The value so calculated is $\Delta H^0_{\text{ReBr}_3} = -39.3 \pm 0.8$ kcal. mole^{-1}. Brewer[19] had estimated a value of -40 ± 15 kcal. mole^{-1} for this heat.

In summary, new thermodynamic functions are given for rhenium trichloride and rhenium tribromide at 25° in Table IV.

This method for obtaining heats of formation appears to be quite general and can be applied to fluorides and iodides as well. Thus it should be applicable to the halides of molybdenum, technetium, ruthenium tungsten, osmium and perhaps zirconium and hafnium iodides and bromides.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY, CHEMICAL RESEARCH LABORATORIES, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, MELBOURNE, AUSTRALIA]

The Preparation of the Anhydrous Zirconium Trihalides

BY I. E. NEWNHAM AND J. A. WATTS

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A new process for preparing pure, anhydrous zirconium trichloride, tribromide and triiodide is described. The appropriate tetrahalide vapor is mixed with hydrogen at a pressure of 3–4 mm. and passed through a glow discharge. The zirconium trihalide which is formed is subsequently freed from adsorbed or unreduced contaminants by heating *in vacuo.*

The important role which zirconium trichloride can play in the separation of zirconium and hafnium[1] has drawn attention to the paucity of thermodynamic data concerning not only the trichloride but also the analogous tribromide and triiodide. One obstacle to the accurate study of the properties of these compounds has been the absence of a method for preparing them in the pure anhydrous state.

The first preparation of a zirconium trihalide was attempted by Ruff and Wallstein[2] who reduced zirconium tetrachloride with aluminum, but their product was contaminated with 2.5–4% aluminum; moreover, the brown color of the compound which these early workers described indicated that partial hydrolysis had occurred. Larsen and Leddy[3] eliminated the aluminum contamination but, even under the most favorable reaction conditions, the trichloride which they prepared contained 15% unreacted zirconium. The brown color of their product also showed that they were unable to avoid a certain amount of hydrolysis. Larsen and Leddy pointed out that their trihalides were formed as a layer on the surface of finely-divided zirconium, and Newnham[4] has shown that the caking which occurs under these conditions makes complete elimination of the zirconium metal an extremely slow process.

Young[5] realized that one of the first essentials in the preparation of the pure trihalides was their complete isolation from the reactants. By making use of the St. Claire-Deville "hot-cold" tube, he prepared zirconium tribromide in a part of the apparatus not occupied by the aluminum reducing agent. Unfortunately he was not able to control the degree of reduction of his tetrabromide, so that the blue-black powder which he obtained was a mixture of tribromide, dibromide and finely divided zirconium metal. Young found that his tribromide turned brown when subjected to a slight amount of hydrolysis, and his prediction that the trichloride should be blue-black rather than brown subsequently was confirmed by Newnham.[4]

From the foregoing it is apparent that any method for preparing the pure trihalides must eliminate contamination by the reductant, closely control the degree of reduction and guard against any trace of hydrolysis. Since the trihalides are comparatively involatile, it is obvious that contamination can be avoided by using a gaseous reductant. Hydrogen presents itself as a likely choice in view of the work of Schumb and Sundström[6] on the analogous reduction of titanium tetrachloride by hydrogen. However, attempts to prepare zirconium trichloride by either Schumb's method or by the closely related technique of Young[5] have proved unsuccessful, and attention therefore has been directed to the possibility of using atomic hydrogen as the reductant. The dissociation of hydrogen into free atoms in an electric glow discharge was first described by Wood,[7] and Poole[8] has made a thorough study of the energy efficiency when atomic hydrogen is produced in this way. It has not proved practicable to adopt all the recommendations of these earlier workers (for example, they used hydrogen which had been saturated with water-vapor), but a careful adaptation of their technique has led to the development of a new process for preparing the pure zirconium trihalides.

Experimental

Raw Materials.—Zirconium tetrachloride was prepared by chlorinating reactor-grade zirconium at 500°. Since the reaction between chlorine and zirconium can be quite violent, the chlorination was initiated with a 10% mixture of chlorine in oxygen-free nitrogen, and the ratio of chlorine to nitrogen was increased as the reaction proceeded. Both gases were dried by passing them through magnesium per-

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[1] I. E. Newnham (a) *Research*, **10**, 424 (1957); (b) U. S. Patent 2,791,485, *C. A.*, **51**, 11227 (1957).

