675. *Simple and Complex Fluorides of Some Noble Metals.*

By A. G. Sharpe.

Bromine trifluoride has been used as fluorinating agent in the preparation of platinum tetrafluoride, rhodium tetrafluoride, and palladium trifluoride from halides of these metals. Platinum tetrafluoride dissolves in the reagent, yielding a compound $PtBr_2F_{10}$, which undergoes partial reaction with potassium tetrafluorobromite (bromotetrafluoride), forming a mixture from which pure potassium hexafluoroplatinate may be separated by a procedure based on the widely different rates of hydrolysis of PtF_4 and the $[PtF_6]^{--}$ ion. Rhodium tetrafluoride and palladium trifluoride also yield complex fluorides, but these are unstable to water and have not been obtained pure. Complex fluoride ions are generally the least stable of complex halide ions of noble metals, the stability increasing from fluoride to iodide; the value of this stability sequence is illustrated in the preparation of sodium hexabromoplatinate and potassium tetrabromopalladite by heating the accessible complex chlorides with hydrobromic acid. Substitution reactions of the hexafluoroplatinate ion:

$$[PtF_6]^{--} + 6X^- = [PtX_6]^{--} + 6F^-$$

where X = Cl, Br, or I are hydrogen-ion catalysed; the rate-determining step is the first, and *X*-ray powder photography shows that products intermediate in composition between K_2PtF_6 and K_2PtBr_6 are not isolated in the reaction between potassium hexafluoroplatinate and hydrobromic acid.

The use of bromine trifluoride for the preparation of auric fluoride and the fluoroaurates (Sharpe, *J.*, 1949, 2901) suggested that this reagent might find application in the preparation of fluorides of other noble metals, and with its aid new methods for the production of the highest fluorides of platinum, rhodium, and palladium have been devised. For the preparation of these substances, bromine trifluoride has two main advantages over elemental fluorine: in the first stage of the process, addition compounds between the fluorides and the solvent are formed in solution, thereby ensuring rapid and quantitative reaction; in the second stage, the addition compounds undergo thermal decomposition at temperatures below 200°, so the use of special apparatus is unnecessary, and the whole preparation may be carried out in a quartz flask without significant damage to this vessel.

Metallic platinum is not attacked by bromine trifluoride at room temperature, but if the metal is first converted into its tetrachloride or tetrabromide (which need not be prepared pure) vigorous reactions take place on the addition of the reagent, and a clear red solution results. Evaporation of this *in vacuo* at room temperature yields a red product of empirical formula $PtBr_2F_{10}$, which is vigorously decomposed by water or alcohol but is not attacked by carbon tetrachloride. This substance undergoes rapid decomposition at 180—200°, forming bromine trifluoride and light brown platinic fluoride. The latter compound is identical in properties with that described by Moissan ("Le fluor et ses composés," Paris, 1900); it is rapidly hydrolysed to a hydrated dioxide by boiling water.

In bromine trifluoride solution the compound $PtBr_2F_{10}$ reacts as an "acid" (Woolf and Emeléus, *J.*, 1949, 2865), and with potassium tetrafluorobromite (bromotetrafluoride), a "base," it forms a salt:

$$(BrF_2)_2PtF_6 + 2KBrF_4 = K_2PtF_6 + 4BrF_3$$

As often occurs in such "neutralisations" in bromine trifluoride, interaction of "acid" and "base" is incomplete (Sharpe, *J.*, 1950, 2907) and evaporation of the solution at 20° produces a residue of approximate composition $K_2PtF_6,1{\cdot}1BrF_3$. When pure potassium hexafluoroplatinate, obtained as described below, is dissolved in bromine trifluoride and the solution is evaporated at room temperature, a similar residue remains; this contamination of the salt with the elements of bromine trifluoride is therefore of the nature of an equilibrium state, and the product may be described as partially solvolysed potassium hexafluoroplatinate, *i.e.*, a mixture of K_2PtF_6, $KBrF_4$, and $(BrF_2)_2PtF_6$. The last two of these substances are thermally unstable, and heating at 200° results in removal of all the bromine, leaving a residue in which the atomic proportions are Pt : 2K : 6F. This is not a compound, however, but a mixture of K_2PtF_6, KF, and PtF_4; the last two substances are formed by thermal decomposition of $KBrF_4$ and $(BrF_2)_2PtF_6$ respectively. The action of boiling water on the mixture rapidly hydrolyses the platinic fluoride to the insoluble hydrated dioxide, which is filtered off, and yellow crystals of potassium hexafluoroplatinate (only very slowly hydrolysed by boiling water) are obtained by fractional crystallisation at room temperature. This substance has been made twice previously: by the action of the complex fluoride $3KF,HF,PbF_4$ [which would probably be better represented as $K_3(PbF_6)(HF_2)$] on platinum (Schlesinger and Tapley, *J. Amer.*

