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THE ANHYDROUS LOWER BROMIDES OF ZIRCONIUM

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The present paper is the second¹ of a series dealing with a general study of the lower anhydrous bromides of the elements of the titanium family, and considers the preparation and properties of the lower bromides of zirconium.

The lower chlorides of zirconium were prepared by Ruff and Wallstein,² who allowed aluminum powder to react with zirconium tetrachloride in an evacuated tube in the presence of aluminum chloride as a catalyst. On account of the oxide of aluminum in the powder and because of the method of introducing the reactants into the reaction tube, resulting in hydrolysis, the product obtained by Ruff and Wallstein after sublimation of the unchanged zirconium tetrachloride and aluminum chloride was inevitably rendered impure by aluminum oxide and zirconium oxide.

In order to prevent hydrolysis and oxidation as far as possible, it was planned to prepare the bromides by a method which would enable one to obtain the product without the necessity of transfer from one apparatus to another and also by a method which would not require the placing of the reactants in that part of the apparatus in which the products would be collected.

The general procedure adopted for the preparation of zirconium tribromide consisted essentially of the passing of zirconium tetrabromide with hydrogen over aluminum metal (wire) in a hot tube and of quickly chilling the volatile products of the reaction upon a tube kept cold by a current of water. The apparatus was so devised that the products could then be transferred in the presence of an inert gas to a tube joined to the reaction tube and the *former* tube could then be drawn out and sealed. The procedure and results in detail are described below, after a consideration of the preparation and degree of purity of the zirconium tetrabromide used.

Zirconium tetrabromide was prepared from zirconium dioxide which had been shown by analysis to be free from impurities other than hafnium. Nitrogen saturated with bromine was allowed to pass through a 30-mm. Pyrex tube filled with an intimate mixture of four parts of dry sugar charcoal to one of dry zirconium dioxide, the tube being heated in a combustion furnace to the temperature at which the glass begins to soften. The zirconium tetrabromide sublimed and was collected at the end of the

¹ Young with Schumb, *THIS JOURNAL*, **52**, 4233 (1930).

² Ruff and Wallstein, *Z. anorg. allgem. Chem.*, **123**, 96 (1923).

tube. The crude material was purified by sublimation *in vacuo*, the white product obtained was analyzed for zirconium by the selenious acid method, and found to be pure. The bromine was determined separately as silver bromide.

Anal. Calcd. for $ZrBr_4$: Zr, 22.20; Br, 77.79. Found: Zr, 22.30, 22.33; Br, 77.68, 77.76.

Preparation of Zirconium Tribromide.—Referring to Fig. 1, at A, 30 g. of zirconium tetrabromide was introduced into the curved 22-mm. Pyrex tube which had been sealed directly to the larger (28 mm.) horizontal Pyrex tube. A current (about 200 cc. per min.) of dry, oxygen-free hydrogen was passed through the apparatus which, after the air had been displaced, was heated in a hinged-type electric furnace until the temperature of the furnace measured a minimum of 450° . Then the zirconium tetrabromide was slowly volatilized by means of a free flame and as it passed with the hydrogen through the furnace reacted in part with aluminum wire placed in the tube so that the wire would be in the center of the furnace. The wire consisted of four concentric coils, each coil 5 cm. long, of No. 18 wire, the diameter of the largest coil being 18 mm. The total weight of aluminum was 14 g. The cooling tube through which the water circulated was 9 mm. in diameter and extended to within approximately one inch of the wire. It was noted that satisfactory results were obtained only when this distance was carefully observed. A black to blue mass collected on the cold tube. Some of the aluminum bromide formed was carried by the hydrogen into the tube B and out the smaller tube C. The metal at the end farthest from the cold tube became incandescent during the reaction. Some of the zirconium tetrabromide was reduced to zirconium metal which alloyed with the aluminum.

