

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.<sup>1</sup>

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<sup>2</sup> 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.

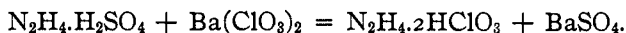
<sup>1</sup> A chapter from the thesis of the author submitted to the Faculty of Cornell University, May 1908, for the degree of Doctor of Philosophy.

<sup>2</sup> *Gazz. chim. ital.*, **37**, 32 (1907).

Salvadori prepared hydrazine monochlorate by treating a solution of chloric acid of known concentration with such a volume of a solution of hydrazine hydroxide as contained an amount of the base equivalent, molecule per molecule, to the chloric acid. After evaporation to an oily consistency over sulfuric acid, the salt was precipitated from the solution by the addition of alcohol and was washed with absolute alcohol. Laminated crystals were obtained. These were shown to be soluble in water, less soluble in alcohol and insoluble in ether, benzene, and chloroform. The salt proved to be instable and easily explosive on being subjected to a percussion.

The monoperochlorate of hydrazine was obtained in crystalline form directly from evaporation on the water bath. It crystallizes from water with one-half molecule of water of crystallization. It melts at  $131-2^{\circ}$ ; at  $13^{\circ}$  water dissolves 67.56% by weight of the salt. The compound was further studied with a view to its explosibility, its rate of decomposition being determined. The explosion of this compound, when induced by percussion, is said to be equal to that of the perchlorate in violence.

**Hydrazine Dichlorate.**—This compound was prepared by treating a solution of hydrazine disulfate with the theoretical amount of barium chlorate in solution, the reaction taking place in agreement with the equation,



The barium sulfate was removed by filtration. The filtrate was subjected to qualitative tests for both sulfate and barium and was found to be free from these two most probable impurities. Portions of this solution were then evaporated *in vacuo* over concentrated sulfuric acid, the temperature of the solution being maintained most of the time at  $0^{\circ}$ , or below. On the appearance of crystals in the concentrated solution, decomposition began to occur with the evolution of chlorine gas and continued with accumulating rapidity, finally resulting in the entire destruction of the hydrazine compound present. When the crystallization was allowed to take place under the microscope, a similar decomposition took place so that the compound could not be further studied there. Attempts to study the crystallized compound were not made.

**Hydrazine Diperochlorate.**—Hydrochloric-acid-free perchloric acid was obtained on treating a solution of perchloric acid contaminated with hydrochloric acid, a decomposition product, with a solution of silver perchlorate. The latter was prepared by dissolving silver carbonate in perchloric acid; it was added titrimetrically to the impure acid until the last drop produced no further precipitation of silver chloride. By means of the purified acid a solution containing 13.5 g. of barium hydroxide,  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , was neutralized and was then treated with the theoretical amount of hydrazine sulfate, 5.56 g.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , in solution to form

hydrazine diperchlorate. After filtering to remove barium sulfate and after testing the solution for traces of sulfate and barium, the solution was evaporated to crystallization.

In the earlier part of this work the solutions of the diperchlorate were evaporated in desiccators over concentrated sulfuric acid and under reduced pressure. But when it was found that the substance was so stable as to permit it, the evaporations were conducted more expeditiously on the water bath, or on steam coils with the aid of an air blast. When evaporated in this way until crystallization begins to take place and then cooled the entire mass becomes solid with laminated crystals. If evaporated more slowly, beautiful, brilliant plates may be obtained.

Hydrazine diperchlorate crystallizes with two molecules of water of crystallization. This was determined by desiccating *in vacuo* over sulfuric acid, until there was no further change in weight, a carefully weighed sample of the crystals which previously had been allowed to come to constant weight in the open air of a dry, steam heated room. Table I gives the figures obtained.

TABLE I.

No.	Wight sample. Gram.	Loss. Gram.	Percentage loss.	Theory for 2 H <sub>2</sub> O.
1.....	0.1065	0.0136	12.77	13.35
2.....	0.1499	0.0190	12.65	13.35

Upon dehydration the crystals effloresced. The effloresced salt, however, did not regain its water of crystallization when again exposed to the open air of the laboratory. It is probable, therefore, that the low results were due to a partial dehydration of the crystals before they were transferred to the desiccators.

**Analysis.**—The nitrogen content of the diperchlorate was determined by the method described by Rimini.<sup>1</sup> The samples for analysis were dissolved in about 25 cc. of water in tall, narrow mouthed Erlenmeyer flasks. An excess of a standard solution of potassium iodate was then run in from a buret. After boiling off the liberated iodine, the solution was cooled and was mixed with 15 cc. 1 : 4 sulfuric acid. Sufficient potassium iodide in crystalline form was then added to completely decompose the excess of iodate and also to dissolve readily the liberated iodine; thereupon the free iodine was rapidly titrated, with starch solution as indicator, with a standard solution of sodium thiosulfate.

TABLE II.