Chem. Soc., 1924, **46**, 276); and in small quantity by thermal decomposition of potassium tetrafluorobromite in a platinum crucible (Sharpe and Emeléus, *J.*, 1948, 2135). The method described above is easily the most convenient and economical of the three.

It is shown below that the equilibrium in the reaction $[PtF_6]^{--} + 6Br^- \rightleftharpoons [PtBr_6]^{--} + 6F^-$ lies over on the right-hand side, and that the reaction is strongly catalysed by acids; this is why removal of all bromine before treatment of the mixture of K_2PtF_6, KF, and PtF_4 with water is necessary. Both potassium tetrafluorobromite and difluorobromonium hexafluoroplatinate are readily decomposed by water, but the hydrobromic acid which is formed in their decomposition would at once convert the potassium hexafluoroplatinate into the hexabromoplatinate and hydrofluoric acid.

Solvolysis, or incomplete reaction between " acid " and " base," in bromine trifluoride imposes serious limitations on the use of this reagent for the preparation of complex fluorides which are unstable towards water and cannot be subjected to any process of purification. It is essential to evaporate the solution of the " salt " at room temperature, and to determine whether bromine is present in the product: if it is not, then a complex salt must have been formed quantitatively, since all free " acids " and " bases " known at present retain some bromine trifluoride at room temperature; if bromine is present, it may originate either in solvolysis or in incorrect choice of relative proportions of " acid " and " base." Solvolysis may lead to any degree of contamination short of that which would result from non-interaction of " acid " and " base; " the initial presence of elements giving rise to " acids " and " bases " in wrong proportions should lead, where the " acid " or " base " is stable at room temperature, to contamination of the product with whole numbers of bromine atoms; *e.g.*, fluorination of potassium sulphate yields an equimolecular mixture of potassium fluorosulphonate, KSO_3F, and tetrafluorobromite, $KBrF_4$ (Emeléus and Woolf, *J.*, 1950, 164). When solvolysis occurs and the nature of the complex ion being formed is unknown (*e.g.*, where no approximately pure salt of any metal or of the nitrosonium or nitronium ions can be prepared), special caution is necessary in interpreting results. The separation of the mixture corresponding in composition to K_2PtF_6 into its components shows that removal of bromine trifluoride from a heated reaction product is no criterion of pure complex fluoride formation: the action of heat on any mixture of K_2PtF_6, $KBrF_4$, and $(BrF_2)_2PtF_6$ would lead to formation of a product containing only potassium, platinum, and fluorine; and in such instances production of further evidence for complex formation is essential. Even where production of pure complex fluorides is impossible, however, it is still possible to obtain useful information about their properties, and it is for this reason that work on complex fluorides of rhodium and palladium is described below. In these studies, liquid bromine trifluoride has always been used as the reagent; it is not unlikely, however, that at higher temperatures the vapour would yield complex fluorides by entirely different reactions similar to those involved in the production of the substances K_3CuF_6, K_2NiF_6, and K_3CoF_7 (Klemm and Huss, *Z. anorg. Chem.*, 1949, **258**, 221) and $NaAuF_4$ (Hoppe and Huss, *Angew. Chem.*, 1950, 339) by the use of fluorine at medium temperatures as the fluorinating agent.