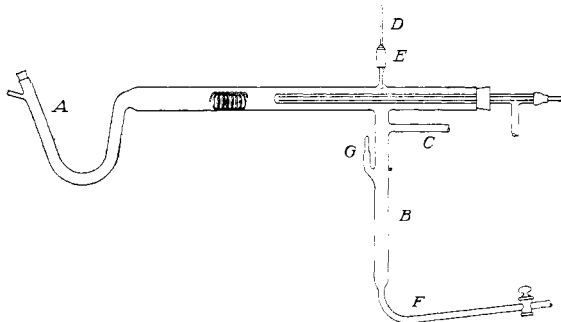


Fig. 1.—Apparatus for the preparation of zirconium tribromide.

After all the zirconium tetrabromide had been volatilized in about one-half to three-quarter hour, the furnace was cooled to room temperature and dry carbon dioxide was substituted for the hydrogen. Tube C was closed and the cooling tube was partially withdrawn through the cork stopper. Part of the product usually clung to the tube, and sometimes it was necessary to use the glass rod D, which could be worked up and down in the tube E, to dislodge it and break the large pieces into smaller ones which would be able to enter tube B. Thick-walled rubber tubing connecting the apparatus with the drying train allowed the apparatus to be tipped so that all the product could be made to enter B, after which it was sealed just below side tube C.

The contents of the tube were now shaken to the end opposite the stopcock and the tube containing aluminum bromide, zirconium tetrabromide and reduced product was

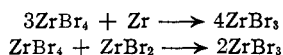
placed in a furnace and evacuated while being heated. About 6 cm. of the large tube was allowed to protrude beyond the furnace and after the temperature had reached approximately 140°, the aluminum bromide began to condense in the cold end. After the temperature had reached 200° the tube was sealed at F and the temperature raised to 290° and held there while the tube was gradually withdrawn from the furnace so that the zirconium tetrabromide which collected in the tube at the end of the furnace would not cause the tube to crack. It was noticed that a blue color always developed where aluminum bromide was in contact with zirconium tetrabromide.

Heating at 290° was continued until no more sublimate formed in the tube just outside of the furnace. In determining this fact, the tube was withdrawn from the furnace a distance of 1 cm., thus presenting a clear and transparent surface. If at the end of fifteen minutes a coating of zirconium tetrabromide formed, the tube was pushed back 1 cm., thus causing the compound to be volatilized forward and after thirty minutes a second test was made as before. About sixteen hours were required for the complete removal of the aluminum bromide and zirconium tetrabromide.

After the volatile products had been sublimed to the cold end of the tube, the furnace was allowed to cool to room temperature and the small tube G was connected by means of thick-walled tubing to a source of dry nitrogen and the narrow part of the tube G was broken thus allowing the gas to enter. The large tube was then sealed just beyond tube G and then tube G also was sealed. The sample now was in a sealed tube in an atmosphere of nitrogen and appeared as a blue-black powder. Crystalline form could not be distinguished with a magnification of 300 diameters.

The tube was filed at the tip, weighed, the tip was broken and the sample weighing approximately 0.5 g. introduced at once into ice water. The reaction was vigorous; a yellow to orange solution was formed, hydrogen was evolved and the color faded and disappeared completely in about five minutes. The solution was filtered and the gray to black residue was ignited. Dilute ammonium hydroxide solution was added to the filtrate and the precipitated hydrous oxide of zirconium was also ignited. The bromide contained in the filtrate from this precipitate was determined as silver bromide. The results of careful investigation showed that the dark insoluble matter amounting to as much as 5% of the sample (which after ignition proved to be zirconium dioxide) could be accounted for by the presence of a small amount of zirconium metal and of zirconium dibromide in the original reaction product. It was found that zirconium dibromide, the preparation of which will be given later, reacts so violently with water even at 0° that some zirconium dioxide is produced directly. The fact that, in the analysis, the zirconium was higher than the theoretical for zirconium tribromide and the bromine lower indicated that zirconium dibromide was present and the fact that the insoluble matter was dark showed the presence of zirconium metal.

To avoid the presence of zirconium metal and zirconium dibromide in the sample, the following procedure was adopted. In the preparation of the tribromide a great excess of the tetrabromide was allowed to accumulate in the product; the usual proportion would be 25 g. of zirconium tetrabromide to 0.5 to 1.0 g. of the reduced material. The tube with contents after being evacuated as described above was sealed and heated for eight hours at 300° in the center of a long electric sleeve with the view of converting any zirconium metal and zirconium dibromide to the tribromide.



