629. *Studies on the Fluorides of Molybdenum and Vanadium.*

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The compound *molybdenum trifluoride* was prepared by heating the tribromide to 600° in hydrogen fluoride. It was not converted into difluoride either by reduction or by thermal disproportionation. Molybdenum dibromide reacted with hydrogen fluoride at 800—860° forming the metal and hexafluoride. Fluorine converted the metal into hexafluoride at 350°. Vanadium dichloride heated in hydrogen fluoride at 700° yielded the trifluoride, which did not disproportionate at 800° and was reduced by hydrogen to the metal. At 300° fluorine converted the metal into pentafluoride, which was also formed by the reaction of bromine trifluoride with the metal or the trichloride. Reaction of bromine trifluoride with mixtures of vanadium trichloride and potassium, silver or barium chlorides gave the *hexafluorovanadates* of these elements, that of potassium also being formed by the interaction of vanadium pentafluoride and potassium fluoride and decomposing into these compounds at 330° in a vacuum.

The only simple anhydrous fluoride of molybdenum known hitherto is the hexafluoride (Ruff and Eisner, *Ber.*, 1905, **38**, 747; 1907, **40**, 2926; Ruff and Ascher, *Z. anorg. Chem.*, 1931, **196**, 413). The known fluorides containing tervalent molybdenum are molybdenyl fluoride $MoOF,4H_2O$ (Wardlaw and Wormell, *J.*, 1927, 1087) and the complex fluorides $K[MoF_4],H_2O$ and $K_3[Mo_2F_9],2H_2O$ (Rosenheim and Li, *Ber.*, 1923, **56**, 2228). It has been found that *molybdenum trifluoride* is formed on heating the tribromide in hydrogen fluoride. This is a non-hygroscopic dark-pink powder, which is only slightly soluble in water and unaffected by 40% hydrofluoric acid, but decomposed by hot concentrated acids or by cold aqua regia. With cold solutions of sodium hydroxide there is a slow reaction, but the compound is dissolved by boiling with a mixture of sodium hydroxide and hydrogen peroxide. This fluoride is unaffected by organic solvents such as alcohol, carbon tetrachloride, or benzene. When it is heated in the air molybdenum trioxide and hydrogen fluoride are formed, but in absence of air it neither melts nor sublimes at 800°.

Molybdenum trifluoride resembles the trifluorides of vanadium, chromium, and iron. The high thermal stability of these compounds makes it impossible to prepare a bivalent and a higher fluoride by thermal decomposition, although the corresponding trichlorides and tribromides of molybdenum and vanadium are unstable at red heat and yield bivalent derivatives. Structurally the trifluorides of vanadium, chromium, molybdenum, iron, cobalt, palladium, and rhodium are closely related. The highest degree of symmetry is found in molybdenum trifluoride, which has the cubic rhenium trioxide structure. This is transformed by heat at 800° in the absence of air and moisture into the distorted structure (unpublished observations with K. H. Jack). Both chromium and iron trifluoride may be reduced by hydrogen quantitatively to the difluorides (Jellinek and Rudat, *Z. anorg. Chem.*, 1928, **175**, 281), but the trifluorides of molybdenum and vanadium yielded only the metal.

Attempts to prepare molybdenum difluoride by the reaction of the dibromide with hydrogen fluoride were unsuccessful: no reaction occurred up to 500°. At 700° there was a slow reaction the product of which was not homogeneous, and above 800° molybdenum hexafluoride and the metal were formed. The hexafluoride was not separated from hydrogen fluoride, but the weight of residual metal was in accord with the reaction scheme:

$$Mo_3Br_6 + 6HF \rightleftharpoons 3MoF_2 + 6HBr$$
$$3MoF_2 \rightleftharpoons 2Mo + MoF_6$$

The molybdenum was characterised analytically and by *X*-ray powder photographs. It was found to be inert to hydrogen fluoride at 860°. Fluorine itself attacks metallic molybdenum at 60°, forming the hexafluoride (Ruff and Ascher, *loc. cit.*). When this reaction was carried out at 350° with fluorine diluted with nitrogen no lower fluoride was formed. Bromine trifluoride attacked molybdenum with incandescence, the main product being the volatile hexafluoride, although a white residue which was probably molybdenum oxytetrafluoride remained in the silica reaction vessel. Molybdenum dibromide reacted with bromine trifluoride similarly, but less vigorously. In the course of these experiments with the molybdenum halides it was shown that the dichloride may be prepared very conveniently by the action of anhydrous hydrogen chloride on the tribromide at dull-red heat.