The action of bromine trifluoride on rhodium bromide produces rhodium tetrafluoride, a purple-red powder which is decomposed by water, forming the olive-green hydrated dioxide and hydrofluoric acid. It oxidises hydrochloric acid to chlorine, with formation of the chloride of tervalent rhodium. This tetrafluoride appears to be identical with the higher rhodium fluoride prepared by Ruff and Ascher (*Z. anorg. Chem.*, 1929, **183**, 206) by the action of fluorine on rhodium at 500°; their product, however, was not obtained pure enough for analysis, and a decision between RhF_4 and RhF_5 for its formula could not be made. Rhodium tetrafluoride is soluble in bromine trifluoride, though no compound with the solvent could be isolated; the solution reacts with sodium fluoride in bromine trifluoride, yielding a complex fluoride which is decomposed by cold water. Isolation of a pure complex fluoride has not been achieved; the action of bromine trifluoride on mixtures corresponding in composition to $2NaCl + RhCl_3$ and $3NaCl + RhCl_3$ yields products containing considerable bromine. These, when heated to 200°, yield residues which analysis shows to be Na_2RhF_6 and Na_3RhF_7 respectively. *X*-Ray powder photography shows the presence of RhF_4 in the former (which is pale pink) but not in the latter (which is pale blue). It therefore seems that the product of composition Na_3RhF_7 consists mainly of a complex fluoride analgous to the cobalt compound K_3CoF_7 described by Klemm and Huss (*loc. cit.*).

Rhodium dioxide is not soluble in hydrofluoric acid, and hydrolysis of the fluororhodate ion thus appears to be irreversible. The only previously reported complex containing quadrivalent rhodium is cæsium hexachlororhodate, Cs_2RhCl_6 (Dwyer and Nyholm, *Nature*, 1947, **160**, 502;

Dwyer, Nyholm, and Rogers, *Proc. Roy. Soc., N.S.W.*, 1947, **81**, 267), which with water liberates chlorine. This suggests that quadrivalent rhodium is unstable with respect to chloride ions in approximately neutral solution; it is, however, incapable of discharging fluoride ions to form fluorine or of liberating oxygen from water under these conditions. In the latter instance the irreversibility of the water–oxygen couple introduces a complication, and it appears that Latimer's estimate of $-1{\cdot}4$ v. for the standard potential for the tervalent–quadrivalent rhodium couple ("The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938) is approximately correct.

Palladous chloride or bromide yields with bromine trifluoride an addition compound of palladium trifluoride and the reagent, approximating in composition to PdF_3,BrF_3. Heating at 180° converts this into black palladium trifluoride (Ruff and Ascher, *loc. cit.*), which is readily soluble in bromine trifluoride. Yellow complex fluorides are formed by interaction of solutions of palladium trifluoride in bromine trifluoride and the tetrafluorobromites of potassium and silver; a pure compound has not yet been made, however, and although it seems likely that the complex fluorides, which are hydrolysed by water, are $KPdF_4$ and $AgPdF_4$, they may be K_2PdF_5 and Ag_2PdF_5, analogous to the complex chlorides of tervalent palladium (Wöhler and Martin, *Z. anorg. Chem.*, 1908, **57**, 398). These substances are being further investigated.

Impure palladous fluoride was prepared by Ruff and Ascher (*loc. cit.*) by reduction of the trifluoride with hydrogen, sulphur dioxide, or iodine. These authors, and later Ebert (*Z. anorg. Chem.*, 1931, **196**, 395), described its structure, but none of its chemical properties has been given; and indeed, its preparation by the action of fluorides on solutions of palladous salts, described by Berzelius but denied by Ruff, is still widely quoted. The brown precipitate formed from sodium fluoride and palladous chloride solution is actually the fluoride-free hydroxide, sodium fluoride functioning only as the salt of a weak acid; ruthenium trichloride, even in the cold, yields a similar precipitate of the hydroxide. Neither hydroxide dissolves in hot 40% hydrofluoric acid. It may therefore be inferred that palladous fluoride is unstable towards water.

Schlesinger and Tapley (*loc. cit.*), in their investigations on potassium fluoroplatinate, noted that the fluoroplatinate ion, unlike the chloroplatinate and bromoplatinate ions, does not yield a brown coloration with potassium iodide solution; and Schlesinger and Palmateer (*J. Amer. Chem. Soc.*, 1930, **52**, 4316), who showed spectrophotometrically that the stability of hexahalogenoplatinate ions increases from chloride to iodide, were unable to observe the transformation of the $[PtF_6]^{--}$ ion into the other hexahalogenoplatinate ions. Now if the true equilibrium in the reaction

$$[PtF_6]^{--} + 6Cl^- \rightleftharpoons [PtCl_6]^{--} + 6F^-$$

were on the left-hand side, it should be possible to prepare potassium fluoroplatinate by evaporation of potassium chloroplatinate with hydrofluoric acid. This is impossible; but investigation of the action of hydrochloric acid on the fluoroplatinate, in which potassium chloroplatinate was produced, showed that the equilibrium is in favour of the complex chloride and that the reaction is hydrogen-ion catalysed. Reactions with bromides and iodides are similar; the complex fluoride is the least stable of the complex halide ions.

