[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM. No. 5.]

A STUDY OF THE ZIRCONATES.

BY F. P. VENABLE AND THOMAS CLARKE.

Received March 6, 1896.

THIS class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl.[1] Of recent years several papers by L. Ouvrard[2]. have appeared. The accounts given in the various text books of these zirconates are based upon the work of Hiortdahl or upon such abstracts of it as were to be found in the Jahresberichte, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watt and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. " Zirconate of potassium thus obtained, dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses, etc., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof

---

[1] *Ann. Chem. Pharm.*, **137**, 34, 236.

[2] *Compt. Rend.*, **112**, 1444-46, and **113**, 1021-22.

that the zirconia was decomposed by the water. In the experiment 0.3910 gram zirconia heated with 0.3130 gram sodium carbonate to a dark redness for nine hours lost 0.1310 gram carbon dioxide, and on treatment with water 0.3871 gram "zirconia," or 99.03 per cent. was left. If an excess of sodium carbonate is used one can drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulas for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid and analyzes the residue, finding in it: ZrO_2, 78.54 per cent.; Na_2O, 5.40 per cent.; and H_2O, 16.89 per cent., corresponding to $Na_2O.8ZrO_2$. He gets the zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:

I. Fusing in boron trioxide, the zirconia and the basic oxide (Ebelmen).

II. Fusing zirconia with alkaline carbonates, (Hiortdahl).

III. Fusing zirconia with alkaline hydroxides.

IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).

V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).

VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

I. FUSION WITH BORON TRIOXIDE.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

II. FUSION OF ZIRCONIA WITH ALKALINE CARBONATES.

The purified zirconia used had been dried at the temperature of the steam bath and therefore was not in the inactive condition brought about by igniting it at a very high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his ziconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form, it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grams of zirconia were used in each case and a large excess of the carbonate. The amount of unattacked zirconia ranged from ninetythree to ninety-nine per cent., showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

I. WITH SODIUM CARBONATE.

Three experiments with sodium carbonate were carried to completion.

1. Two grams zirconia and eight grams sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 gram, or eight per cent. In this $ZrO_2 = 75.70$ per cent.; $Na_2O = 24.30$.

2. Two grams zirconia fused with sixteen grams sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grams. Percentages: ZrO_2, 74.18; Na_2O, 25.81. These correspond fairly with $(ZrO_2)_3(Na_2O)_2$.

3. Two grams zirconia fused with sixteen grams sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid 0.1220 gram, or six per cent. Percentages: ZrO_2, 58.16; Na_2O, 41.84.

II. WITH POTASSIUM CARBONATE.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

III. FUSION OF ZIRCONIA WITH HYDROXIDES.

1. Fusion with sodium hydroxide.

Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grams zirconia fused with eight grams sodium hydroxide. Total amount dissolved 1.1855 grams. An analysis, reduced to dry basis, gave ZrO_2, 92.29, and Na_2O, 7.65.

2. Same amount taken as in Experiment 1. Total amount dissolved 0.7655 gram, containing ZrO_2, 93.19, and Na_2O, 6.22.

3. Two grams zirconia and sixteen grams sodium hydroxide. Amount dissolved 0.8004 gram, containing ZrO_2, 92.57, and Na_2O, 7.38.

4. Two grams zirconia were fused with eight grams of sodium dioxide, instead of the hydroxide. Amount dissolved 0.7074 gram, and this contained 91.21 per cent. ZrO_2.

$Na_2O.(ZrO_2)_6$ contains ZrO_2, 92.20; and Na_2O, 7.80.

$Na_2O.(ZrO_2)_7$ contains ZrO_2, 93.29; and Na_2O, 6.76.

2. *Fusion with potassium hydroxide.*

These were carried out in a manner similar to those with sodium hydroxide and the action seemed to be about the same. In each experiment two grams of zirconia were taken and fused with sixteen grams of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 gram which contained 79.63 per cent. ZrO_2.

