

435. *The Fluorides of Niobium, Tantalum, Tungsten, and Rhenium.*

By H. J. EMELÉUS and V. GUTMANN.

Tantalum trifluoride was prepared by the action of hydrogen fluoride on tantalum powder or "tantalum hydride" at 250–300°. Tantalum pentafluoride was formed simultaneously. Niobium, its "hydride," or the impure trichloride (NbCl_{2-3}) under similar conditions gave only the pentafluoride. The preparation of pure tungsten dibromide is described. It reacted with hydrogen fluoride at 600° forming tungsten and its hexafluoride. Rhenium trichloride reacted with hydrogen fluoride forming the metal and only traces of the volatile hexafluoride. Tungsten and rhenium metals were unattacked by hydrogen fluoride.

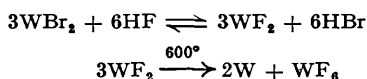
THE fluorides of many transition elements in their lower valency states are at present very incompletely known, though often other halides of the elements in these states have been characterised. It is difficult to decide from the literature if the missing compounds are inherently unstable or if a suitable preparative method has not yet been found. Klemm (F.I.A.T. Review of German Science, 1939–46, *Inorg. Chem.*, Vol. II, p. 15) mentioned that Ehrlich tried unsuccessfully to prepare titanium difluoride, TiF_2 . The instability of vanadium and molybdenum difluorides and the preparation of molybdenum trifluoride were described recently (Emeléus and Gutmann, *J.*, 1949, 2979), but information on the lower fluorides of other transition elements was still lacking. The experiments described below were designed to throw light on the matter. They represent a study of the reaction of hydrogen fluoride with niobium, tantalum, tungsten, and rhenium, or with lower chlorides and bromides of these elements under conditions such that formation of a lower fluoride would be expected.

In the cases of niobium and tantalum only the pentafluorides are known with certainty, though Ruff and Schiller (*Z. anorg. Chem.*, 1911, **72**, 329) observed the formation of a blue "lower fluoride" on heating niobium pentafluoride in hydrogen at its boiling point. On the other hand, tantalum trichloride and tribromide and a lower niobium chloride, said to be the trichloride (Süe, *Bull. Soc. chim.*, 1939, **6**, 830), have been prepared. Lower iodides, the composition of which has not been confirmed, have been described for both niobium and tantalum (Koeroesy, *J. Amer. Chem. Soc.*, 1939, **61**, 838). Süe gave no analysis of the trichloride, and a number of preparations based on his method of reducing the pentachloride by hydrogen gave compounds varying in composition between NbCl_2 and NbCl_3 . This niobium chloride was found to be unattacked by liquid hydrogen fluoride. With gaseous hydrogen fluoride there was no reaction below 400° and little between 400° and 500°, whereas above 500° oxidation to the pentafluoride occurred without formation of trifluoride. Niobium powder also reacted with anhydrous hydrogen fluoride at 250° and 300°, but the only product identified was the pentafluoride. This is in fact a convenient method for the preparation of the pentafluoride, which hitherto has been made by the reaction of the hygroscopic pentachloride with liquid hydrogen fluoride, or by fluorination of the metal with fluorine (Ruff and Schiller, *loc. cit.*). When niobium

previously heated in hydrogen at 250°, was heated at the same temperature in a mixture of hydrogen and hydrogen fluoride the pentafluoride was again formed, but a very thin blue layer was observed on the residual metal; this layer could not be separated and was possibly identical with the blue substances observed by Ruff and Schiller (*loc. cit.*).

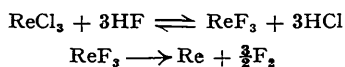
Tantalum powder reacted similarly with hydrogen fluoride. At 300° a 90% yield of the pentafluoride was obtained, but a greyish-white non-volatile and non-hygroscopic residue remained which was found to be tantalum trifluoride. The yield of trifluoride was increased somewhat when the metal was preheated in hydrogen at 250° and the product was then heated in a hydrogen-hydrogen fluoride mixture at 300°, but contamination by unchanged metal became appreciable in this case and the reaction proceeded at a much lower rate. The trifluoride neither melted nor sublimed in nitrogen or hydrogen fluoride at 650°. It was converted into the pentoxide when ignited in air and was insoluble in water and acids, except aqueous hydrofluoric acid. It was decomposed by aqua regia or hot nitric acid and also dissolved in a boiling mixture of sodium hydroxide and hydrogen peroxide. The compound has the cubic rhenium trioxide structure (Gutmann and Jack, unpublished observations) and thus resembles molybdenum trifluoride. Tantalum trifluoride could probably also be prepared from tantalum trichloride or tribromide by a method similar to that used for molybdenum trifluoride (Emeléus and Gutmann, *loc. cit.*).