Weight taken, g.....	0.0201	0.0201	0.0201	0.0201	0.0201	0.0201	0.0117	0.0117
Nitrogen found.....	11.00	10.23	11.00	10.85	10.48	10.41	10.41	10.14%
Average.....	10.56%		Theory..... 10.41%					

<sup>1</sup> *Gazz. chim. ital.*, [1] 29, 265 (1899); *Atti. accad. Lincei*, [5] 15, II, 320; *Chem. Zentr.*, 11, 1682 (1906).

Chlorine was determined in the perchlorate by the following method: A weighed sample of the salt was transferred to a platinum crucible and was intimately mixed with ten times its weight of pure, chlorine-free sodium carbonate. On account of the difficulty of mixing the dry crystals of the salt with the sodium carbonate and the danger of an explosion on grinding the salt in a mortar, the crystals, after being transferred to the crucible, were dissolved in a drop of warm water and the sodium carbonate was added all at once so as to absorb immediately all the solution and thus prevent any loss of it by the rapid effervescence which took place on adding the carbonate to the acid perchlorate solution. The carbonate with the absorbed perchlorate could then be mixed easily with a stirring rod. After covering the crucibles tightly, they were heated on a sand bath for several minutes to drive off the excess moisture from the contained carbonates and were gradually heated to bright redness over Bunsen flames. The crucibles and fused mass, while still hot, were plunged into cold water in a beaker, to loosen the mass from the crucible and were heated on the sand bath until the fused substance had completely dissolved. The resulting solutions were then made slightly acid with nitric acid, the chlorine was precipitated with silver nitrate in slight excess, more nitric acid was added, and the solutions were boiled. The silver chloride was filtered, dried and weighed on a Gooch filter. In Table III are given the results obtained, calculated on the basis of the hydrated salt containing two molecules of water of crystallization.

TABLE III.

No.	Sample taken. Gram.	AgCl found. Gram.	Chlorine found. Per cent.
1.....	0.1385	0.1458	26.01
2.....	0.1388	0.1465	26.09
3.....	0.1155	0.1222	26.15
4.....	0.0768	0.0759	26.06
5.....	0.0560	0.0609	26.87
6.....	0.1163	0.1259	26.74
Average.....			26.32
Theory.....			26.36

TABLE IV.

No.	Sample taken. Gram.	AgCl found. Gram.	Chlorine found. Per cent.
1.....	0.0257	0.0276	30.67
2.....	0.0868	0.1069	30.44
3.....	0.0675	0.0826	30.26
Average.....			30.46
Theory.....			30.44

Analyses were also made of the anhydrous salt. These are shown in Table IV.

These results established a formula for hydrazine diperchlorate as  $N_2H_4 \cdot 2HClO_4 \cdot 2H_2O$ .

Hydrazine diperchlorate is not only efflorescent but is also deliquescent. In moist air it takes up water rapidly and dissolves in it. A portion of 0.079 g. exposed to the open air, gained in three and one-half hours 0.48 g. in fifteen and one-half hours, 0.53 g. of absorbed water.

Its solubility is indicated by the following figures determined without

the use of the more refined methods: At  $29^{\circ}$ , 100 parts of water dissolve 102 parts of the hydrated salt. Solution in water takes place with an absorption of heat. In absolute alcohol, 2.8 parts are soluble in 100 parts of the solvent; in ether, about 1 part is soluble in 100 parts of the solvent. It was not determined whether the salt which crystallized from absolute alcohol was the anhydrous or the hydrated diperchlorate, or the monoperchlorate.

Considerable difficulty was encountered in determining the true melting point of hydrazine diperchlorate. When this operation was conducted in capillary melting point tubes, incipient fusion took place at  $95^{\circ}$ . But so gradual was the change from the solid to the liquid condition, and so marked was the decomposition before the distinctly molten condition had been reached, that it is not safe to say at what temperature the pure salt actually melts.

**Crystalline Structure.**—Professor A. C. Gill, of the Department of Geology, Cornell University, has had the very great kindness to make a crystallographic examination of both the mono- and the diperchlorate of hydrazine.

The diperchlorate forms colorless, tabular crystals which are shown by their optical behavior to be orthorhombic.

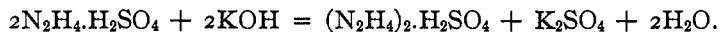
The acute bisectric emerges exactly normal to the large faces, and extinction is parallel to the longer sides. The substance is optically negative with an optical angle of  $30^{\circ}$  to  $40^{\circ}$ (?) and remarkably strong dispersion of the optical axes.

On attempting to extend and verify these observations two or three weeks later, only crystals of the monacid salt could be found. (As the platinum wire with which they were taken out had also been used with the monacid salt, it is possible that the change may have been in a measure induced by the presence of that compound.) An examination of the crystals of the monoperchlorate showed that they were probably monoclinic. The somewhat elongated tablets showed the oblique emergence of one axis of a negative biaxial interference figure, with large optical angle. The plane of the optical axis is the clinio-pinacoid. Like the diacid compound, the double refraction is strong, but the dispersion is not marked. In the prism zone, the following angles were observed (in the sequence given), starting from the large tabular face:  $49^{\circ} 10'$ ,  $57^{\circ} 20'$ ,  $38^{\circ} 50'$ ,  $19^{\circ} 30'$ , and  $15^{\circ} 10'$ .