The relationship between the stabilities of complex chloride, bromide, and iodide ions of noble metals has been recognised for some time (for a review, see J. Bjerrum, *Chem. Reviews*, 1950, **46**, 381). The dissociation constants decrease steadily from the chlorides to the iodides—the reverse of the order for most metals. Until recently, however, few complex fluorides of noble metals (used here to denote silver, gold, mercury, and the six platinum metals) were known. Ruff and Tschirch (*Ber.*, 1913, **46**, 929) obtained (but did not analyse) complex fluorides of quadri- and octa-valent osmium; Schlesinger and Tapley (*loc. cit.*) prepared potassium hexafluoroplatinate and hexafluoroiridate(IV); and Meyer and Kienitz (*Z. anorg. Chem.*, 1939, **242**, 281) made hexafluororhodites. No information about the relative stabilities of these substances has, however, been published.

The complex fluorides of gold are immediately decomposed by water, and even by hydrofluoric acid, with the precipitation of auric hydroxide (Sharpe, *J.*, 1949, 2901), whereas the chloroaurates are stable in hot aqueous solution. Hydrofluoric acid is without action on sodium chloroaurate, but hydrobromic acid at once converts this substance into the bromoaurate; the effect of these acids on chloroplatinates is similar. Here, therefore, the order of stability of the complex ions is quite definitely

$$[AuF_4]^- < [AuCl_4]^- < [AuBr_4]^-$$

and

$$[PtF_6]^{--} < [PtCl_6]^{--} < [PtBr_6]^{--}$$

It now becomes possible to correlate certain scattered facts about compounds of other elements. The insolubility of palladous hydroxide (like auric and platinic hydroxides) in hydrofluoric acid, and the absence of any action of hydrofluoric acid on potassium tetrachloropalladite, K_2PdCl_4, suggest that the $[PdF_4]^{--}$ ion is unstable relatively to water and to other halide ions. The hexafluororhodite ion is not easily hydrolysed by water, but it is unstable in the presence of chloride ions; it is therefore impossible to prepare a hexafluororhodite by the action of hydrofluoric acid on a hexachlororhodite, and the complex chloride must first be converted into the hydroxide or into the complex nitrite. In the latter instance (Meyer and Kienitz, *loc. cit.*) one of the products of the reaction

$$K_3Rh(NO_2)_6 + 6HF = K_3RhF_6 + 6HNO_2$$

is unstable and is continuously removed. The yellow solution of the complex fluoride, however, is converted into a red solution of the complex chloride by addition of a chloride. The insolubility of the hydroxide of quadrivalent iridium in hydrofluoric acid, and the lack of reaction between this acid and sodium hexachloroiridate(IV), suggest that the fluoride is the least stable of the complex halide ions of iridium.

The value of the stability sequence for complex halide ions of noble metals has not always been recognised in preparative inorganic chemistry. It should, for example, be possible to prepare complex bromides very easily by treatment of the complex chlorides (which, owing to the solubilities of most noble metals in aqua regia, are readily available) with hydrobromic acid; this preparation has been illustrated by making sodium hexabromoplatinate and potassium tetrabromopalladite.

Rates of substitution in complex ions, other than the ammines of cobalt and palladium investigated by Anderson, Briscoe, and Spoor (*J.*, **1943**, 361) and Anderson, Briscoe, Cobb, and Spoor (*J.*, **1943**, 367), respectively, have hitherto been little studied. Reactions of the hexafluoroplatinate ion are not typical, because of the extreme slowness of thermodynamically possible substitutions in the absence of hydrogen ions. They are, however, relatively easily investigated, since dilute solutions of potassium hexafluoroplatinate are almost colourless, while solutions of the other complex halides are more or less deeply coloured. Preliminary experiments on the hexfluoroplatinate–iodide reaction

$$[PtF_6]^{--} + 6I^- = [PtI_6]^{--} + 6F^-$$

indicate that the initial rate is approximately proportional to the first powers of the fluoroplatinate and hydrogen-ion concentrations, and almost independent of the iodide-ion concentration. The rate-determining step thus appears to be formation of $[HPtF_6]^-$ or $[PtF_5]^-$ by addition of a proton or withdrawal of a fluoride ion. Hydrofluoric acid (like acetic acid) is a poor catalyst; since it might be expected to be a poor source of protons but a good absorber of fluoride ions, the formation of $[HPtF_6]^-$ appears somewhat more likely.

