VOL. XX. [MAY, 1898.] NO. 5.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, NO. 9.]

THE OXYHALIDES OF ZIRCONIUM.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received March 12, 1898.

I. ZIRCONIUM OXYCHLORIDES.

WE have examined three of these. The first is secured by the evaporation of an aqueous solution of the salt obtained by dissolving zirconium hydroxide in hydrochloric acid. Very large handsome crystals can be secured on slow evaporation over sulphuric acid. These crystals easily dry on porous plates or on filter-paper. Analysis gave:

Zr	28.05
Cl	21.59
Loss	50.46

This loss represents both water and combined hydroxyl or oxygen. These figures correspond to the formula $ZrOCl_2.8H_2O$. One difficulty in the way of securing a correct analysis lies in the constant loss of water on standing exposed to the air. This loss is shown in the following weighings:

	Dates.					
	Oct. 9.	Oct. 11.	Oct. 12.	Oct. 13.	Oct. 15.	Oct. 18.
Weighings	1.2806	1.2796	1.2792	1.2787	1.2779	1.2758

By heating to 135°–140° for six hours a large amount of chlorine is driven off and yet not all of the water. The mass is left only partly soluble. Heated to 100° under a stream of hydrogen chloride the weight was constant and the loss corresponded to

26.84 per cent. of the original weight. The residue is entirely soluble in water. Five molecules of water are thus lost at 100°, and the compound left is $ZrOCl_2.3H_2O$. This formula was confirmed by determinations of both ZrO_2 and Cl. The first formula, $ZrOCl_2.8H_2O$, is the one assigned by Paykull[1] and confirms his results as against those of Melliss.[2] The formula gotten by Herrmann, $ZrOCl_2.9H_2O$, was manifestly obtained from imperfectly dried crystals.

Various experiments on the dehydration of this salt were carried out. Thus a portion placed in a desiccator over fused calcium chloride had lost a large part of its water and was still losing weight after seven months. Another portion was placed over fused calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued although it was very slight. Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear, colorless solution. It contained 53.30 per cent. of zirconium dioxide. This corresponds very nearly to the formula $ZrOCl_2.3H_2O$.

Another form of the oxychloride is gotten by crystallization from concentrated hydrochloric acid. The form of the crystals is apparently similar to that of the crystals from an aqueous solution. It is difficult to free these from excess of acid. Linnemann,[3] by treatment of this with alcohol and ether, secured a fine, crystalline, snow-white, silky body, leaving fifty per cent. of its weight on ignition. This is, however, far from an accurate method for removing the water.

---

[1] *Ber. d. chem. Ges.*, 6, 1467.

[2] *Ztschr. Chem.* (2), 6, 196.

[3] *Chem. News*, 52, 224.

Bailey[1] tried various methods of drying these crystals without success.

It was found that these crystals could be dried under hydrogen chloride at 100°–125° C. At this temperature a white mass soluble in water was gotten which gave on analysis :

	Calculated for $ZrOCl_2.3H_2O$.	Found.
Zr	39.12	38.99
Cl	30.66	29.98

The amorphous (?) form, insoluble in concentrated hydrochloric acid, but easily soluble in water, has been analyzed by Paykull, and he has calculated the formula $2ZrOCl_2.13H_2O$. This insoluble oxychloride is nearly always present during the process of purification by recrystallization from concentrated hydrochloric acid. Repeated boilings with hydrochloric acid fail to dissolve it. A sample was prepared by allowing a very concentrated aqueous solution of the oxychloride to fall drop by drop into concentrated hydrochloric acid. It was washed with hydrochloric acid and then boiled with it. After pouring off the acid the mass was washed with a mixture of nine parts ether and one part alcohol. It was dried between filter-paper. Little assurance could be felt that this mode of drying removed all the hygroscopic moisture. It was analyzed in this condition. Another portion was placed over caustic alkali (after pressing between filter-paper) and yet another portion was dried at 105° in a stream of hydrogen chloride.