Tungsten hexafluoride has been known for some time (Ruff and Eisner, *Z. anorg. Chem.*, 1907, **52**, 256; Ruff and Ascher, *ibid.*, 1931, **196**, 416) and the tetrafluoride has been described recently (Priest and Schumb, *J. Amer. Chem. Soc.*, 1948, **70**, 3378). No lower fluorides are, however, known, although the dichloride, dibromide, and di-iodide have all been recorded. Tungsten powder differed from tantalum in that it was unattacked by hydrogen fluoride up to 700°, and an attempt was therefore made to prepare lower fluorides from the other dihalides. Tungsten dichloride could not be prepared in a pure state by reduction of the hexachloride (Biltz and Fendius, *Z. anorg. Chem.*, 1928, **172**, 385) and attempts were made to obtain tungsten dibromide. The product obtained by Roscoe's method (*Annalen*, 1872, **162**, 349) was found to contain unattacked metal and higher bromides. A pure product was, however, obtained by reducing the pentabromide in hydrogen at 400–450° and heating the product in a stream of dry nitrogen at 550°. The dibromide was a greenish-yellow powder, insoluble in water and unattacked by acids except hot nitric acid, which reacted with precipitation of yellow tungsten trioxide. It resembled molybdenum dibromide in its chemical inertness. It sublimed unchanged in nitrogen above 600°, but was converted into the trioxide when ignited in air. No reaction occurred with hydrogen fluoride up to 500°, but at 550° there was a slow reaction and, at intermediate stages of the reaction, the product contained fluorine. Probably the difluoride is formed but, since it is probably non-volatile, attack on the dibromide is incomplete. At 600°, however, the reaction went to completion and hexafluoride distilled off, though it could not be separated from hydrogen fluoride by distillation (b. p. 19°). The residue in the boat was metallic tungsten and not the difluoride. The weight of metal was less than would be expected for disproportionation according to the equations:



but this could be accounted for by sublimation of unchanged dibromide at 600°. This behaviour parallels that of the corresponding molybdenum compound (Emeléus and Gutmann, *loc. cit.*). No anhydrous trihalides of tungsten (*e.g.*, WCl_3) are known and many experiments designed to prepare them were unsuccessful.

Two simple fluorides of rhenium are known: the hexafluoride (Ruff and Kwasnik, *Z. anorg. Chem.*, 1932, **209**, 113) and the tetrafluoride (*idem, ibid.*, 1934, **219**, 65). Rhenium powder was unattacked by anhydrous hydrogen fluoride at 500°, and an attempt was made to prepare a lower fluoride from the trichloride. This was insoluble in liquid hydrogen fluoride. With gaseous hydrogen fluoride no reaction occurred at 100°. At 240° an intermediate product was obtained, consisting mainly of unchanged trichloride and probably some metal. At 350° reaction was complete but the product in the boat was metallic rhenium. In this case very little hexafluoride was formed and the rhenium in the residue accounted for almost all of that in the trichloride taken. The probable course of the reaction is shown by the equations:



In this case, as in that of tungsten difluoride, there is evidence that the lower fluoride is formed under conditions when it is decomposed. The experiments thus throw some light on the stability of these compounds, though clearly some other preparative methods operating at lower temperatures will be needed to produce the lower fluorides in states of purity.

EXPERIMENTAL.

Reactions with Gaseous Hydrogen Fluoride.—These reactions were carried out in a platinum-lined Monel tube, the exit of which had a constriction and was water-cooled to trap any sublimate. The tube was connected to a cylinder of hydrogen fluoride by a copper T-piece, through which either nitrogen or hydrogen could be admitted to the stream of hydrogen fluoride. The tube was heated in an electric furnace, and samples for treatment were contained in a platinum boat.