X-Ray powder photography has been used to obtain evidence compatible with the view that the first step in the substitutition governs the overall rate. Its use is made possible by potassium hexafluoroplatinate not being isomorphous with the other hexahalogenoplatinates. When, in the reaction $K_2PtF_6 + 6HBr = K_2PtBr_6 + 6HF$, quantities of hydrobromic acid sufficient to effect only partial conversion are taken, the product is a mixture of unchanged fluoroplatinate and hexabromoplatinate, and solid products of the type $K_2(PtF_xBr_{6-x})$ are not isolated. In the analogous substitution $K_2PtCl_6 + 6HBr = K_2PtBr_6 + 6HCl$, the complex halides are isomorphous, and substitution results only in a progressive increase in the size of the unit cell, the structure type remaining constant. *X*-Ray powder photography therefore fails to distinguish between formation of intermediate compounds such as $K_2(PtCl_4Br_2)$ and formation of solid solutions of chloroplatinate and bromoplatinate. There can be little doubt that substitution in these complex ions takes place in stages, but the value of some of the evidence quoted as supporting this, *e.g.*, the preparation of a salt analysing as $K_2PtCl_4Br_2$ by the action of bromine water on potassium tetrachloroplatinite (Klement, *Z. anorg. Chem.*, **1927**, **164**, 195), is very doubtful.

It seems likely that hydrolysis of the hexafluoroplatinate ion $[PtF_6]^{--} + 4H_2O = Pt(OH)_4 + 4HF$ is another very slow reaction which proceeds almost to completion. Platinic hydroxide is insoluble in hot 40% hydrofluoric acid, even in the presence of potassium fluoride; and prolonged heating of potassium hexafluoroplatinate solution results in the deposition of a little platinic hydroxide. The equilibrium therefore appears to be in favour of the hydrolysis products, but it is approached only extremely slowly—behaviour which, so far as is known, has no parallel among other complex halide ions, but which recalls that of sulphur hexafluoride (Yost and Claussen, *J. Amer. Chem. Soc.*, **1933**, **55**, 888).

More detailed investigations of reactions of the hexfluoroplatinate ion are being carried out by means of spectrophotometric methods, and these will be reported in a later communication.

EXPERIMENTAL.

Platinic Fluoride and Related Compounds.—Platinum, even when finely divided, is not noticeably attacked by bromine trifluoride at room temperature. A known weight of the metal was dissolved in aqua regia in a silica flask; the chloroplatinic acid so obtained was converted into bromoplatinic acid by addition of hydrobromic acid, and the solution was evaporated *in vacuo* at 70°, yielding crude platinic bromide. This (which is more reactive than the chloride) was treated with an excess of liquid bromine trifluoride. The clear red solution which resulted was evaporated *in vacuo* at room temperature, the technique described by Sharpe and Emeléus (*loc. cit.*) being used; at about 0·01 mm. pressure, bromine trifluoride was removed only extremely slowly after the composition of the red *product* reached $PtBr_2F_{10}$. Analysis was effected by decomposition with sodium carbonate solution, filtration, and ignition of the platinic hydroxide produced to the metal, and determination of bromine and fluorine in the filtrate. Bromine was precipitated as silver bromide after reduction with sulphurous acid; fluorine was determined as calcium fluoride (Treadwell and Hall, " Analytical Chemistry," Vol. II, 9th English edn., p. 397) (Found: Pt, 36·6; Br, 30·1; F, 33·0. $PtBr_2F_{10}$ requires Pt, 36·0; Br, 29·2; F, 34·7%). Properties of this substance are described above. When it was heated at 200° *in vacuo* until the product had a constant weight, it yielded platinic fluoride, a light brown powder which reacted only slowly with water at ordinary temperature but was decomposed, with some frothing, at 100° (Found: Pt, 75·3; F, 24·5; Br, 1·0. Calc. for PtF_4: Pt, 72·0; F, 28·0%).

