride ($CuN_6.2C_6H_5N$), crystallin compounds.

In the corrosion of copper anodes in sodium trinitride solution, copious precipitates, yellow in color, were obtained.[3] This was taken to indicate that copper was dissolving from the anode in the cuprous condition and was being precipitated subsequently as cuprous hydroxide by interaction with sodium hydroxide from the cathode region.

Experimental.

Preparation of Material.—Hydronitric acid was prepared by the distillation of a solution of sodium trinitride (commercial), obtained from Raschig, acidified with sulfuric acid. The distillate was diluted to an approximately 2% concentration.

Cuprous oxide was precipitated by glucose from an alkaline double tartrate solution. This was washed repeatedly with distilled water. Other portions were prepared by electrolyzing a cold solution of sodium chloride between copper electrodes.

The Interaction of Hydronitric Acid and Cuprous Oxide.—On the addition of hydronitric acid to yellow cuprous oxide, the latter quickly changed from the granular to a flocculent condition, becoming much more bulky. Its color changed simultaneously from the reddish yellow of the cuprous oxide to a brown yellow.[4] The precipitate reacted with concentrated hydrochloric acid, yielding a white solid, presumably cuprous chloride. With concentrated sulfuric acid, a precipitate of dark red, metallic cop-

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[1] *Ber.*, 23, 3023.

[2] THIS JOURNAL, 29, 18 (1907).

[3] *Ibid.*, 33, 803 (1911), see p. 824.

[4] The color of the precipitate as first formed appears to be a function of the color of the cuprous oxide used. If that be yellow, the color of the precipitate obtained with hydronitric acid is more yellow; if the color be red, the precipitate obtained is at first red. This fact probably accounts for Curtius' statement (*Ber.*, 23, 3023) that cuprous trinitride is red. As the transformation from cuprous oxide to the nitrogen compound is, of course, not an instantaneous one—one of the reacting substances being a solid—the first colors obtained are composit of those of the oxide and the nitrogen compounds resulting. In the light, the color of the cupric trinitride eventually prevails and the substances become dark brown.

per resulted. These reactions are characteristic of cuprous compounds and show the presence within the precipitate of some cuprous compound. The compound was soluble in ammonium hydroxide and ammonium chloride solutions. In the latter a colorless solution resulted, turning blue in contact with the air. The solid, on exposure to air, rapidly became dark brown and on drying was extremely explosive (CuN_6?); on standing in a test tube, covered with its mother liquor, but exposed to diffused sunlight, its color changed from yellow to the dark brown of cupric trinitride. The darkening in color occurred earlier, and was more intense on the side toward the source of light. This change was accompanied by a slow *evolution of gas*. The supernatant liquid was straw-yellow in color,[1] from which, by the very careful addition of dilute ammonium hydroxide, with heating, there was produced a slight yellow precipitate, soluble in a slight excess of the precipitant. This was taken to be cuprous hydroxide. To other portions of the supernatant liquid was added potassium hydroxide. On warming, *ammonia was evolved*, as was attested both by litmus paper and the sense of smell. Tests for hydrazine with Fehling's solution, applied to the supernatant liquid, gave negative results.

The presence of sulfuric acid (5 cc. 6 N to 10 cc. 2% HN_3 soln.) retarded the color changes; however, the effervescence produced by the reaction between the cuprous oxide and hydronitric acid was more marked in its presence, and the production of ammonia was quite as marked. Dilute sulfuric acid added to the solid after it had become black from exposure to the light restored the original pale yellow color, the superficial coating of dark brown solid dissolving in the acid to a blue solution.

While in every instance where the precipitate was exposed to the light it turned dark brown, when kept in the dark it became white and remained so seemingly indefinitely. Its supernatant liquid, acidified with hydronitric and sulfuric acids, gradually assumed the blue color of the cupric ion.

Small portions of the white precipitate were exposed to the focused light of a carbon arc (15 amp., 110 volt) for various lengths of time, an exposure of 5 sec. being sufficient to turn the solid a dark brown. At the same time there was a marked evolution of gas. The coloration was only superficial, the dark color on the surface protecting the colorless compound beneath. This became evident on stirring.

In order to determin the nature of the gas evolved, a portion of the cuprous oxide, in a 15 cc. test tube, was treated with 10 cc. hydronitric acid solution and 5 cc. 6 N sulfuric acid.[2] The tube was closed with a

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[1] THIS JOURNAL, 33, 803 (1911), see p. 824.

[2] The sulfuric acid was added because in its presence, it has been noted, the effervescence is more rapid. The presence of the acid, however, is not essential to the effervescence.

one-holed rubber stopper through which was inserted a capillary delivery tube. This was bent at the proper angles so as to deliver the gas into an inverted buret, filled with water, to serve as a gas holder. The test tube was so filled that when the stopper was forced into position all of the gas and some of the liquid were forced out through the capillary. Thereafter, any gas delivered into the gas holder was only that evolved fron the reacting substances within the tube.

At the end of about one week 14 cc. of gas had been collected. This was analyzed in separate portions for oxygen and hydrogen, respectively, by shaking with alkaline pyrogallol in a Hempel pipet and by passing over freshly ignited palladium black, at a temperature near 100°. The first portion of 5.8 cc. was mixed with 12.6 cc. of pure nitrogen,[1] making a total volume of 18.4 cc. The volume remaining after the absorption in alkaline pyrogallol and palladium black was 18.2 cc., showing a contraction of 0.2 cc. The second portion, 8.8 cc., was added to the residues from the preceding analysis, making a total volume of 27.0 cc. The residue from the palladium absorption measured 26.8 cc. showing an absorption of only 0.2 cc., a value hardly outside the limits of experimental error. On the basis of these analyses (and on others of volumes of gas obtained under like conditions from other compounds reacting with hydronitric acid) the gas evolved under these experimental conditions was taken to be practically pure nitrogen.[2]

The foregoing observations indicate that cuprous oxide reacts with hydronitric acid to form an unstable compound containing nitrogen which, in contact with an excess of the acid, undergoes gradual transformation into cupric trinitride. The transformation, being an oxidation, results in the reduction of the oxidizing agent, hydronitric acid, and yields, as the reduction products of that acid, ammonia and nitrogen.