[2] O. Ruff and R. Wallstein, *Z. anorg. Chem.*, **128**, 96 (1923).

[3] E. M. Larsen and J. J. Leddy, THIS JOURNAL, **78**, 5983 (1956).

[4] I. E. Newnham, *ibid.*, **79**, 5415 (1957).

[5] R. C. Young, *ibid.*, **53**, 2148 (1931).

[6] W. C. Schumb and R. F. Sundström, *ibid.*, **55**, 596 (1933).

[7] R. W. Wood, *Phil. Mag.*, **44**, 538 (1922).

[8] H. G. Poole, *Proc. Roy. Soc.*, **163A**, 424 (1937).

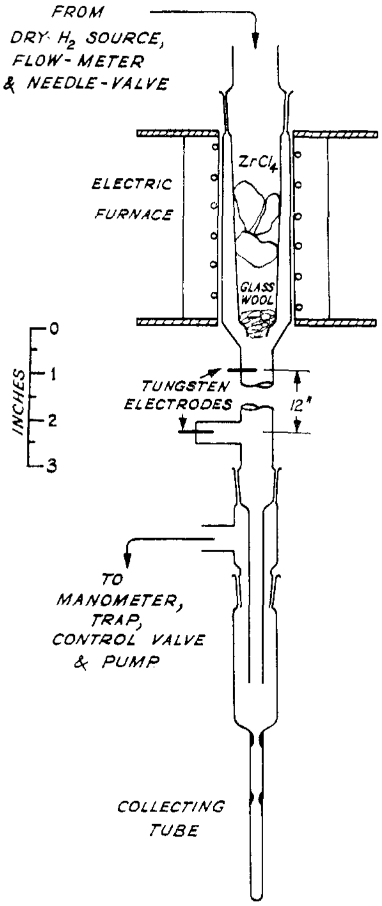

Fig. 1.—Reduction apparatus.

chlorate towers and the tetrachloride was purified and densified by slow vacuum sublimation at 250°.

Zirconium tetrabromide was prepared by bubbling dry nitrogen through liquid bromine and passing the nitrogen-bromine mixture over reactor-grade zirconium heated to 850°; in this case the nitrogen diluent also acted as a suitable carrier for the bromine vapor. The product was vacuum sublimed at 270°.

Zirconium tetraiodide was prepared by passing a stream of dry nitrogen over iodine heated to 165° and then leading the mixture of nitrogen and iodine vapor through a jacketed tube and over reactor-grade zirconium heated to 750°. The product was vacuum sublimed at 400°.

The hydrogen used as a reducing agent was passed through a heated bed of copper and then through successive towers filled with silica gel, phosphorus pentoxide and magnesium perchlorate. The resultant oxygen-free dry gas was metered into the reduction apparatus through a needle-valve at the rate of 100 cc. per minute at N.T.P.

Apparatus.—The apparatus, consisting essentially of a halide generator, a reduction zone and a collecting tube,.is shown in Fig. 1. A low-pressure stream of hydrogen was drawn through a heated bed of the tetrahalide and the mixture of halide vapor and hydrogen then passed through a constricted tube into the glow discharge. Reduction was instantaneous and care was necessary to prevent back diffusion of the atomic hydrogen, with resultant deposition of the trihalide above the upper electrode. Provided the trihalide was deposited on the walls of the tube between the tungsten electrodes, it gradually flaked away during the progress of the reaction and fell into the collecting tube. In passing it should be noted that the type of discharge zone used by Ingraham[9] in his reduction of titanium tetrachloride with atomic hydrogen proved quite unsuitable for the production of zirconium trihalides. The electrodes rapidly became coated with a black deposit which completely inhibited the formation of the trihalides.

Power for the electrodes was provided by a high frequency a.c. induction coil. Input to the coil came from a 0–240 v. variable transformer connected to the primary of a step-up transformer capable of supplying 2240 v. at 550 ma. Voltage from this transformer was fed through an isolating capacitor of 0.6 μfd. on to an oscillatory discharge circuit, which was composed of a 0.04 μfd. capacitor discharging through the primary of the induction coil. The primary winding consisted of 16 turns of 7-strand, 17-gauge copper wire on a 3" diameter former, and the secondary of 1600 turns of 33-gauge wire on a 2" diameter former.

Prior to each run the electrodes were cleaned by immersing them in a 20% aqueous solution of caustic soda and passing a 6 v. current for 3 minutes.

