

613. Auric Fluoride and Related Compounds.

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Bromine trifluoride dissolved gold to yield the compound AuBrF_6 , which decomposes at 180° forming auric fluoride. In bromine trifluoride solution AuBrF_6 behaves as an "acid," and with bromotetrafluorides ("bases") forms fluoroaurates such as silver fluoroaurate, AgAuF_4 .

EVIDENCE for the existence of a fluoride of gold was noted by Moissan (*Compt. rend.*, 1889, **109**, 807), who heated gold wire in fluorine at a dull-red heat and observed the formation of a hygroscopic crust of orange powder on the metal. At a slightly higher temperature decomposition occurred, and the powder was not identified. Later attempts to obtain a fluoride were made by Lenher (*J. Amer. Chem. Soc.*, 1903, **25**, 1136) and by Ruff (*Ber.*, 1913, **46**, 922). Lenher studied the reaction between argentous fluoride and auric chloride in water, but obtained only auric hydroxide; Ruff unsuccessfully attempted the fluorination of gold dichloride with hydrogen fluoride and with potassium hydrogen fluoride. Gold-coated copper has been used as a fluorination catalyst, but no details of a fluoride of gold have hitherto been published.

It has been shown (Sharpe and Emeléus, *J.*, 1948, 2135) that bromine trifluoride is a powerful fluorinating agent at room temperature and converts thallic, plumbous, and cobaltous halides into thallic, plumbic, and cobaltic fluoride, respectively. It therefore seemed likely that this reagent would convert gold or its halides into auric fluoride at a temperature well below that required for the decomposition of the last-named compound.

Auric chloride reacted vigorously with bromine trifluoride, but it was soon found that conversion of the metal into the chloride was unnecessary and that gold dissolved readily in bromine trifluoride, with evolution of bromine, when gently warmed. Evaporation of the solution at 50° *in vacuo* gave a lemon-yellow compound of empirical formula AuBrF_6 . This substance underwent immediate decomposition by water, with the precipitation of auric hydroxide; it reacted violently with carbon tetrachloride and with benzene, and exploded in contact with alcohol. Its structure is considered below. When the compound was heated at 120° , bromine trifluoride was liberated, and at 180° production of auric fluoride was rapid and quantitative.

Auric fluoride, so prepared, is an orange powder. Water decomposes it immediately, with the evolution of heat and the formation of auric hydroxide and hydrofluoric acid. Even 40% hydrofluoric acid effects immediate hydrolysis, and it is thus clear why Lenher's attempts to prepare it in the wet way failed. Thermal decomposition to gold and fluorine is rapid only above 500° . Auric fluoride is a powerful fluorinating agent; carbon tetrachloride reacts quietly at 40° , but with benzene and with alcohol reaction is violent and the organic liquid takes fire.

The reactivity of the compound AuBrF_6 suggests that it is not to be formulated as $\text{AuF}_2(\text{BrF}_4)$, and a clear indication that, in bromine trifluoride solution at least, it ionises according to the equation $\text{AuBrF}_6 = [\text{BrF}_2]^+ + [\text{AuF}_4]^-$ is given by the immediate formation of a precipitate of *silver fluoroaurate*, AgAuF_4 , when solutions of AuBrF_6 and silver bromotetrafluoride (Sharpe and Emeléus, *loc. cit.*) in bromine trifluoride are mixed. Instantaneous reactions in solution are usually reactions between oppositely charged ions, for which the activation energy is extremely low, and this reaction, therefore, may reasonably be represented by the equation $[\text{BrF}_2]^+[\text{AuF}_4]^- + \text{Ag}^+[\text{BrF}_4]^- = \text{Ag}^+[\text{AuF}_4]^- + 2\text{BrF}_3$. It is, then, a further example of a neutralisation reaction in bromine trifluoride solution, in which "acids" and "bases" contain $[\text{BrF}_2]^+$ and $[\text{BrF}_4]^-$ ions respectively (Woolf and Emeléus, this vol., p. 2865). Instead of preparing and mixing solutions of AuBrF_6 and AgBrF_4 , the preparation may be carried out by mixing equivalent quantities of gold and silver or silver chloride, and treating the mixture with bromine trifluoride; there can be little doubt that the course of this reaction remains as described above.

