174. *The Fluorination of Compounds of Vanadium, Chromium, and Manganese by Bromine Trifluoride.*

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New complex fluorides $KCrOF_4$, $AgCrOF_4$, and $KMnF_5$ are obtained by the action of bromine trifluoride on potassium dichromate, silver dichromate, and potassium permanganate; all are readily hydrolysed. Unsuccessful attempts to prepare manganese tetrafluoride are described; quadrivalent manganese is, however, stabilised in bromine trifluoride, as in aqueous solvents, by complex formation, yielding, *e.g.*, $KMnF_5$ and K_2MnF_6. Removal of oxygen from vanadium pentoxide and vanadates by bromine trifluoride is usually slow, and owing to the formation of oxygen-containing complexes these substances are not suitable starting materials for the preparation of hexafluorovanadates; nitrosonium hexafluorovanadate is, however, obtained from nitrosyl chloride, vanadium pentoxide, and bromine trifluoride.

Preliminary experiments on the action of bromine trifluoride on chromium compounds were made in this laboratory by Banks (Thesis, Cambridge, 1948), who showed that this reagent converts chromium trioxide and potassium dichromate into oxygen- and fluorine-containing chromium compounds in an oxidation state between four and six. This paper describes detailed work on these reactions and those of compounds of vanadium and manganese; the principles and technique of the preparation of complex fluorides by bromine trifluoride have previously been discussed (Woolf and Emeléus, *J.*, 1949, 2865; Sharpe, *J.*, 1950, 3444).

Emeléus and Gutmann (*J.*, 1949, 2979) showed that bromine trifluoride, vanadium trichloride, and alkali-metal halides yield hexafluorovanadates, *e.g.*, KVF_6. When bromine trifluoride reacts with vanadium pentoxide, however, the volume of oxygen evolved, measured by Emeléus and Woolf's method (*J.*, 1950, 164), corresponds to only three atoms of oxygen per molecule of the pentoxide. The composition of the product from sodium vanadate varies from $NaVOF_4$ to $NaVF_6$ according to the time for which the vanadate is boiled with bromine trifluoride. Similar results were obtained with other vanadates. In view of the difficulty of determining combined oxygen, it is inadvisable to replace vanadium trichloride by the pentoxide or an oxy-salt in the preparation of hexafluorovanadates.

Chromium trioxide reacts with bromine trifluoride with liberation of two-thirds of its oxygen. The residue slowly volatilises *in vacuo* at temperatures necessary for removal of the excess of bromine trifluoride, and the isolation of a chromium oxyfluoride has not been achieved. If, however, the solution obtained from chromium trioxide and bromine trifluoride is treated with one mole of a "base" on the bromine trifluoride system (*e.g.*, $KBrF_4$, $AgBrF_4$) complex oxyfluorides of quinquevalent chromium are obtained. The action of bromine trifluoride on a mixture of potassium chloride and chromium trioxide in equimolecular proportions, for example, yields a residue of composition $KCrOF_4,0{\cdot}5BrF_3$ if the solution is evaporated *in vacuo* at 20°; heating at 130—150° effects removal of all the combined bromine trifluoride, and potassium tetrafluoro-oxychromate(V), $KCrOF_4$, remains. This substance is also produced by fluorination of potassium dichromate with bromine trifluoride, five-sevenths of the oxygen initially present being eliminated. It is immediately hydrolysed by water, forming a solution containing ter- and sexa-valent chromium in 1 : 2 proportion. The corresponding silver salt, $AgCrOF_4$, is similarly obtained from silver dichromate; a pure nitrosonium salt could not be made. Potassium chromate and bromine trifluoride appear to yield a mixture of potassium tetrafluoro-oxychromate(V) and tetrafluorobromite: there is no evidence for the formation of another complex, K_2CrOF_5, although this would be more likely to contain six-co-ordinated chromium. Thus the valency of chromium in complex halide ions decreases with decreasing oxygen content: potassium fluorotrioxychromate(VI), $KCrO_3F$, is well known, but the highest complex fluoride is K_2CrF_6 (Huss and Klemm, *Z. anorg. Chem.*, 1950, **262**, 25).