Preparation and Fluorination of "Niobium Trichloride."—The pentachloride was prepared by the action of chlorine on heated niobium powder in a Pyrex tube, and the product was reduced by repeated sublimations in hydrogen through a zone of the tube heated to *ca.* 500°, as in the reduction of tungsten hexachloride to dichloride (Biltz and Fendius, *Z. anorg. Chem.*, 1928, **172**, 385). This yielded a greyish-green solid which was non-hygroscopic and non-volatile at 550°. It was analyzed for chlorine by precipitation as silver chloride after precipitation of niobium with aqueous ammonia. The niobium precipitate was ignited to pentoxide and weighed. The results for several preparations showed the product to be intermediate in compositions between NbCl₅ and NbCl₃ (Found : Nb, 53.2, 53.6, 52.0, 55.2; Cl, 47.2, 46.5, 48.1, 46.0. Calc. for NbCl₃ : Nb, 46.7; Cl, 53.3. Calc. for NbCl₅ : Nb, 56.7; Cl, 43.3%). When treated with anhydrous hydrogen fluoride at 500°, the chloride was converted almost completely into the volatile niobium pentafluoride, which collected near the constriction of the cooled part of the reaction tube. It was analyzed for fluorine by the Willard–Winter method (*Ind. Eng. Chem. Anal.*, 1933, **5**, 7), 50% sulphuric acid being used for decomposition, and the distilled fluorosilicic acid titrated by 0.05N-thorium nitrate (Found : Nb, 49.2; F, 50.5. Calc. for NbF₅ : Nb, 49.5; F, 50.5%). The very small residue remaining in the platinum boat at 500° was green and contained chlorine. At 600° conversion into the pentafluoride was complete.

Fluorination of Niobium with Hydrogen Fluoride.—Niobium powder reacted with hydrogen fluoride at 250°, the volatile product being the pentafluoride and the residue unattacked metal. At 300° 3 g. of the metal were converted quantitatively into pentafluoride in 6 hours (Found : Nb, 49.6, 49.1; F, 50.2, 50.6%). This method is a useful alternative to the reaction of fluorine with niobium or of liquid hydrogen fluoride with the hygroscopic pentachloride. When the niobium was first heated at 250° in hydrogen and then at the same temperature in hydrogen–hydrogen fluoride, the pentafluoride was again formed, though in lower yield. The surface of the residual metal was coated with a thin blue layer which could not be separated. An X-ray powder photograph of the residue showed only lines due to the metal and no evidence could be obtained for the formation of trifluoride.

Preparation of Tantalum Trifluoride.—Tantalum powder reacted with anhydrous hydrogen fluoride below 200°, the product being a mixture of unattacked metal, tantalum pentafluoride, and probably some trifluoride. The pentafluoride could be separated by distillation in nitrogen at 250°. At 300° complete reaction of the metal occurred, about 90% yielding the volatile pentafluoride, while about 10% remained as non-volatile tantalum trifluoride. For analysis the trifluoride was dissolved in a mixture of sodium hydroxide and hydrogen peroxide, and tantalum determined as tantalum pentoxide. It was analyzed for fluorine by the Willard–Winter method (*loc. cit.*) (Found : Ta, 75.4, 75.8; F, 22.8, 24.1. TaF₃ requires Ta, 76.1; F, 23.9%). The volatile pentafluoride was collected near the constriction of the tube and was analyzed similarly after dissolution in sodium hydroxide (Found : Ta, 65.4; F, 34.4. Calc. for TaF₅ : Ta, 65.7; F, 34.3%). The reaction followed a similar course when the metal was preheated in hydrogen at 250° and then fluorinated with hydrogen–hydrogen fluoride, but was appreciably slower.

Preparation of Tungsten Dichloride and Dibromide.—Tungsten powder, previously heated in hydrogen to 1000° to remove any oxidic impurities, was converted into the hexachloride by heating it in chlorine in a Pyrex tube, and this salt was reduced by hydrogen under the conditions given by Biltz and Fendius (*loc. cit.*). The product was not pure, however, and appeared to contain higher chlorides. Tungsten was determined as tungsten trioxide after treatment of the chloride with nitric acid, evaporation to dryness, and ignition at 850°. For halogen determination the substance was dissolved in a mixture of sodium hydroxide and hydrogen peroxide and evaporated to dryness, and the residue digested with 20% nitric acid (Cooper and Wardlaw, *J.*, 1932, 636). Tungsten trioxide was filtered off and chloride determined as silver chloride in the filtrate after addition of phosphoric and nitric acids (Found : W, 70.1, 68.9; Cl, 30.7, 32.0. Calc. for WCl₂ : W, 72.2; Cl, 27.8%).