Known quantities of platinum were dissolved in aqua regia as before; equivalent quantities of potassium chloride were added, and the mixture was evaporated with hydrobromic acid. Alternatively, potassium hexabromoplatinate, prepared by a method analogous to that described below for the sodium salt, was used as starting material. Reaction with bromine trifluoride yielded a clear solution, which on evaporation *in vacuo* at 20° gave a product whose weight indicated a composition approximating to $K_2PtF_6,1{\cdot}1BrF_3$; the action of heat at 200° removed all the bromine, but the product was not homogeneous, and only part of the platinum was precipitated by boiling with water. From the weights of platinum and potassium in the reactants the composition of the whole residue was known to approximate to K_2PtF_6 (Found: K, 19·8; Pt, 49·5. Calc. for K_2PtF_6: K, 20·1; Pt, 50·4%). Evaporation of the solution obtained by treatment of the residue with boiling water yielded sparingly soluble yellow crystals of potassium hexafluoroplatinate, very much less soluble than potassium fluoride and freed from the latter substance by washing with water. Evaporation of the solution was best carried out over silica gel at room temperature; at higher temperatures slight hydrolysis occurred and the product was contaminated with a little platinic hydroxide. Potassium hexafluoroplatinate was decomposed by fusion with sodium carbonate; the insoluble residue from the fusion was ignited to the metal, and fluoride was precipitated as calcium fluoride (Found: Pt, 50·0; F, 29·1%); yield of K_2PtF_6 from 1 g. of Pt, 0·8 g. (40%). Solvolysed sodium and silver fluoroplatinates were obtained by the action of bromine trifluoride on mixtures of platinic chloride and sodium chloride or silver; these salts appear to be decomposed by water to a slightly greater extent than the potassium salt, and they were not isolated pure.

Potassium hexafluoroplatinate is readily soluble in bromine trifluoride; evaporation of a solution of a known weight of the salt in bromine trifluoride yielded a residue of approximate composition $K_2PtF_6,0{\cdot}95BrF_3$ (Found: Pt, 37·3; Br, 13·5. Calc.: Pt, 37·7; Br, 14·6%). The residue was visibly heterogeneous; presence of potassium tetrafluorobromite in another solvolysed salt has recently been demonstrated (Sharpe, *J.*, 1950, 2907).

Rhodium Tetrafluoride and Related Compounds.—Sodium chlororhodite dodecahydrate (water of crystallisation determined by heating at 105° to constant weight, 35·8. Calc. for $Na_3RhCl_6,12H_2O$: H_2O, 36·0%) was converted into rhodium hydroxide by warming with sodium carbonate solution. The precipitate was thoroughly washed with hot water, and, in order to obtain some idea of its purity, chloride was determined on the filtrate (Found: Cl, 53·3. Calc. for $Na_3RhCl_6,12H_2O$: Cl, 53·3%). The rhodium hydroxide was dissolved in hydrobromic acid, and this solution was evaporated on the steam-bath; the residue was dried at 100° *in vacuo* and then treated with bromine trifluoride; the product was readily soluble in excess of the reagent, yielding a red solution. Evaporation of this under the conditions described for platinum compounds gave a pink product (which could not be isolated), rapidly decomposing into purple-red rhodium tetrafluoride; even after being heated at 180°, however, this still contained a little bromine. After decomposition by fusion with sodium carbonate, rhodium was reduced to the metal, and fluoride and bromide were determined by precipitation as calcium fluoride (calcium acetate being used as precipitant) and silver bromide, respectively (Found: Rh, 53·5; F, 40·2; Br, 5·8. Calc. for RhF_4: Rh, 57·4; F, 42·5%). Divergence from calculated results is not serious; the formula calculated from these data is $RhF_{4{\cdot}05}Br_{0{\cdot}1}$. Rhodium tetrafluoride does not react with ether or carbon tetrachloride at room temperature; it gives a blue-green aqueous solution which deposits an olive-green precipitate of the hydrated dioxide. Alkalis yield a similar precipitate. Iodine is liberated from potassium iodide solution, and a black precipitate (rhodium tri-iodide) is formed; hydrochloric acid is oxidised to chlorine with the production of a red solution of the chloride of tervalent rhodium.

Fluorination by bromine trifluoride of a sodium chloride–rhodium trichloride mixture containing the substances in molecular proportions of 2 : 1, and of anhydrous sodium chlororhodite, gave products containing appreciable amounts of bromine; after heating at 180°, the residues corresponded in composition to Na_2RhF_6 (Found : Rh, 38·7; F, 43·8; Br, trace. Calc. for Na_2RhF_6 : Rh, 39·1; F, 43·4%) and Na_3RhF_7 (Found : Rh, 33·0; F, 43·5; Br, trace. Calc. for Na_3RhF_7 : Rh, 33·7; F, 43·7%), respectively. Both were hydrolysed to the dioxide by warm water; both liberated chlorine from hydrochloric acid. The evidence in favour of Na_3RhF_7 as the complex fluoride has been given above.