The analysis of the portion dried between filter-paper was as follows (no difference was observed in that over caustic alkali after two days) :

	Calculated for $ZrOCl_2.6H_2O$.	Found.
Zr	31.70	31.72
Cl	21.01	20.81

This is therefore in close accord with the formula $ZrOCl_2.6H_2O$. The portion dried under hydrogen chloride was small and only the zirconium was determined. The percentage of this corresponded fairly well with $ZrOCl_2.3H_2O$.

Summarizing our examination of these oxychlorides then, we find that there are three :

---

[1] *Chem. News*, 60, 17.

1. An oxychloride gotten in large, well-formed crystals by crystallization from water. These crystals lose both water and hydrochloric acid on exposure to the air. Their formula is $ZrOCl_2.8H_2O$.

2. An oxychloride gotten by precipitation with hydrochloric acid from an aqueous solution. This is insoluble in hydrochloric acid. It is seen in silky crystals or a white mass of very fine crystals. The formula is $ZrOCl_2.6H_2O$.

3. An oxychloride gotten by crystallization from hydrochloric acid. This has the formula $ZrOCl_2.3H_2O$.

When any one of these is dried at 100°–125°, with a stream of dry hydrogen chloride passing over it, three molecules of water of crystallization are left and the oxychloride has the formula given under 3, namely $ZrOCl_2.3H_2O$. These last molecules of water are lost at a temperature of 180°–210°.

Weibull[1] gives the measurements of the crystals of the oxychloride formed from water. They belong to the tetragonal system, and are optically uniaxial with double refraction.

Several times during the examination of these oxychlorides the formation of a hydrogele was observed. The exact conditions under which it was formed were not determined. The tendency to form this hydrogele is much less than in the case of the bromides and iodides. Similar compounds will be mentioned there.

II. ZIRCONIUM OXYBROMIDES.

Zirconium oxybromides may be formed by decomposing the tetrabromide with water and also by dissolving zirconium hydroxide in hydrobromic acid.[2] It crystallizes from the aqueous solution in fine, transparent, needle-like crystals containing water of crystallization.[3]

Weibull gives the following analyses:

	Calculated for $ZrOBr_2.8H_2O$.	Found. I.	II.
Zr	21.87	20.35	20.83
Br	39.05	41.16	38.70

He says that the crystals are isomorphous with those of the oxy-

---

[1] *Ber. d. chem. Ges.*, *1887*, 1394.

[2] Berthemot: *Ann. chim. phys.*, **44**, 393.

[3] Weibull: *Ber. d. chem. Ges.*, *1887*, 1394.

chloride which seems to be true. They are much more hygroscopic. His two analyses are decidedly discordant and one would judge that the amount of water of crystallization had been decided upon from the analogy to the oxychloride.

The oxybromides described in the following experiments belong to two types with varying degrees of hydration—$ZrOBr_2 + xH_2O$, where $x = 3$, 13 or 14 and $ZrBr(OH)_3 + yH_2O$ where $y = 1$ or 2. All of these compounds are deliquescent and decompose on exposure to moist air, the clear white crystals, often colored pink by free bromine present, melting to a gum, frequently with the evolution of hydrobromic acid. The salts are unstable even in dry air as was found on exposing dried crystals upon a watch-glass in a desiccator containing sulphuric acid. Much hydrobromic acid was evolved in the decomposition.

The crystals were prepared in two ways: either by dissolving pure $Zr(OH)_4$ in dilute hydrobromic acid evaporating upon a water-bath with subsequent additions of forty-eight per cent. hydrobromic acid and repeated evaporation, or a concentrated solution of hydrobromic acid was saturated with $Zr(OH)_4$, evaporated, and the crystals obtained on cooling.

As a rule the crystals obtained were quite soluble in the hot acid but separated at once on cooling. In the heating necessary for the thorough saturation of the hydrobromic acid by the $Zr(OH)_4$, the solution first becomes straw-colored then a deeper red, depending upon the time of the heating. This is evidently due to bromine from the decomposition of some hydrobromic acid.