Recent work on manganese fluorides has been reported by Aynsley, Peacock, and Robinson (*J.*, 1950, 1622) and by Huss and Klemm (*loc. cit.*). The former authors state that fluorine and potassium permanganate at 150° yield a mixture of potassium, manganese(II), and manganese(III) fluorides, but no potassium hexafluoromanganite(IV), K_2MnF_6; the latter authors obtained the hexafluoromanganite by heating a mixture of composition $2KCl : MnCl_2$ in fluorine.

Manganous iodate reacts vigorously with bromine trifluoride, with evolution of all the oxygen and formation of iodine pentafluoride. The solution which remains contains quadrivalent manganese, as is shown by its successive conversion into the complex fluorides $KMnF_5$ and K_2MnF_6 by treatment with potassium tetrafluorobromite in pure (pale yellow) bromine trifluoride: in these reactions, no bromine is liberated. Since any increase in the oxidation number of the manganese would require simultaneous reduction of some bromine trifluoride to bromine (readily detectable by its colour) the manganese must be in the oxidation state +4 throughout. From the solution, however, isolation of manganese tetrafluoride is impossible: the unstable addition product, probably $(BrF_2)(MnF_5)$, decomposes when gently heated, and removal of the bromine trifluoride yields only a residue of manganese trifluoride.

A more convenient preparation of potassium pentafluoromanganite(IV), $KMnF_5$, is from potassium permanganate and bromine trifluoride. Oxygen evolution from the permanganate is quantitative, and removal of the solvent *in vacuo* leaves the fluoromanganite as a pinkish powder which is decomposed by water with the production of hydrated manganese dioxide and hydrofluoric acid. *X*-Ray powder photography shows its freedom from KF, MnF_3, and K_2MnF_6. Fluorination of a mixture of equimolecular proportions of potassium permanganate and potassium chloride with bromine trifluoride yields yellow potassium hexafluoromanganite(IV), and there are thus two complex fluorides of potassium and quadrivalent manganese.

Treatment of dinitrogen tetroxide and manganous iodate with bromine trifluoride, in the way used by Woolf and Emeléus (*J.*, 1950, 1050) for the preparation of nitronium complex fluorides, yielded a nitrogen-containing product which was probably an impure nitronium fluoromanganite: its thermal decomposition at 150° again yielded only manganese trifluoride. Manganese trifluoride is found by *X*-ray powder photography to be isomorphous with cobalt trifluoride and hence with the other trifluorides of metals of the first transition series.

The failure to prepare manganese tetrafluoride strongly suggests that quadrivalent manganese is stable in bromine trifluoride only when in a complex anion. This recalls the similar stability in aqueous solvents: quadrivalent manganese appears only in very sparingly soluble compounds (*e.g.*, MnO_2) or in complex ions (*e.g.*, MnF_6^{--}, $MnCl_6^{--}$, and $Mn(CN)_6^{--}$).

The relatively light colour of the salts $KCrOF_4$ and $AgCrOF_4$ apparently precludes the possibility of the presence of chromium in two valency states in these compounds, and indicates that they are derivatives of quinquevalent chromium. The absence of any evidence from *X*-ray data for finite complex ions of the type (MX_5) makes it desirable to produce more evidence before formulating the compounds of empirical formulæ $KCrOF_4$ and $KMnF_5$ with such finite ions. Complexes Tl_2AlF_5 (Brosset, *Z. anorg. Chem.*, 1937, **235**, 139) and Cs_3CoCl_5 (Powell and Wells, *J.*, 1935, 359), for example, contain anion chains of (AlF_6) octahedra, and individual ions Cs^+, $(CoCl_4)^{--}$, and Cl^- respectively. Further discussion of the structures of the new complex fluorides reported here is therefore postponed until additional information is available.

EXPERIMENTAL.