**Other Properties.**—The diacid salts of hydrazine exhibit strong acid properties. Bach<sup>1</sup> has shown that the dichloride of hydrazine produces the inversion of cane sugar in the same way as does hydrochloric acid in the presence of a chloride. This salt in dilute solutions yields 4 ions.

<sup>1</sup> *Z. physik. Chem.*, 9, 258 (1892).

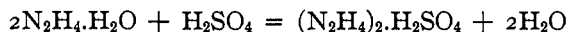
Stolle<sup>1</sup> suggests the use of the disulfate for standardizing solutions of caustic alkalis. On titration, the disalts go over into the monosalts, as indicated by the equation,



Curtius<sup>2</sup> makes use of this fact to determine titrimetrically hydrazine hydrate with standard sulfuric acid. His statement of the reaction by the equation,



however, is manifestly incorrect, as Stolle's work, as well as numerous titrimetric determinations of hydrazine hydrate in this laboratory, show. The hydrazine disulfate, being largely hydrolyzed in aqueous solution, indicated as the final product in the reaction represented in Curtius's formula, must needs give an acid reaction to indicators. One must, then, necessarily regard this error in the paper of Curtius's as simply an oversight, especially as, when one examines his calculations, it is seen that actually they are not based on this equation, but rather on the equation,



which is the correct one.

In Table V are given the results of a comparison of the methods of Curtius and Rimini when applied to the analysis of anhydrous hydrazine. These analyses were made incidentally in a different research and are used here in substantiation of the preceding statements. The figures in Col. 1 are arrived at from calculations based on Curtius's equation, those in Col. 2, on the corrected equation as given above, and those in Col. 3, are obtained from calculations based on Rimini's iodate method. Each sample of the anhydrous hydrazine served for two analyses. The weighed samples of the anhydrous substance were dissolved in water and titrated with standard acid. On the same solution was then conducted an analysis by the method of Rimini.

TABLE V.

Weight in grams of  $\text{N}_2\text{H}_4$  found by

No.	Curtius's method.		Rimini's method. 3.
	1. As stated.	2. Corrected.	
1.....	0.030	0.060	0.061
2.....	0.0294	0.0588	0.0605
3.....	0.02998	0.0596	0.0601
4.....	0.0304	0.0608	0.0597
5.....	0.007	0.014	0.0142
6.....	0.012	0.024	0.0204
7.....	0.0298	0.0596	0.0600
Average.....	0.02406	0.04812	0.04799

<sup>1</sup> *J. prakt. Chem.*, [2] 66, 332-8 (—)

<sup>2</sup> *Ibid.*, 42, 521 (1890).

An examination of the hydrazine dichloride, dichlorate and diperchlorate revealed the fact that these salts also are susceptible of titration with solutions of alkali, methyl orange being used as indicator, and of being thereby quantitatively determined, as was shown by Stolle to be the case for the disulfate. Hydrazine diperchlorate also dissolves carbonates with the evolution of carbon dioxide. The dichloride on heating to  $180^{\circ}$  gives up quantitatively one molecule of its acid,<sup>1</sup> thus resulting in the monochloride. The diperchlorate probably possesses the same property, this surmise being founded on the observation that in a vacuum desiccator and over sulfuric acid the diperchlorate exhibits a marked vapor pressure of perchloric acid, the desiccator becoming filled with the vapor of this acid.

While the pure and dry hydrazine diperchlorate seems to be quite stable, the impure salt, after standing for several months at room temperature, deteriorates, and becomes discolored, assuming a yellow hue. In solution a gradual loss of perchloric acid occurs and crystals of the monoperochlorate form.

The substance, on being struck with a metal hammer, explodes with a loud report.

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[CONTRIBUTION FROM THE HOSPITAL OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK.]

## A METHOD FOR THE TITRATION OF SMALL AMOUNTS OF HALIDES.

BY FRANKLIN C. MCLEAN AND DONALD D. VAN SLYKE.

Received March 5, 1915.

The accuracy, convenience, and wide applicability of the Volhard method for titration of halides has made its use nearly universal. The fact that 1 drop, or about 0.05 cc., of 0.1 *N* solution is required to give the color change satisfactorily at the end point, however, makes it necessary to have under ordinary conditions at least 0.5 milligram molecule of halide, equivalent to 5 cc. of 0.1 *N* silver nitrate, in order that the accuracy of the titration may be within 1%.

The necessity for an accurate means of determining chlorides in small amounts has forced us to seek a titrimetric method with a more sensitive end point, so that less material than is required by the Volhard method may be analyzed with equal percentage accuracy. An iodometric method, with a manipulation almost identical to that of the Volhard titration, proved thoroughly practicable. Like the Volhard, it permits titration in an acid solution, and requires the use only of stable standard solutions, while because of the more sensitive color change it permits one to use

<sup>1</sup> Cartius, *J. prakt. Chem.*, [2] 39, 27 (1889).