A difficult problem was the removal of the strong hydrobromic acid mother-liquor and the free bromine nearly always present with the crystals. Of the methods tried to effect this, none proved satisfactory. The crystalline mass in one case was six times washed with ether, the yellowish-red solution, due to dissolved bromine, being decanted. Filtering proved too slow, permitting a rather long exposure of the crystals to the moisture of the air. After this washing with ether the crystals, still slightly yellow colored, were placed in a vacuum desiccator for the removal of the remaining ether. The small glass dish containing the material was allowed to remain thirty-six hours in the vacuum desiccator. The substance was then removed, dried between filter-paper, and analyzed.

	Calculated for $ZrOBr_2.13H_2O$.	Found. I.	II.	III.
ZrO_2	24.01	24.15	24.50	24.60
Br	31.93	....	32.29	....
Loss at 124° C. less HBr evolved	....	....	24.44	....

This substance gave evidence of decomposition after being placed in the weighing bottle.

Another method used for the removal of bromine was washing the colored crystals three times with strong (forty-eight per cent.) solution of hydrobromic acid. Most of the bromine was thus removed although the salt remained slightly yellow, possibly due to the remaining hydrobromic acid. An interruption of the work at this point required the salt in this state to be placed in a desiccator over sulphuric acid. It remained there for several days when the work was resumed. All moisture seemed to be removed and great volumes of hydrobromic acid were given off when the desiccator was opened. The substance had taken on a brownish-red color around the edges but the central portion was perfectly white. To remove the excess of acid the substance was washed quickly three times with small amounts of water. All of these salts are exceedingly soluble in water and the utmost care is necessary to avoid the entire re-solution of the substance. The wash-water was deeply colored by the bromine removed and the salt remained pinkish. It was dried on filter-paper and an analysis gave 24.54 per cent. zirconium dioxide.

This shows that the method of removing the bromine and hydrobromic acid and drying the crystals, did not materially alter their composition. Alcohol did not give satisfactory results.

The ether-washed crystals, after being allowed to stand in a glass-stoppered weighing bottle in the balance case for several weeks, showed evidence of absorbed moisture. They were dried again by pressure between folds of bibulous paper, but they could not in this way be brought back to the same state as before, as shown by the analysis:

	Calculated for $ZrOBr_2.14H_2O$.	Found.	Previously found.
ZrO_2	23.70	23.49	24.50(av.)
Br	30.82	30.58	......

About four grams of these crystals were dried in a glass-stoppered flask under a rapid stream of dry hydrobromic acid at a temperature varying between 100° and 120°. The average temperature was about 110°, and the drying lasted continuously through three and a half days. After cooling, perfectly dry air was drawn through the flask for a little over ten minutes. This was supposed to be but was not long enough as the analysis showed that all the free hydrobromic acid had not been removed. It requires at least thirty minutes for thorough removal. The substance dried down to a hard, white, crystalline solid which was quite soluble in water. The composition of this salt was as follows :

	Calculated for $ZrOBr_2.4H_2O$.	Found. I.	Found. II.
ZrO_2	36.21	34.91	34.82
Br	47.30	50.05	....

It is evident that the assignment of such a formula is largely guess work, but the cost in time and materials was too great for us to repeat the experiment.

Another experiment was carried out as follows :

One hundred cc. of forty-eight per cent. hydrobromic acid solution were saturated with wet $Zr(OH)_4$ by continuous boiling. The solution was never perfectly clear until it was twice filtered through compact filter-paper doubly folded. The clear yellow solution was concentrated by evaporation on the water-bath. The more concentrated it became the redder it was; finally the color was so deep that it appeared almost black. This was due to decomposition of the hydrobromic acid.