Tests had been carried out to show that the first of these reactions will take place and it had been shown previously that the second reaction proceeds in the case of the titanium bromides.

After the eight hours' heating at 300° , the aluminum bromide and unchanged zirconium tetrabromide were sublimed away from the reduced product and the resulting sample was analyzed as described. The water insoluble matter now amounted to only a milligram in a 0.2-g. sample, the solution being clear and transparent.

Anal. Calcd. for $ZrBr_3$: Zr, 27.55; Br, 72.45. Found: Zr, 27.79, 27.77; Br, 72.35, 72.27.

The zirconium tribromide with the dibromide and metal eliminated appeared as a blue-black powder similar in color to the tribromide of titanium. When subjected to a slight amount of hydrolysis it took on a brown appearance and upon further hydrolysis turned red.³ It dissolved in water to give a yellow to orange colored solution which was acid to litmus and evolved hydrogen. The color faded quickly. On the addition of the compound to a cold dilute solution of ammonium hydroxide, an orange precipitate was formed which persisted only momentarily.

In the formation of a 0.5-g. sample of the tribromide, 3 to 5 g. of aluminum bromide was obtained; the aluminum metal gained in weight slightly due to the substitution of some zirconium metal for the aluminum. Larger yields of the tribromide were obtained by volatilizing the tetrabromide more slowly. The production of 1 g. was the maximum obtained in one hour.

As a test of its reducing power small samples were added to the following dilute solutions arranged in order of increasing difficulty of reduction: sodium chromate, ferric chloride, bismuth chloride, copper chloride, titanium tetrabromide, stannous chloride and zinc sulfate. The change from yellow to green in the first case showed that chromium had been reduced from valence 6 to valence 3. A blue precipitate formed on the addition of potassium ferrocyanide in the second test solution proved that ferric iron had been reduced to ferrous. Metallic bismuth was obtained in the third test; a precipitate of cuprous chloride in the fourth. A violet color formed in the test with titanium bromide indicated reduction to trivalent titanium. Negative results were obtained with stannous chloride and zinc sulfate. Since zirconium tribromide caused the evolution of hydrogen from water—due to hydrolysis, the solution is acid—the molal reduction potential of Zr^{+++}/Zr^{++++} can be approximately placed as above that of hydrogen but below that of tin.

Other reducing substances were tried in place of aluminum in the preparation of zirconium tribromide. Iron wire reacted with the zirconium tetrabromide to produce the lower bromides and ferrous bromide.

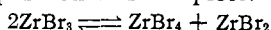
³ Ruff and Wallenstein² describe the trichloride of zirconium as brown in color. Inasmuch as the tribromide and trichloride of titanium and the tribromide of zirconium have all been found to be blue-black in color, it seems possible that the brown color of the trichloride of zirconium prepared by these authors was due to partial hydrolysis.

The product, however, was freed from the latter with great difficulty. An alloy of zirconium and aluminum was successfully used. Magnesium metal produced a much larger percentage of the dibromide than did aluminum.

Zirconium tetrabromide is insoluble in carbon tetrachloride, benzene, and ethyl bromide and the metals mercury, aluminum, and silver caused no reducing action, when added to the tetrabromide in the presence of these liquids, even when heated to the boiling point of the liquid. In solvents in which the salt did dissolve, such as glacial acetic acid, acetic anhydride, and acetone there was no indication of any tribromide formation by the reducing action of the metals given above.

Considerable effort was made to reduce zirconium tetrabromide with hydrogen alone by use of the hot-cold tube principle and a resistance-wound silica tube as the reaction tube, which was heated to 1100°. No evidence of reduced product was obtained, nor did any reaction occur when the tube was heated to such a temperature that the silica softened in spots.

Zirconium Dibromide.—The preparation of the dibromide of zirconium involved heating the tribromide, obtained in the evacuated tube as previously described, to a temperature at which decomposition into the dibromide and tetrabromide took place and of keeping the material at that temperature until decomposition was complete.