In the preparation of tungsten dibromide, tungsten was first brominated at 600° by bromine vapour carried in a nitrogen stream. The pentabromide sublimed and was then reduced by heating it in hydrogen as described by Biltz and Fendius (*loc. cit.*) for the preparation of the dichloride. It was necessary to avoid temperatures above 500°, as otherwise metallic tungsten was formed. The reduced material was then heated to 550° in a stream of purified nitrogen to remove more volatile higher halides. A yellowish-green solid—pure tungsten dibromide—remained. It was analyzed as described for the dichloride (Found : W, 53.2; Br, 46.9. Calc. for WBr₂ : W, 53.5; Br, 46.5%).

Reaction of Tungsten Dibromide with Hydrogen Fluoride.—Reaction commenced at *ca.* 550° and was incomplete even after 30 hours' heating at 580°. At 600° the dibromide commenced to sublime. The non-volatile product of the reaction at 600° contained no fluorine and was shown analytically and by an X-ray powder photograph to consist of tungsten. It was assumed that tungsten hexafluoride was the other reaction product. A blue layer of tungsten oxides was observed near the outlet of the reaction

tube, which was probably produced by hydrolysis of tungsten hexafluoride. In one experiment the tungsten dibromide which sublimed unchanged was recovered and weighed. The weight of dibromide used was 2.4816 g., that of sublimed unchanged dibromide was 0.4178 g., and that of tungsten metal remaining in the boat was 0.6920 g. This corresponds to a 94% recovery of tungsten on the basis of the equation already given. It was shown that tungsten powder was unattacked by anhydrous hydrogen fluoride up to 700°.

Preparation and Fluorination of Rhenium Trichloride.—Rhenium trichloride was prepared as described by Geilmann, Wrigge, and Biltz (*Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl.*, 1932, 579). Metallic rhenium, previously heated to redness in hydrogen, was heated in a porcelain boat in a tube furnace, first in nitrogen and then in purified chlorine. The black distillate of pentachloride was distilled into the first of a series of Pyrex bulbs, in which it was carefully heated in dry nitrogen to bring about decomposition into the trichloride and chlorine. The completion of the decomposition was indicated by the absence of brown vapour when the solid was heated gently. The residual trichloride sublimed when heated more strongly, giving a green vapour, and could be purified in this way. It was obtained in a yield of about 60%. It was analyzed for chlorine as silver chloride, after oxidation of the rhenium to per-rhenate as described by Geilmann and Lange (*Z. anorg. Chem.*, 1937, **234**, 289) (Found: Cl, 36.5, 36.3. Calc. for ReCl_3 : Cl, 36.4%). Rhenium trichloride was insoluble in liquid hydrogen fluoride. No reaction occurred with gaseous hydrogen fluoride at 100°. When the trichloride was heated at 240° an intermediate product was obtained which, however, consisted mainly of unchanged trichloride. Above 350° reaction of the trichloride, which is stable at 500° in nitrogen, was complete and metallic rhenium remained in the boat. This was identified by an X-ray powder photograph. Traces of a fluoride appeared to be present, however, since on exposure to air in glass tubes the latter were slightly etched within a few weeks. No fluorine was found on analysis. The amount of rhenium remaining corresponded almost quantitatively to that contained in the trichloride, as is shown by the following results:

ReCl_3 taken (g.)	0.2244	0.4288	0.3000
Re in ReCl_3 taken (g.)	0.1468	0.2729	0.1910
Re from the reaction (g.)	0.1440	0.2612	0.1885

Only traces of the volatile hexafluoride were formed, probably by a secondary reaction of the fluorine set free in the thermal decomposition of rhenium trifluoride formed as an intermediate.

One of the authors (V. G.) thanks the British Council for a Scholarship. The authors also thank Messrs. Johnson Matthey & Co. Ltd. for the loan of a quantity of rhenium and of the platinum-lined reaction tube.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, May 10th, 1950.]