Vanadium Compounds.—Sodium vanadate dissolved quietly in boiling bromine trifluoride. The product obtained by immediate removal of the solvent at 45° *in vacuo* contained a considerable quantity of bromine [Found : wt. equiv. to $NaVO_3$ (= 122), 220; V, 22·0; F, 45·2; Br, 13·2%]. Vanadium was determined by reduction to the quadrivalent state by sulphur dioxide, and titration with permanganate; fluorine was determined by the Willard–Winter method, bromine by precipitation as silver bromide. The residue obtained by heating the first product at 100° approximated in composition to $NaVOF_4$ (Found : equiv., 163; V, 29·8; F, 45·2%; Br, nil. Calc. for $NaVOF_4$: equiv., 166; V, 30·7; F, 45·8%). If, however, the solution of the vanadate in bromine trifluoride was heated under reflux in a long-necked quartz flask for 30 minutes before removal of the solvent at 45°, the composition of the residue approximated to $NaVF_6$ (Found : equiv., 186; V, 28·3; F, 57·0%. Calc. for $NaVF_6$: equiv., 188; V, 27·2; F, 60·7%). Nitrosyl chloride (in excess), vanadium pentoxide, and bromine trifluoride yielded ***nitrosonium hexafluorovanadate*** when the solution was evaporated at 20° (Found : N, 7·9; V, 26·6; F, 57·8. $NOVF_6$ requires N, 7·2; V, 26·2; F, 58·4%). Nitrosonium hexafluorovanadate is a white solid, rapidly hydrolysed by water and decomposing at 60°. Attempts to obtain silver and nitronium hexafluorovanadates gave products intermediate in composition between the tetrafluoro-oxyvanadates and the hexafluorovanadates.

Chromium Compounds.—When chromium trioxide, dried at 120°, was treated with bromine trifluoride, 64% (in a second experiment, 57%) of the oxygen was evolved; a little chromium was volatilised, presumably as an oxyfluoride. Evaporation of the solution in the usual way gave a product which retained some bromine even after being heated for four hours at 200° (Found : Cr, 37·5; F, 44·8; Br, 9·3%). On prolonged boiling, bromine trifluoride solutions of the product from chromium trioxide become pasty and then solidified; the residue from one of these was analysed after attaining a constant weight *in vacuo* at 20° (Found : Cr, 23·8; F, 43·5; Br, 27·2%). Both analysed products gave aqueous solutions containing ter- and sexa-valent chromium and hydrofluoric acid. The most satisfactory explanation of these observations, in accord with experiments on oxy-salts, appears to be the formation of a thermally unstable compound between $CrOF_3$ and BrF_3 [the calculated composition for $(BrF_2)(CrOF_4)$ is Cr, 19·7; F, 43·5; Br, 30·3%]. If it is assumed that, in both products, each bromine atom is equivalent to one molecule of combined bromine trifluoride, then the ratios of chromium to (fluorine not present as BrF_3) are 1 : 2·8 (high-temperature product) and 1 : 2·85 (low-temperature product).

The action of bromine trifluoride on chromium trioxide–boric oxide and chromyl chloride–boric oxide mixtures yields boron-free residues; thse results are similar to those obtained with sulphuryl chloride and boric oxide, and show that salts containing CrO_2^{++} and SO_2^{++} ions are not formed.