After all the unchanged zirconium tetrabromide had been evolved from the tribromide as already described, the temperature of the furnace was gradually raised and at 310° the tetrabromide began to deposit again at the end of the furnace, but very slowly. The rate increased as the temperature was further raised. At 350° from ten to fifteen hours were required to decompose a 0.5-g. sample of zirconium tribromide and at 390° about six hours.

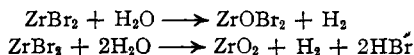
In appearance the dibromide is a lustrous black powder. It was obtained in an atmosphere of nitrogen in a sealed tube exactly as in the case of the tribromide. On exposure to the air the dibromide catches fire. It was therefore introduced into ice water saturated with nitrogen by breaking the tube under water. As the water vapor came in contact with the solid there was a very vigorous reaction, part of the solid became incandescent and hydrogen was liberated.⁴

There was in this case considerable dark gray to white insoluble residue consisting mainly of the oxide of zirconium with a very small amount

⁴ J. H. de Boer and J. D. Fast⁵ in an article on the preparation of pure metals of the titanium group through the thermal decomposition of their iodides briefly mention the preparation of the dibromide of zirconium by the action of zirconium tetrabromide on zirconium metal. They however report the dibromide of zirconium as reacting slowly with water to give off hydrogen, and as forming an orange colored solution which slowly decolorized. The analyses given differ considerably from the theoretical.

⁵ J. H. de Boer and J. D. Fast, *Z. anorg. allgem. Chem.*, **187**, 177 (1930).

of zirconium metal, which caused the dark appearance of the oxide. In the analysis of a sample of the dibromide weighing 0.1745 g., 0.0282 g. of zirconium dioxide was obtained on ignition of the water-insoluble material and 0.0604 g. was obtained on ignition of the precipitate formed by addition of ammonium hydroxide solution to the filtrate from the water-insoluble matter. The total zirconium calculated from these two weights gives a percentage of zirconium of the sample as 36.41%, the theoretical percentage of zirconium in zirconium dibromide being 36.18. Since the percentage of bromine determined as silver bromide corresponded with that required for the dibromide, it is evident that not all of the zirconium dibromide dissolves as zirconyl bromide but that part of the compound reacts with the water to form zirconium dioxide with the formation of hydrogen bromide and liberation of hydrogen.



Anal. Calcd. for ZrBr_2 : Zr, 36.33; Br, 63.67. Found: Zr, 36.41, 36.34; Br, 63.98, 63.45.

If the decomposition of zirconium tribromide is carried out at too high a temperature, considerable zirconium metal will be formed due to the reaction $2\text{ZrBr}_2 \longrightarrow \text{ZrBr}_4 + \text{Zr}$. This takes place very slowly at 350° but does go on as the somewhat dark appearance of the zirconium dioxide before ignition indicates. At temperatures of 400° and above, the decomposition of the dibromide proceeds quite rapidly. One sample heated at 410° for twenty-four hours gave, on analysis, 44.5% of zirconium and 57.2% of bromine.

Summary

Anhydrous zirconium tribromide has been prepared by the reduction of the tetrabromide with aluminum in an atmosphere of hydrogen in the hot-cold tube. Appropriate apparatus and manipulation are described. The compound is a blue-black powder which dissolves in water with the evolution of hydrogen, producing a yellow to orange colored solution, the color of which quickly disappears. Trivalent zirconium was found capable of bringing about the following reductions: $\text{CrO}_4^{=}$ to Cr^{+++} , Fe^{+++} to Fe^{++} , Bi^{+++} to Bi , Cu^{++} to Cu^+ , TiO^{++} to Ti^{++} and 2H^+ to H_2 . Negative results were obtained in the attempts to reduce stannous chloride.

The dibromide of zirconium is formed by the decomposition of the tribromide at 350° , the tetrabromide being formed at the same time. Zirconium dibromide is a lustrous black powder which catches fire in the air and reacts with water so vigorously as to cause incandescence even in an atmosphere of nitrogen. Hydrogen is evolved and considerable dioxide of zirconium is formed.