By similar methods impure *fluoroaurates* of *sodium* and *potassium* have been obtained. These, however, are more soluble than the silver salt in bromine trifluoride, and the products obtained by evaporation of their solutions have compositions such as $\text{KAuF}_4 \cdot 0.1\text{BrF}_3$. Similar retention of the elements of bromine trifluoride by other salts was observed by Woolf and Emeléus (*loc. cit.*). Since the bromine trifluoride is relatively firmly bound, a possible explanation appears to be solvolysis by bromine trifluoride, but this awaits experimental confirmation.

The fluoroaurates are very pale yellow in colour; they are rapidly decomposed by cold water, *e.g.*, $\text{AgAuF}_4 + 3\text{H}_2\text{O} = \text{Au}(\text{OH})_3 + \text{AgF} + 3\text{HF}$. The silver salt is without action on carbon tetrachloride but is slowly reduced to gold and silver by benzene.

EXPERIMENTAL.

Analysis.—A general method found suitable for the compounds described below was decomposition with dilute aqueous sodium hydroxide containing a little formaldehyde, filtration and ignition of the gold which was precipitated, and determination of bromine and fluorine in the filtrate as silver bromide and as calcium fluoride respectively. From silver tetrafluoroaurate both gold and silver were precipitated; they were separated by dissolution of the silver in nitric acid.

Preparation of AuBrF₆.—Gold powder (1–2 g.) and an excess of bromine trifluoride (15–20 g.) were warmed together in a quartz flask until evolution of bromine began. The gold dissolved quietly and a clear yellow solution resulted. From this the excess of bromine trifluoride was removed and recovered by distillation *in vacuo* into a quartz trap cooled in liquid air. The silica flask and its contents were heated at 50° until the product had a constant weight. The weight of product equivalent to Au = 197 was 386 (AuBrF_6 requires 391) (Found: Au, 51.4; Br, 19.9; F, 28.5. AuBrF_6 requires Au, 50.4; Br, 20.4; F, 29.2%). Reactions of the compound with organic liquids and water are described above. The scarlet residue from the reaction with carbon tetrachloride was identified as auric chloride.

Auric Fluoride.—When the compound AuBrF_6 was heated to 120°, bromine trifluoride was evolved and an orange residue remained in the flask. At this temperature decomposition was slow, but at 180° liberation of bromine trifluoride was rapid and *auric fluoride* containing only a trace of bromine remained (Found: Au, 77.1; F, 22.3; Br, <0.5. AuF_3 requires Au, 77.6; F, 22.4%). The approximate temperature at which decomposition of auric fluoride took place was determined by heating samples in sealed tubes and examining the residues. At about 500° fluorine (identified by its action on a crystal of potassium iodide) was evolved and a residue of gold (distinguished from auric fluoride by its insolubility in concentrated hydrochloric acid) remained. When auric fluoride was warmed with dry carbon tetrachloride a quiet reaction ensued, and the characteristic sharp smell of organic chlorofluoro-compounds was noticed. Benzene and alcohol reacted violently in the cold.

Silver Fluoroaurate.—The most convenient preparation was from gold and silver. Equivalent quantities of the two metals were weighed into a quartz flask and treated with bromine trifluoride; a vigorous reaction took place and a pale yellow precipitate settled. Removal of the solvent in the usual manner left a residue of *silver fluoroaurate* (Found: Ag, 28.0; Au, 51.5; F, 19.7. AgAuF_4 requires Ag, 28.3; Au, 51.8; F, 19.9%). The use of silver chloride in place of silver, and precipitation from separately prepared solutions of AuBrF_6 and AgBrF_4 , gave the same product. Its reactions are described above.

Other Salts.—Impure potassium fluoroaurate was obtained by the action of bromine trifluoride on a mixture of equivalent quantities of gold and potassium chloride. Since the constituents of this mixture, when caused to react separately, yield respectively AuBrF_6 and KBrF_4 (a mixture of equivalent proportions of which would contain Au, 33.6; Br, 27.3; F, 32.5%), the formation of a product approximating in composition to KAuF_4 is clear evidence for a neutralisation reaction, and the retention of small quantities of bromine trifluoride (indicated by analysis and by the weight of product formed) must be due to a secondary effect (Found: Au, 59.0; Br, 3.0; F, 25.5. Calc. for KAuF_4 : Au, 63.2; F, 24.3%). Anhydrous sodium chloroaurate was similarly converted into impure sodium fluoroaurate (Found: Au, 58.3; Br, 3.5; F, 28.3. Calc. for NaAuF_4 : Au, 66.6; F, 25.6%).