Potassium dichromate was a convenient starting material for the preparation of a complex oxyfluoride derived from the postulated " acid," $(BrF_2)(CrOF_4)$. This salt evolved 71·5% of its oxygen on treatment with bromine trifluoride. After removal of the solvent *in vacuo* at room temperature, the purple residue, of composition $KCrOF_4,0{\cdot}5BrF_3$, was hydrolysed by sodium hydroxide solution. Bromine was determined as silver bromide after reduction with sulphurous acid. A portion of the reduced solution was oxidised to chromate by sodium peroxide, and total chromium was determined iodometrically. Fluorine was determined by decomposition with sodium hydroxide solution and precipitation by calcium fluoride in weakly alkaline carbonate-containing solution; the mixed calcium carbonate–calcium fluoride precipitate was washed free from chromate and then treated in the usual way. The alternative Willard–Winter method gave the same result [Found : wt. equiv. to $\frac{1}{2}K_2Cr_2O_7$ (= 147), 253; Cr, 20·2; Br, 14·3; F, 41·0%. $KCrOF_4,0{\cdot}5BrF_3$ requires equiv., 251; Cr, 20·7; Br, 15·9; F, 41·5%]. After being heated *in vacuo* for two hours at 70° the residue had the approximate composition $KCrOF_4,0{\cdot}3BrF_3$; at 130—150° elimination of bromine was rapidly completed, and *potassium tetrafluoro-oxychromate*(V) remained as a light purple powder, shown by *X*-ray powder photography to be free from potassium fluoride. After hydrolysis with sodium hydroxide, sexavalent chromium was determined iodometrically; tervalent chromium was precipitated as hydroxide by the potassium cyanate–ammonium chloride method, and, after oxidation to chromate, determined iodometrically. Total chromium and fluorine were determined as above [Found : wt. equiv. to $\frac{1}{2}K_2Cr_2O_7$ (= 147), 185; Cr, 28·1; Cr^{III}, 9·2; Cr^{VI}, 18·2; F, 39·8%. $KCrOF_4$ requires equiv., 183; Cr, 28·4; Cr^{III}, 9·5; Cr^{VI}, 19·0; F, 41·5%]. Bromine trifluoride and an equimolecular mixture of potassium chloride and chromium trioxide gave the same product. Silver dichromate was similarly converted into *silver tetrafluoro-oxychromate*(V), a light purple powder which was instantly hydrolysed by moist air, with the formation of silver chromate [Found : wt. equiv. to $\frac{1}{2}Ag_2Cr_2O_7$ (= 216), 254; Ag, 42·4; Cr, 20·5; Cr^{VI}, 13·9; F, 29·5%. $AgCrOF_4$ requires equiv., 252; Ag, 42·8; Cr, 20·6; Cr^{VI}, 13·9; F, 30·2%]. Attempts to obtain a pure nitrosonium salt were unsuccessful.

Manganese Compounds.—Potassium permanganate reacted vigorously with bromine trifluoride; in three experiments the volume of oxygen evolved was 99, 103, and 100% of the theoretical value. Removal of the solvent *in vacuo* at 20° left pink *potassium pentafluoromanganite*(IV) $KMnF_5$, contaminated to a slight extent with the elements of bromine trifluoride. In several preparations the weight of product equivalent to $KMnO_4$ = 158 varied from 185 to 210. One specimen was analysed by decomposition with sodium carbonate solution, and determination of manganese, fluorine, and bromine as the oxide Mn_3O_4, calcium fluoride, and silver bromide respectively [Found : wt. equiv. to $KMnO_4$ (= 158), 195; Mn, 28·7; F, 46·0; Br, 3·8%. $KMnF_5$ requires equiv., 189; Mn, 29·1; F, 50·2%].

Bromine trifluoride and an equimolecular mixture of potassium permanganate and chloride yielded yellow potassium hexafluoromanganite(IV) (Found : Mn, 21·6; F, 44·0; Br, 1·2. Calc. for K_2MnF_6 : Mn, 22·3; F, 46·2%). Its identity was confirmed by comparison of its *X*-ray powder photograph with that of a sample of K_2MnF_6 prepared in the wet way [Bellucci, *Atti R. Accad. Lincei*, 1913, **22**, (ii), 579] by Dr. W. G. Palmer.

Potassium pentafluoromanganite(IV) is, like the hexafluoromanganite, decomposed by cold water with the precipitation of hydrated manganese dioxide; the salt is stable *in vacuo* at 180°. The action of bromine trifluoride on a 1 : 2 mixture of potassium permanganate and chloride yielded the hexafluoromanganite and the tetrafluorobromite.

In view of this formation of derivatives of quadrivalent manganese, the action of bromine trifluoride on manganous iodate (Emeléus and Woolf, *loc. cit.*) was re-investigated. The iodate dissolved in boiling bromine trifluoride, yielding a clear solution which reacted with dry potassium fluoride (without liberation of bromine), forming successively $KMnF_5$ and K_2MnF_6. This indicated that the solution contained quadrivalent manganese; evaporation of the solution at 20° gave only a red product containing much less bromine than would be required for $(BrF_2)(MnF_5)$. This at 140° lost nearly all its bromine, yielding manganese trifluoride (Found : Mn, 46·5; F, 47·5; Br, 4·0. Calc. for MnF_3 : Mn, 49·2; F, 50·8%). The action of heat on the product obtained from bromine trifluoride, manganous iodate, and excess of dinitrogen tetroxide yielded a similar residue.

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