Palladium Trifluoride and Related Compounds.—Potassium tetrachloropalladite was used as a source of palladium compounds. Since it proved impossible to prepare palladous hydroxide from this in a state even approaching purity, the hydroxide was ignited to the metal, which was purified by washing with dilute formic acid and reignition (Found : Pd, 32·5. Calc. for K_2PdCl_4 : Pd, 32·6%). The metal was dissolved in aqua regia, and the solution was evaporated with hydrobromic acid; the residue, dried at 70°, was treated with bromine trifluoride; the brown product obtained at room temperature yielded black palladic fluoride at 200°. This was analysed by decomposition with sodium hydroxide solution and determination of palladium as the metal and fluoride as calcium fluoride (Found : Pd, 64·5; F, 33·0; Br, trace. Calc. for PdF_3 : Pd, 65·2; F, 34·7%). The brown addition *complex* of palladium trifluoride and bromine trifluoride, stable *in vacuo* at 20°, was PdF_3,BrF_3 or $(BrF_2)(PdF_4)$ (Found : Pd, 34·2; Br, 25·3; F, 40·4. $PdBrF_6$ requires Pd, 35·5; Br, 26·5; F, 38·0%).

The action of bromine trifluoride on potassium tetrachloropalladite yielded a light brown bromine-containing product of approximate composition (determined from the weight of K_2PdCl_4 taken and the weight of product formed) $K_2PdF_5,0{\cdot}5BrF_3$; the action of heat at 280° converted this into a pale yellow substance of composition K_2PdF_5 (Found : Pd, 38·0; F, 32·9. Calc. : Pd, 38·2; F, 33·8%). From a mixture of chlorides containing potassium and palladium in 1 : 1 proportion, the product on evaporation of the solution at room temperature appeared to be $KPdF_4,0{\cdot}8BrF_3$; at 200° it was converted into a brown residue (Found : Pd, 45·0. Calc. for $KPdF_4$: Pd, 48·3%). The quantity of bromine trifluoride retained at room temperature indicates that in each instance complex salt formation must have taken place to a considerable extent. From information at present available it is impossible to assign a formula to the complex fluoride; what is clear, however, is that all the palladium in these products is precipitated on addition of water; it will be essential, therefore, to continue the investigation in non-aqueous solvents or in the absence of a solvent. The action of bromine trifluoride on silver–palladous chloride mixtures yields orange products which at 20° correspond to compositions $AgPdF_4,1{\cdot}2BrF_3$ and $Ag_2PdF_5,0{\cdot}8BrF_3$; these do not merit further discussion now.

Preparation of Complex Bromides.—Sodium hexachloroplatinate hexahydrate was dissolved in hydrobromic acid, and the solution was evaporated on the steam-bath. After one repetition of this process, further treatment with hydrobromic acid (weighing after drying at 105°) was shown to be without effect. Platinum was determined by precipitation with formic acid in the presence of ammonium acetate, and bromine as silver bromide (Found : Pt, 27·5; Br, 67·4. Calc. for Na_2PtBr_6 : Pt, 27·0; Br, 66·6%). Four evaporations of the product with concentrated hydrochloric acid reversed the reaction only to a negligible extent. Similar treatment of potassium tetrachloropalladite with hydrobromic acid yielded potassium tetrabromopalladite, analysed by reduction to palladium and precipitation of silver bromide (Found : Pd, 20·9; Br, 63·2. Calc. for K_2PdBr_4 : Pd, 21·2; Br, 63·3%).

Reactions of Potassium Hexafluoroplatinate.—Qualitative information on some of these, and on various compounds of tervalent rhodium, bivalent palladium, and quadrivalent iridium, has been given above and is not repeated or amplified here.

Although repeated evaporation of potassium chloroplatinate with 40% hydrofluoric acid does not lead to the production of any complex fluoride, the reverse reaction is readily accomplished; and treatment of potassium hexafluoroplatinate with hydrochloric acid produces the hexachloroplatinate (Found : Pt, 39·9; Cl, 44·0. Calc. for K_2PtCl_6 : Pt, 40·2; Cl, 43·8%). Use of this transformation in the analysis of fluorine-containing platinum compounds has been made occasionally; whereas reduction methods for platinum in the fluoride complexes lead to low results (Schlesinger and Tapley, *loc. cit.*), normal results are obtained on complex chlorides.