After concentration the liquid was cooled and white crystals separated out. On allowing it to stand twenty-four hours, or always when made too concentrated by further evaporation, a red jelly separated on top of these crystals. In trying to wash this jelly from around the crystals, for it was very soluble in water, the crystals were also dissolved. The whole was therefore redissolved and after several attempts a set of prismatic needles one to two mm. in length separated free from the jelly. This jelly was not silicic acid as feared. The mother-liquor was poured off, the crystals quickly washed three times with small amounts of water, dried between filter-paper, and analyzed:

	Calculated for $ZrBr(OH)_3.2H_2O$.	Found. I.	II.
ZrO_2	35.23	34.90	34.34
Br	31.01	30.79	....

The solution was further evaporated and another crop of needle crystals similar to, but much smaller than, the above obtained. They were washed four times in cold water, dried to a powder between filter-paper and analyzed :

	Calculated for $ZrBr(OH)_3.H_2O$.	Found. I.	II.
ZrO_2	37.91	36.86	36.35
Br	33.33	32.49	....

An investigation of the gelatinous oxybromide of zirconium showed that it was a hydrogele. On dialysis the small amount of crystalline oxybromide present passed through the membrane. At the same time the gelatinous compound, if it may be so termed, slowly decomposed into zirconium hydroxide and hydrobromic acid, the latter gradually passing through the septum while the former remained behind.

III. ZIRCONIUM OXYIODIDES.

According to Melliss, zirconium oxyiodide is not formed by dissolving $Zr(OH)_4$ in hydriodic acid. Hinzberg[1] secured an oxyiodide by precipitating a solution of zirconium sulphate with barium iodide in equivalent amounts. The solution was evaporated over sulphuric acid and the crystals washed with carbon bisulphide. The analysis gave $ZrI(OH)_3.3H_2O$.

In our experiments we found that zirconium hydroxide, when precipitated cold, was soluble to a small extent in strong aqueous hydriodic acid or could be dissolved by passing hydrogen iodide into water in which the zirconium hydroxide was suspended. Evaporation of this solution over sulphuric acid or calcium chloride gave needle-like crystals strongly colored with iodine and very hygroscopic. Every attempt failed at getting these freed from excess of iodine and properly dried. Washing with ether or with carbon bisulphide was ineffective. A hydrogele was gotten by acting upon zirconium hydroxide with hydrogen iodide, which formed on drying a hard, horn-like, colored mass insoluble in water and acids. This contained :

---

[1] *Ann. Chem.* (Liebig), 239, 253.

	Per cent.
Zr	32.14
I	27.88
H_2O (by difference)	28.64

It lost only 11.07 per cent. of its weight after three hours' heating at 100°-120°.

UNIVERSITY OF NORTH CAROLINA.

ATROPINE PERIODIDES AND IODOMERCURATES.

BY H. M. GORDIN AND A. B. PRESCOTT.[1]

Received March 12, 1898.

I. ATROPINE ENNEAIODIDE.

IT has been known for a long time that in solutions of atropine salts, as in those of the salts of most other alkaloids, a solution of iodine in potassium iodide gives an insoluble precipitate. The nature of this precipitate has so far as we know not been thoroughly investigated. Jörgensen[2] has obtained and described two periodides of atropine : a triiodide and a pentaiodide Our experience has taught us that in aqueous solutions the capacity of atropine for combining with iodine varies very widely, and the quantities taken up seem to depend upon the concentration of the liquids and even the order of mixing them.

The highest number of iodine atoms which a molecule of atropine can combine with, seems to be nine ; between this and the above-mentioned triiodide lie the other compounds of atropine with iodine which are formed in aqueous solution. The same is true when chloroform is used as a solvent. We reserve for a later date a report upon the exact conditions which are necessary for the formation of any particular periodide of atropine. For the present we wish to say that under the conditions described below we were able to obtain the enneaiodide of atropine, $C_{17}H_{23}NO_3.HI.I_8$, as the sole combination of all the alkaloid, and sufficiently stable.

These conditions are the following : The concentration of the aqueous solution of the atropine salt should not exceed five-tenths per cent.; that of the iodine solution must not exceed one

---

[1] In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopeia of the United States.

[2] *J. prakt. Chem.* [2], 3, 329.