2. Dissolved 1.5241 grams which contained ZrO_2, 82.98; K_2O, 17.00.

3. Dissolved 1.2078 grams which contained ZrO_2, 78.59; K_2O, 21.40.

4. Dissolved 0.9297 gram which contained ZrO_2, 85.51; K_2O, 14.49.

In analyzing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for ZrO_2, 93.51, and Na_2O, 6.49, or very nearly the numbers gotten in Experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it can not be claimed from the analyses that definite zirconates have been prepared. Some allowance must be made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(Na_2O)_2(ZrO_2)_3$. In the fusion with sodium hydroxide the results range from $(Na_2O)(ZrO)_5$ [$ZrO_2 = 90.76$; $Na_2O = 9.24$], to $(Na_2O)(ZrO)_8$ [$ZrO_2 = 94.08$; $Na_2O = 5.92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not very clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from $(K_2O)(ZrO_2)_3$ [$ZrO_2 = 79.57$; $K_2O = 20.43$], to $(ZrO_2)_5(K_2O)$, [$ZrO_2 = 86.74$; $K_2O = 13.26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing ZrO_2, 78.59 per cent., and K_2O, 21.41 per cent. was left. This nearly corresponds to the formula $K_2O.(ZrO_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:

Two grams ZrO_2 were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis ZrO_2, 89.11 per cent.; Li_2O, 10.99 per cent. Percentage of ZrO_2 calculated for $Li_2O.2ZrO_2$ is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia and gave the following results:

	I.	II.	Calculated for $CaO.ZrO_2$.
ZrO_2	70.11	70.83	68.54
CaO	29.88	29.14	31.46

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analyzed with the following result :

	Found.	Calculated for $BaO.ZrO_2$.
ZrO_2	55.51	55.95
BaO	44.49	44.05

This is a grayish white powder, very fine and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained :

	Found.	Calculated for $SrOZrO_2$.
ZrO_2	54.22	54.55
SrO	45.77	45.45

7. The magnesia (eight grams) and zirconia (two grams) was heated together for about four hours and then treated in the same manner as the calcium fusion, *i. e.*, first leached with dilute acetic acid and then washed with water until free from magnesia. The residue gave evidence of being crystalline.

	Found.	Calculated for $MgO.ZrO_2$.
ZrO_2	76.28	75.30
MgO	23.70	24.70

IV. FUSION OF ZIRCONIA WITH CHLORIDES.

This method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium and lithium. According to the latter they all gave zirconates of the form M_2ZrO_3.

1. Fusion with sodium chloride.

There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When two grams of zirconia were fused with sixteen grams of sodium chloride, it was found that less than two per cent. had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than two-tenths of a per cent.

2. Fusion with potassium chloride.

No action was observable. When two grams of zirconia were heated a number of hours with an excess of potassium chloride and the mass then treated as above, only three-tenths of a gram had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. Fusion with alkaline earths.

Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths except where these chlorides are decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

V. PRECIPITATION FROM THE SOLUTION OF A ZIRCONIUM SALT BY MEANS OF AN ALKALINE HYDROXIDE.

Watts speaks of this method but no experiments are recorded. It seemed to us upon examination of the question that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It, therefore, seemed to be quite useless to make analyses of the precipitates gotten with different degrees of washing; especially as somewhat similar experiments were carried out under the next heading.

VI. THE SOLUTION OF ZIRCONIUM HYDROXIDE IN CAUSTIC ALKALI.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off and the amount of zirconia present determined.

A 50 per cent solution potassium hydroxide dissolved per cc. 0.00233 gram.
33 " " " " " " " " 0.00097 "
25 " " " " " " " " 0.00075 "
12 " " " " " " " " 0.00009 "

In the case of sodium hydroxide there seemed to be a stronger solvent action.

A 33 per cent solution dissolves per cc. 0.00245 gram.
25 " " " " " " 0.0012 "
12 " " " " " " 0.0005 "

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralization with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a liter of water used.) The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxide with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed and then decomposed by the action of the water during the washing, but it seems more probable that this is, as is true in the case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with. This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, as CaO.ZrO, etc. The same is true of the magnesium compound. For lithium the compound obtained was LiO.ZrO. For the alkalies it seemed to be possible to obtain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of the water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

DOUBLE ZIRCONATES.

Two attempts at the formation of double zirconates were made.

1. Potassium calcium zirconate.

About two grams each of zirconia, potassium hydroxide and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then on treatment with dilute hydrochloric acid nearly the whole residue went into solution. The analysis gave ZrO_2, 67.21 per cent.; CaO, 31.06; K_2O, 1.11. This is a calcium zirconate, ($CaO.ZrO_2$), with a small part of the CaO substituted by K_2O.

2. Potassium aluminum zirconate.

Two grams of zirconia were fused for eight hours with two grams of potassium hydroxide and three grams of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid and the insoluble portion removed by filtration. The analysis gave ZrO_2, 72.38 per cent.; Al_2O_3, 7.66; K_2O, 20.00. These experiments indicate the possible existence of double zirconates, and when time admits this point will be further examined.

UNIVERSITY OF NORTH CAROLINA.