Vanadium difluoride was not obtained by the action of hydrogen fluoride on the dichloride. The product was the trifluoride, which is believed to result from the reactions:

$$VCl_2 + 2HF \rightleftharpoons VF_2 + 2HCl$$
$$VF_2 + HF \rightleftharpoons VF_3 + \tfrac{1}{2}H_2$$

This mechanism, involving the decomposition of hydrogen fluoride by the strongly reducing difluoride, corresponds with observations by Manchot and Fischer (*Annalen*, 1907, **357**, 129). They prepared a violet-red solution by the action of hydrofluoric acid on vanadium aluminium silicide in the absence of air. This contained bivalent vanadium, presumably in the form of a difluoride, but on admission of air or addition of an excess of hydrogen fluoride a green solution containing tervalent vandium resulted. Hydrogen fluoride did not react with vanadium metal at a red heat, though chromium readily forms its difluoride under these conditions (Poulenc, *Ann. Chim. Phys.*, 1894 [vii], **2**, 60). Reduction of the trifluoride by hydrogen occurred above 500°, but only the metal was formed.

Vanadium trifluoride was first prepared by Ruff and Lickfett (*Ber.*, 1911, **44**, 2539) by the action of hydrogen fluoride on the trichloride at red heat. It was found to be formed in small amounts by heating the metal in fluorine at 450°, whereby mainly the pentafluoride was formed.

Vanadium pentafluoride was first obtained by Ruff and Lickfett (*loc. cit.*) by the thermal disproportionation of the tetrafluoride into tri- and penta-fluoride. The action of fluorine on the metal, which has not been studied previously, has been found to give the pentafluoride almost quantitatively at 300°. Bromine trifluoride also converted the metal into pentafluoride with incandescence and reacted similarly, but much less vigorously, with vanadium trichloride. It proved difficult, however, to separate the products by simple distillation. Vanadium pentoxide or vanadium oxytrichloride on the other hand formed mainly vanadium oxytrifluoride, VOF_3.

An interesting new reaction of the pentafluoride was that with potassium fluoride, which yielded *potassium hexafluorovanadate*, KVF_6. Since the pentafluoride is also formed by the action of bromine trifluoride on vanadium trichloride, it would be expected that the same salt would be formed from bromine trifluoride and a mixture of potassium fluoride (or chloride) and vanadium trichloride. This proved a very convenient preparative method, and, by use of barium chloride and silver or silver chloride in place of potassium chloride, both *barium hexafluorovanadate*, $Ba(VF_6)_2$, and *silver hexafluorovanadate*, $AgVF_6$, were obtained. The potassium and silver salts were soluble in bromine trifluoride and in these cases the formation of hexafluorovanadate was quantitative. The barium salt, however, was insoluble and was not obtained completely pure but contained some barium bromofluoride. The three hexafluorovanadates were extremely hygroscopic and fumed in moist air, losing hydrogen fluoride and leaving an orange residue which contained vanadium pentoxide. The potassium and silver salts were soluble in cold water, undergoing hydrolysis, but the barium salt dissolved only with difficulty owing to the low solubility of barium fluoride, which was formed by hydrolysis. The potassium and the barium salt were white solids, whilst the silver salt was orange-red. All were decomposed by 50% sulphuric acid with precipitation of vanadium pentoxide. The potassium salt was stable in a vacuum up to 300° but decomposed at 330° into potassium fluoride and vanadium pentafluoride. The pentafluoride attacks glass readily at this temperature, but in suitable metal or refractory containers this decomposition could probably be developed as a preparative method for the pentafluoride.

Structurally the hexafluorovanadates probably resemble the hexafluorophosphates. It has been shown that the latter are formed by the action of bromine trifluoride on phosphates of cations which form stable bromofluorides and a reaction mechanism involving the neutralisation of the bromofluoride by the hypothetical acid $BrF_2^+PF_6^-$ has been postulated (Emeléus and Woolf, in the press). In the formation of the potassium salt from potassium metaphosphate and bromine trifluoride, for example, the essential reaction is believed to be :

$$K^+BrF_4^- + BrF_2^+PF_6^- = KPF_6 + 2BrF_3$$

Vanadates do not react with bromine trifluoride in an analogous manner, but it is likely that the formation of hexafluorovanadates in presence of bromine trifluoride involves a similar unstable acidic substance $BrF_2^+VF_6^-$. The investigation is being continued to obtain further evidence for the existence of this compound and also to determine whether the behaviour of the fluorides of columbium and tantalum is similar.

EXPERIMENTAL.