Reduction Procedure.—With the pump control valve fully open and the needle valve closed, the apparatus was evacuated and outgassed. The two valves then were adjusted to give the required hydrogen pressure and flow-rate, the pressure being measured by means of a silicone oil manometer. While these adjustments were in progress the glow discharge was commenced and the halide generator furnace turned on. The temperature of the latter was raised to a level slightly below that at which unreduced tetrahalide condensed on the lower walls of the reduction zone. Trihalide collected at the rate of 0.5 g./hr. and gentle heating was used to dislodge any of the reduced halide which showed a tendency to adhere to the wall of the discharge tube.

The time for an average run was 45 minutes, after which the generator was switched off and, five minutes later, the discharge was stopped. With the needle valve closed and the pump valve open the trihalide in the collecting tube was heated for an hour to sublime off any unreduced tetrahalide and strongly adsorbed hydrogen halide. The tube was then sealed off and heated for 20 hr. with its upper end protruding from the furnace. This ensured that the last traces of tetrahalide condensed in the top of the tube, which was subsequently sealed off from the part containing the pure trihalide.

Analysis.—The trihalides were so pyrophoric that special care was necessary in the preparation of samples for analysis. Because of the tendency of the trihalides to ignite under water, the collecting tubes for analytical samples were flattened on one side so that they could be easily broken along their full length. In this way instantaneous flooding of the whole sample was made possible and the formation of insoluble zirconium oxide was prevented.

Zirconium was determined by the EDTA back titration method[10] and halide by the Volhard process; in the case of the chloride samples the Caldwell modification[11] was used.

Results

Zirconium Trichloride.—When zirconium tetrachloride was heated in the halide generator, a blue film appeared on the walls of the discharge zone as soon as the generator temperature reached 190°. At 200° this film became a dense opaque blue-black layer which broke away from the glass in a steady stream. At temperatures above 220° white tetrachloride started to condense in the reaction zone and 200° was therefore adopted as the most suitable generator temperature. The hydrogen pressure throughout the reduction was 3 mm.

A series of empirical tests showed that 200° was also a satisfactory temperature for the vacuum sublimation and the subsequent 20-hour heating period which was used to free the trichloride from contaminants.

The blue-black zirconium trichloride powder dissolved completely in water, with violent evolution of hydrogen, to give a yellow-brown solution. The color faded on standing and the resultant solution was crystal clear and free from any traces of an in-

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[9] T. R. Ingraham, K. W. Downes and P. Marier, *Can. J. Chem.*, **35**, 850 (1957).

[10] W. C. Milner and P. J. Phennah, *Analyst*, **79**, 475 (1954).

[11] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

soluble residue. Chemical analysis established the composition of the trichloride. Calcd. for $ZrCl_3$: Zr, 46.2; Cl,53 .8. Found: (1) Zr, 45.8; Cl, 54.2; (2) Zr, 46.0; Cl, 54.0. There was no indication of the brown color mentioned in the description of previous trichloride preparations[2,3] but the blue-black compound changed to brown if left standing in an inert atmosphere to which traces of moist air were admitted.

Zirconium Tribromide.—This compound first appeared in the reduction zone as a light blue film at a generator temperature of 210°. Unreduced tetrabromide did not condense on the tube walls until the generator reached 250°, and 230° was adopted as a satisfactory working temperature. A hydrogen pressure of 3 mm. gave erratic results but consistent reproducibility was obtained when the pressure was raised to 4 mm. A temperature of 200° proved satisfactory for the subsequent purification of the tribromide.

Zirconium tribromide was obtained as a blue powder, much lighter in color than the trichloride and chemical analysis established its composition. Calcd. for $ZrBr_3$: Zr, 27.6; Br, 72.4. Found: (1) Zr, 27.2; Br, 72.8; (2) Zr, 27.0; Br, 73.0.

Zirconium Triiodide.—The preparation of this compound did not follow the pattern of the trichloride and tribromide. At a generator temperature of 255° unreduced tetraiodide started to condense on the walls of the discharge tube. No reaction was apparent until the generator reached 290° at which temperature a green-black deposit formed in the reduction zone. As soon as this compound appeared it was found that the reduction proceeded in a normal fashion provided the generator temperature was reduced to 235°. The hydrogen pressure for the reaction was 4 mm. and the purification temperature was 260°. Chemical analysis established the composition of the greenish-black zirconium triiodide powder. Calcd. for ZrI_3: Zr, 19.3; I, 80.7. Found: (1) Zr, 19.4; I, 80.6; (2) Zr, 19.1; I, 80.9.