The following equation is proposed to represent qualitatively the reduction of hydronitric acid by cuprous oxide:

$$Cu_2O + 5HN_3 = 2CuN_6 + H_2O + NH_3 + N_2.$$

They indicate further that this transformation takes place more readily in the presence of sulfuric acid, a fact which would be explicable on the supposition that the protective coating of cupric trinitride, difficultly soluble in water, is constantly being removed by solution in sulfuric acid.

There is evidence also that the oxidation of cuprous trinitride by hydronitric acid is a reaction that is greatly accelerated by light.

Analysis.—Numerous attempts were made to determin quantita-

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[1] From previous analyses; added to secure a convenient volume.

[2] The activity of the palladium black was repeatedly tested with volumes of hydrogen prepared from zinc and sulfuric acid; the hydrogen was invariably absorbed quantitatively.

tively the copper and nitrogen content of the compound produced from cuprous oxide. On account of its lack of stability in the air and light, portions were prepared and were filtered, washed and dried in an atmosphere of hydrogen, the entire operation being carried out in red light, or in the dark. Because of its supposed explosive character, it was filtered in small amounts on separate filters. To this purpose a Bruehl receiver for use in vacuum distillations was adapted. The rack for holding the receiving tubes was supported on a single glass foot and was held upright by wedges. In it were placed five funnels containing tared filter papers. The side apertures were provided with rubber stoppers through which were inserted glass tubes for the entrance and exit of a stream of hydrogen. The tube in the lower side aperture was so bent as to enter a slight depression in the lowest part of a sloping false bottom of paraffin, and was provided at its inner end with a short section of rubber tubing to make a closer contact with the bottom of the depression. Thus all liquids coming from the various filters were made to flow into the depression and were forced thence out through the exit tube. In this way the last drop of liquid could be blown out by the issuing stream of hydrogen. The stem of a dropping funnel entered through the opening in the lid. It was bent at an angle and could be turned so as to deliver solutions and suspended precipitates into the various filters as desired. Wash liquids were admitted in a similar manner.

The air was displaced in the filtration vessel by hydrogen. Portions of the yellow substance prepared and filtered in the manner indicated were washed with distilled water, absolute alcohol and ether, previously freed from air by shaking with, and maintaining under hydrogen. They were then dried for 48 hours by passing a stream of hydrogen, dried over concentrated sulfuric acid, through the apparatus. After the washing, the vessel was enveloped in black paper to exclude light. The precipitates, together with the papers holding them, were then weighed between tared watch-glasses. It was noted that they lost weight rapidly on the balance pan. They were transferred to graduated flasks containing ammonium hydroxide; after they had dissolved, the flasks were filled to the mark with water.

For the determination of hydronitric acid, aliquot portions were transferred rapidly to distilling flasks containing sulfuric acid in excess over that requisite to the neutralization of the ammonium hydroxide and were distilled in the usual way into receiving solutions of silver acetate.

Copper was determined electrochemically from the solution remaining in the distilling flask after the distillation.

Strictly concordant results were obtained for both nitrogen and copper; these were found to be present in approximately equivalent amounts, with copper in slight excess; of nitrogen there was found 29.6 % and of copper 49.1%, equaling 78.7%. If water of combination be considered as making up the balance, these values are in close agreement with the formula $CuN_3.2H_2O$.

From a sample representing 0.0348 g. material was obtained 0.0368 g. AgN_3, equivalent to 0.0103 g. N_3 (= 29.6%). This weight of nitrogen, on the basis of the formula $CuN_3.2H_2O$, is equivalent to 0.0156 g. copper, (found, 0.0167 g. copper) and to 0.0088 g. water; total, 0.0347 g.

Under the conditions existing in these experiments, one would expect to obtain cuprous trinitride. In the absence of a determination of water, it cannot be said with definiteness whether the formula proposed represents the actual composition of the compound, or is in agreement with the values obtained only through a coincidence.

The excess in copper over nitrogen, it may be pointed out, is to be expected when it is remembered that a reaction between a solid and a liquid may quite easily be incomplete, due to the protective coating on the solid of the product of the reaction, where the product is likewise a solid. It is to be expected, then, that a small amount of cuprous oxide would still be present.

The application of the results described in the foregoing paragraphs to the anomalous electrochemical corrosion of magnesium and zinc in sodium trinitride solution has been made, through predicted analogies, in the preamble. They tend to support, furthermore, the interpretation of the phenomena observed when copper is made anode in that solution. The formation of the highly explosive black compound on the anode may be explained as the result of the nitridation of the soluble cuprous trinitride to the insoluble cupric compound.

Summary.

In the reaction between hydronitric acid and cuprous oxide the acid plays the role of an oxidizing agent and is reduced to ammonia and nitrogen.

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THE ACTION OF HYDRONITRIC ACID ON CUPROUS CHLORIDE AND METALLIC COPPER.

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Cuprous Chloride.—When cuprous chloride is treated with dilute hydronitric acid it is transformed from the white, crystalline form into a bulky, yellow and flocculent condition. When the latter substance is treated with hydrochloric acid, the white crystalline condition is resumed, a fact which indicates that the reaction is reversible.

Cuprous chloride, prepared by one of the well known methods, was washed by decantation with distilled water until yellow tints began to