Preparation of Molybdenum Tribromide and Dibromide.—Molybdenum powder, previously heated in hydrogen at 1000°, was heated at 450—500° with a stream of bromine vapour carried by dry nitrogen. The tribromide sublimed and was purified by treatment with cold water containing hydrobromic acid, filtration, and drying in a vacuum (Muthmann and Nagel, *Ber.*, 1898, **31**, 2009) (Found: Mo, 29·9; Br, 70·5. Calc. for $MoBr_3$: Mo, 28·5; Br, 71·5%). The dibromide was prepared in the same way but at a temperature of 600—650° (Lindner and Helwig, *Z. anorg. Chem.*, 1925, **142**, 180). Some tribromide sublimed and the involatile dibromide remained in the reaction tube as an orange residue containing some unchanged molybdenum. It was ground and re-treated with bromine to complete the conversion (Found : Mo, 37·9; Br, 62·5. Calc. for $MoBr_2$: Mo, 37·4; Br, 62·6%).

Preparation of Molybdenum Dichloride.—Preparations were made by the method of Lindner, Haller, and Helwig (*Z. anorg. Chem.*, 1923, **130**, 209; *Ber.*, 1922, **55**, 1458). This and other published methods appear to be less satisfactory than a new method involving the reaction of molybdenum tribromide with anhydrous hydrogen chloride at 500°. At 400° some trichloride and some unreacted tribromide is present in the reaction product, but at the higher temperature a yellow residue of anhydrous dichloride remains in the reaction tube, higher chlorides formed by disproportionation of the trichloride subliming off (Found : Mo, 57·3; Cl, 42·8. Calc. for $MoCl_2$: Mo, 57·5; Cl, 42·5%).

Preparation and Reduction of Molybdenum Trifluoride.—A platinum boat containing the tribromide was heated in a stream of hydrogen fluoride in a copper tube (65 cm. long, 2 cm. in diameter), the exit end of which was cooled to trap any sublimate. As a preliminary the tube and its contents were heated in a stream of dry nitrogen to expel air and moisture. The course of the fluorination was followed roughly by holding a drop of silver nitrate solution on a loop of platinum wire in the escaping fumes. At 350° the molybdenum tribromide became coated with a film of fluoride which retarded volatilisation of the tribromide. Owing to this factor it was possible to raise the temperature gradually to 500° without any considerable loss from the boat. The product was cooled, ground, and reheated in hydrogen fluoride to 600° for 7 hours. This process was repeated and the conversion was then complete. When the molybdenum halide contained oxybromide as an impurity a sublimate of oxyfluoride was deposited in the cooled part of the tube, but with pure starting material the yield of trifluoride was 95%. *Molybdenum trifluoride* was analysed for molybdenum by dissolution in a mixture of sodium hydroxide and hydrogen peroxide, precipitation as sulphide, and convertion of this into oxide. Fluorine determination by the Willard–Winter method using 20% perchloric acid for distillation gave results about 20% low. The determination was therefore made by precipitation of calcium fluoride, followed by washing with 3% acetic acid to remove calcium molybdate (Found : Mo, 62·2, 62·8; F, 36·1, 35·7. MoF_3 requires Mo, 62·8; F, 37·2%).

Molybdenum trifluoride was reduced in pure hydrogen in the same apparatus. After treatment for

2 hours at 400° the compound was unchanged. At 440° there was a slight loss in weight and at 650° there was a 34% decrease in weight in 1 hour, indicating reduction to the metal. Reduction to difluoride would require a loss of only 12·4% in weight. The presence of molybdenum was confirmed by *X*-ray powder photographs.

Action of Hydrogen Fluoride on Molybdenum Dichloride and Dibromide.—At 500° the halides were practically unattacked by hydrogen fluoride, although a thin black layer was formed on the solid surface. At 730° reaction was very slow, small amounts of an unidentified green intermediate reaction product being observed. Prolonged reaction at this temperature gave a black powder, which still contained bromine or chlorine. When the dibromide was heated in hydrogen fluoride at 800—860° without previous heating at lower temperature, a grey powder remained. This was shown by analysis to contain 97·2% of metallic molybdenum and traces of bromine. An *X*-ray powder photograph showed only molybdenum lines.

Action of Fluorine on Molybdenum.—Molybdenum powder in a platinum boat was heated to 350° in nitrogen, which was then replaced in successive experiments by varying proportions of fluorine. In every case the metal was converted into a volatile fluoride and there was no indication of the formation of an involatile lower fluoride.