Hydrobromic acid similarly converts the hexafluoroplatinate into the hexabromoplatinate; the products obtained by using sufficient dilute hydrobromic acid to effect only partial conversion were studied by *X*-ray powder photography. Potassium hexafluoroplatinate (0·0532 g.) was dissolved in hot water, and 7·0 ml. of 0·0520N-hydrobromic acid were added; the solution was then slowly evaporated on the steam-bath. The product (0·0634 g.) was visibly heterogeneous; a small sample was taken for *X*-ray investigation, and the remainder was analysed (Found : Pt, 32·1; Br, 50·7%). This corresponds to $K_2PtBr_{3\cdot9}F_{2\cdot1}$; powder photography showed that only the end hexahalogenoplatinates were present in the product. A similar result was obtained with a mixture corresponding to $K_2PtBr_{2\cdot3}F_{3\cdot7}$. The quantitative introduction of bromine under these conditions confirms that the equilibrium in the fluoroplatinate–bromide reaction strongly favours formation of the bromoplatinate.

Similar treatment of the hexachloroplatinate with insufficient hydrobromic acid yielded products which were homogeneous to the eye and were intermediate in colour between the complex chloride and the complex bromide. The same type of powder pattern was retained throughout the series K_2PtCl_6, $K_2PtBr_{2\cdot1}Cl_{3\cdot9}$, $K_2PtBr_4Cl_2$, and K_2PtBr_6, while the spacing of the lines progressively decreased.

Preliminary Experiments on the Hexafluoroplatinate–Iodide Reaction.—Potassium hexafluoroplatinate and potassium iodide in neutral solution gave no coloration, even when kept at 90° for one hour; this confirms Schlesinger and Tapley's observations. Addition of a drop of hydrochloric acid, however, soon resulted in the production of a brown colour similar to that obtained from the chloroplatinate in absence of added acid. The colour was not extracted by chloroform and therefore could not have been due to iodine. Addition of sodium fluoride solution did not produce any appreciable lightening of the colour, *i.e.*, reversal of the reaction, and hydrofluoric acid was also without effect.

Visual estimation of colour intensities, by the dilution method, was used to investigate the effect of ionic concentrations on the development of the colour. Formation of the complex iodide was chosen for a first exploration because of the intense colour of the $[PtI_6]^{--}$ ion; for more accurate work, however, spectrophotometric determination of the complex chloride, which is more stable in aqueous solution, would probably be more suitable. All measurements were made at 25°; at this temperature, equilibrium is not established until after several days, and initial rates were compared. The isolation method was used to fix the order of the reaction with respect to each reactant. Beer's law being assumed to be obeyed, the initial rate was found to be approximately proportional to the first powers of the hexafluoroplatinate and hydrogen-ion concentrations, and nearly (but not quite) independent of the iodide-ion concentration. This suggested the mechanism discussed above: a slow reaction between acid and complex fluoride, followed by a fast (though not instantaneous) substitution reaction in several stages.

In conformity with this, when the hexafluoroplatinate and hydrochloric acid were heated together for one hour at 60° before being cooled and mixed with the iodide solution, the colour appeared within a few seconds. Pre-treatment with hydrofluoric acid or acetic acid had a much smaller effect, but sulphuric acid appeared (under comparable concentrations) to be about as effective as hydrochloric acid.

The conversion of hexachloroplatinates into hexaiodoplatinates is a very fast reaction even in the absence of added acid; in the presence of a strong acid, however, it is noticeably accelerated. It may be that hydrogen ions are essential for a rapid reaction between chloroplatinate and iodide, and that these are present owing to partial hydrolysis of the chloroplatinate ion and the formation of a little hydrochloric acid. The slowness of the hexafluoroplatinate–iodide reaction could then be correlated with the slow hydrolysis of the fluoroplatinate ion and the production, thereby, of only a weak acid. The effect of pH on other substitutions in complex ions therefore appears to deserve examination.

Grateful acknowledgment is made to Messrs. Johnson, Matthey, and Company, Limited, for the loan of compounds of precious metals.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, August* 23*rd*, 1950.]