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Stabilities of Divalent Metal Complexes of 4-Hydroxybenzothiazole

BY PAO KUO FENG AND QUINTUS FERNANDO

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The acid dissociation constants of 4-hydroxybenzothiazole and the formation constants of its chelates with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Mg(II) have been determined potentiometrically in 50% v./v. dioxane-water. The order of decreasing stability of the metal chelates Cu > Pb, Ni, Co > Zn > Cd > Mn > Mg is similar to the stability sequence generally obtained for divalent metals. The chelates of 4-hydroxybenzothiazole with Co(II), Ni(II) Cu(II), Zn(II), Cd(II) and Pb(II) have been prepared and their infrared spectra determined.

The reactions of divalent metal ions with 4-hydroxybenzothiazole have a marked resemblance to those with 8-hydroxyquinoline, with some noteworthy exceptions. The magnesium complex of 4-hydroxybenzothiazole is much more soluble in water than magnesium oxinate, and the copper, nickel and zinc complexes of 4-hydroxybenzothiazole are insoluble in chloroform in contrast to the corresponding oxinates.[1] The presence of the sulfur atom in the 4-hydroxybenzothiazole ring system undoubtedly will affect the basicities of the ligand and also give rise to resonance interactions which can cause the properties of the metal complexes to be drastically altered. The present study was initiated in order to obtain more information on the factors that cause certain metal chelates of 4-hydroxybenzothiazole to behave differently from the corresponding oxinates.

Experimental

Preparation of 4-Hydroxybenzothiazole.—4-Hydroxybenzothiazole was prepared by the method described by Erlenmeyer and Ueberwasser,[2] with several modifications.

123 g. of *o*-anisidine was dissolved in 93 ml. of HCl (d. 1.19) and 500 ml. water, to which was added 160 g. of ammonium thiocyanate in 3.5 l. of water. The resulting solution was heated in a 5 l. beaker on a hot plate for 8 hr., with constant addition of water to maintain a volume of about 2 l. On cooling, crystals of *o*-methoxyphenylthiourea separated out. The crystals were filtered, washed thoroughly with water and recrystallized from water; yield 90%, m.p. 146°.

A solution of 82 g. of bromine in 200 ml. of chloroform was added slowly and with shaking to a suspension of 90 g. *o*-methoxyphenylthiourea in 400 ml. of dry chloroform in a 3 l. round-bottomed flask. The temperature of the mixture was kept below 30°. After all the bromine was added, a red liquid layer was formed at the bottom of the vessel. This mixture was refluxed for about an hour until the evolution of HBr ceased. The solution was cooled, the supernatant chloroform layer decanted and a fresh 200 ml. portion of chloroform added and refluxed again for another hour. This sequence of operations, of cooling, decantation, addition of a fresh portion of chloroform and finally refluxing, was repeated several times until a solid, 2-amino-4-methoxybenzothiazole, was obtained. At this stage the chloroform in the flask was decanted and the small amount of chloroform remaining in the solid was removed by means of a vacuum pump. The solid was transferred to a beaker with a small amount of sulfurous acid, stirred thoroughly and neutralized with a dilute solution of sodium hydroxide, filtered and recrystallized from water; yield 70%, m.p. 144°.

Forty-five g. of 2-amino-4-methoxybenzothiazole was dissolved in 225 ml. of phosphoric acid (88–92%), the mixture cooled to 0°, and 64 ml. of nitric acid added with stirring, keeping the temperature at 0°. A solution of 18 g. of sodium nitrite in 25 ml. of water was added very slowly to this mixture with constant stirring when a dark red viscous solution was obtained. This diazotized mixture was added slowly and with constant stirring to a solution containing 100 g. of copper in 500 ml. of HCl (d. 1.19). The mixture was allowed to stand for an hour, diluted to 2 l. with water and allowed to stand overnight. The solid, 2-chloro-4-methoxybenzothiazole, obtained was filtered, washed thoroughly with water and recrystallized from a methanol-water mixture; yield 60%, m.p. 140°.

Twenty g. of 2-chloro-4-methoxybenzothiazole was refluxed with 6 g. of red phosphorus and 100 ml. of hydriodic

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(1) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 192.

(2) H. Erlenmeyer and H. Ueberwasser, *Helv. Chim. Acta*, **25**, 515 (1942).