Preparation of Vanadium Di- and Tri-chloride.—Vanadium trichloride was prepared by a modification of Ruff and Lickfett's method (*Ber.*, 1911, **44**, 506). A mixture of vanadium pentoxide (12 g.) and sulphur (6 g.) was heated in a current of dry chlorine at a temperature which was increased gradually to 550°. The dark brown distillate, consisting of $VOCl_3$, VCl_4, and S_2Cl_2, was collected and refluxed for 10 hours with sulphur (11 g.). Sulphur chloride was distilled off and free sulphur was removed from the residual trichloride by heat in a vacuum at 300° (Found : V, 32·2, 32·5; Cl, 67·8, 67·1. Calc. for VCl_3 : V, 32·4; Cl, 67·6%). Vanadium dichloride was prepared by thermal disproportionation of the trichloride (Ruff and Lickfett, *loc. cit.*). Reduction of the trichloride (Klemm and Hoschek, *Z. anorg. Chem.*, 1936, **226**, 361) gave a less pure product (Found : V, 41·3; Cl, 59·1. Calc. for VCl_2 : V, 41·8; Cl, 58·2%). Vanadium oxytrichloride was prepared by the action of chlorine on vanadium pentoxide (Ruff and Lickfett, *loc. cit.*).

Reactions of Vanadium Di- and Tri-chloride with Hydrogen Fluoride.—Anhydrous hydrogen fluoride reacted slowly with the dichloride at 700°, the product being the pure trifluoride (Found : V, 47·6; F, 53·4. Calc. for VF_3 : V, 47·2; F, 52·8%). The trifluoride was also prepared from hydrogen fluoride and vanadium trichloride at 600° (Ruff and Lickfett, *Ber.*, 1911, **44**, 2539). Fluorine was determined by the Willard–Winter method using 20% perchloric acid for distillation, since decomposition with 50% sulphuric acid was incomplete.

Preparation of Vanadium Pentafluoride and Potassium Hexafluorovanadate.—Vanadium powder in a nickel boat, contained in a heated copper tube connected to a cooled nickel trap, was allowed to react with fluorine at 300° (at 160° the metal remained unattacked). The crude distillate was purified by trap-to-trap vacuum-distillation in a silica apparatus. It was analysed for vanadium by dissolution in sodium hydroxide and titration with potassium permanganate. Fluorine was precipitated as calcium fluoride, which was then decomposed with 20% perchloric acid to separate it from calcium vanadate (Found : V, 35·1; F, 64·0. Calc. for VF_5 : V. 34·9; F, 65·1%).

To potassium fluoride (0·3 g.) in a Pyrex tube attached to the vacuum system an excess of vanadium pentafluoride was added. The tube was sealed off in a vacuum and kept at room temperature for 3 days, after which unchanged pentafluoride was distilled off in a vacuum. A hygroscopic white residue of *potassium hexafluorovanadate* remained (Found : V, 25·5, 25·7; F, 55·2, 55·0. KVF_6 requires V, 25·0; F, 55·7%).

Preparation of Hexafluorovanadates by use of Bromine Trifluoride.—The experimental procedure was similar to that used in the preparation of bromofluorides (Sharpe and Emeléus, *J.*, 1948, 2135). Bromine trifluoride was added cautiously to accurately weighed quantities of vanadium trichloride and potassium chloride cooled by liquid air in a silica flask, attached by a ground joint to the vacuum system. When the bromine trifluoride was allowed to melt a reaction set in which was completed, after the addition of an excess of the reagent, by heat at 130°. Excess of bromine trifluoride was removed in a vacuum, the last traces being removed by warming the residue to 50°. Fluorine was determined by decomposing the *salt* with 50% sulphuric acid and silica, and titrating the fluosilicic acid distilled with thorium nitrate solution. Vanadium was determined by titration with potassium permanganate (Found : K, 19·7; V, 24·9; F, 55·1; equiv., 203. KVF_6 requires K, 19·2; V, 25·0; F, 55·8%; equiv., 204). *Silver hexafluorovanadate* was prepared similarly from metallic silver, or silver chloride, and vanadium trichloride. Silver was precipitated as silver bromide and the filtrate used for determination of vanadium (Found : Ag, 38·7; V, 19·2; F, 41·6%; equiv., 267. $AgVF_6$ requires Ag, 39·3; V, 18·8; F, 41·9%; equiv., 272). *Barium hexafluorovanadate* was prepared by use of barium chloride (Found : Ba, 31·7; V, 21·8; F, 46·1%; equiv., 442. BaV_2F_{12} requires Ba, 29·3; V, 21·9; F, 48·8%; equiv., 467).

Thermal Decomposition of Potassium Hexafluorovanadate.—A weighed amount of the salt was heated in a Pyrex tube connected by a cooled silica trap to the vacuum line, a small plug of glass wool being placed in the top of the heated tube to prevent the carry-over of solids. No reaction occurred up to 300°, but at 330° reaction was rapid, vanadium pentafluoride collected in the trap, and potassium fluoride containing only a trace of vanadium remained in the heated tube. The pentafluoride was analysed (Found : V, 35·1; F, 64·9. Calc. for VF_5 : V, 34·9; F, 65·1%).

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