215. *The Preparation of Complex Fluoro-acid Salts of Metals and of the Nitronium Ion by Means of Bromine Trifluoride.*

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Salts of complex fluoro-acids have been prepared by two general methods. In the first an oxy-salt is treated with bromine trifluoride, and in the second, of wider application, mixtures of substances, which may be metals, oxides, oxy-salts, or halides, capable of reacting as " acids " and " bases " in bromine trifluoride, are treated with the latter. The conversion of borates into tetrafluoroborates is an example of the first method; the reaction of a mixture of silver and arsenious oxide with bromine trifluoride to yield *silver hexafluoroarsenate* is an example of the second. The second procedure has also been used in the production of nitronium salts. Dinitrogen tetroxide, boric oxide, and bromine trifluoride, for instance, yielded *nitronium tetrafluoroborate*. *Nitronium tetrafluoroaurate, hexafluorostannate, hexafluorophosphate, hexafluoroarsenate,* and *hexafluoroantimonate* were produced similarly.

The formation of certain salts of complex fluoro-acids by neutralization reactions in liquid bromine trifluoride has already been described (Woolf and Emeléus, *J.*, 1949, 2865). These observations have now been extended by the preparation of tetrafluoroborates, hexafluorophosphates, hexafluoroarsenates, and hexafluoroantimonates. Salts of complex fluoro-ions of aluminium, indium, thallium, zirconium, hafnium, thorium, lead, bismuth, selenium, tellurium, molybdenum, tungsten, uranium, iodine, and manganese could not be prepared by the methods described below, on account of the insolubility of the resulting fluorides in bromine trifluoride, or the displacement of a less stable complex by the tetrafluorobromite (bromotetrafluoride) ion. It has also been shown that mixtures of metallic nitrates and compounds capable of yielding anions of the above acids when treated with bromine trifluoride gave salts of the nitronium ion NO_2^+.

There are two general preparative methods available. In the first, equivalent amounts of substances which produce the " acid " and " base " in bromine trifluoride are mixed in that solvent, and the excess is removed *in vacuo* after the reaction has been completed. If, for example, silver and phosphorus pentabromide are mixed with excess of bromine trifluoride the salt, *silver hexafluorophosphate*, results. The reaction mechanism is believed to involve an ionic reaction between the base $AgBrF_4$ and an unstable acid $(BrF_2)PF_6$ (Emeléus and Woolf, *J.*, 1950, 164). Similarly, to quote another example, a mixture of lithium carbonate and antimony trioxide gives *lithium hexafluoroantimonate*: again it is believed that there is a reaction between the base $LiBrF_4$ and the acid $(BrF_2)SbF_6$. The element, its oxide, carbonate, or halide can be used as the source for " acid " or " base." The second preparative method, which is less general, involves the reaction between bromine trifluoride and a suitable oxy-acid salt, in which the elements need be present in the correct proportions only when the component fluorides produced are non-volatile. Borax, for example, yields sodium tetrafluoroborate, the excess of boron being removed as boron trifluoride, while potassium perdisulphate and pyrosulphate are converted into the fluorosulphonate.

The nitrates of potassium, silver, and barium are converted by bromine trifluoride into the corresponding fluorobromites which suggested that they could act as sources of " bases " in the first of the above preparative methods. When, however, a nitrate was mixed with a material capable of forming an " acid " and then treated with bromine trifluoride, a product containing nitrogen remained when all the volatile residue had been removed. Potassium nitrate and excess of boric oxide, for example, gave a product of composition $K(NO_2)(BF_4)_2$, which was presumably a mixture of KBF_4 and NO_2BF_4. From this observation a method for preparing nitronium salts was developed. Dinitrogen tetroxide and " acid "-forming substance were mixed and treated with bromine trifluoride to give the following compounds: nitronium tetrafluoroborate,

$(NO_2)BF_4$; nitronium hexafluorostannate, $(NO_2)_2SnF_6$; nitronium hexafluorophosphate, $(NO_2)PF_6$; nitronium hexafluoroarsenate, $(NO_2)AsF_6$; nitronium hexafluoroantimonate, $(NO_2)SbF_6$, and nitronium tetrafluoroaurate, $(NO_2)AuF_4$.

The existence of the nitronium ion and its functioning as the electrophilic entity in aromatic nitration is now well established. That this ion can also exist in normal salts is shown by physical evidence for the structure of nitronium perchlorate (Cox, Jeffrey, and Truter, *Nature*, 1948, **162**, 259). No direct evidence has yet been obtained to confirm the existence of the nitronium ion in the new compounds described here. This is however strongly indicated by the presence of two NO_2 groups in the tin compound, as would be expected for a salt of the dibasic acid H_2SnF_6, and of one NO_2 group in the gold compound. Sharpe has recently shown that gold is converted into a monobasic " acid " in bromine trifluoride which contains the tetrafluoroaurate ion (*J.*, 1949, 2901). The analogous nitrosyl derivatives $(NO)_2SnCl_6$ (Klinkenburg, *Rec. Trav. chim.*, 1937, **56**, 749) and $(NO)AuCl_4$ (Sudborough, *J.*, 1891, 662) are known. The hydrolysis of these compounds to form nitric acid also indicates the presence of nitronium ions $[(NO_2)_xAF_y + HOH \longrightarrow xHNO_3 + H_xAF_y]$. If these nitronium derivatives are formed by an ionic reaction it is necessary to postulate the existence in bromine trifluoride of the unstable base $(NO_2)BrF_4$ which, by reaction with various " acids," produces the salts which have been isolated.

EXPERIMENTAL.

Preparation of Tetrafluoroborates.—The preparative method was, unless otherwise stated, similar to that already described (Emeléus and Woolf, *loc. cit.*). Anhydrous borax, prepared from the AnalaR decahydrate, gave sodium tetrafluoroborate when treated with bromine trifluoride. The BF_4^- content of the product was determined by precipitating the nitron salt, which was characterised analytically (Lange, *Ber.*, 1926, **59**, 2110) (Found: Na, 20·9; BF_4, 78·4%; equiv., 111. Calc. for $NaBF_4$: Na, 20·9; BF_4, 79·1%; equiv., 110. Found: C, 59·8; H, 4·1; N, 13·9. Calc. for $C_{20}H_{17}N_4F_4B$: C, 60·0; H, 4·3; N, 14·0%). Tetrafluoroborates could also be made by the reaction of metallic halides and excess of boric oxide with bromine trifluoride. The potassium salt, for example, was prepared from potassium chloride in this way (Found: BF_4, 67·8%; equiv., 128. Calc. for KBF_4: BF_4, 69·0%; equiv., 126. Found: C, 60·0; H, 4·5; N, 13·8. Calc. for $C_{20}H_{17}N_4F_4B$: C, 60·0; H, 4·3; N, 14·0%).

Preparation of Hexafluorophosphates.—These may be obtained from metaphosphates and bromine trifluoride (Emeléus and Woolf, *loc. cit.*), or by reaction of bromine trifluoride with a mixture of phosphorus pentabromide and a halide of the metal. For example, barium chloride mixed with an excess of red phosphorus was cooled and bromine was added dropwise to produce phosphorus pentabromide. Bromine trifluoride was then added in excess and the mixture boiled to drive off excess of phosphorus as the pentafluoride. The product was analysed for barium by precipitation of the sulphate in a large volume of water, to prevent co-precipitation of barium fluoride formed by hydrolysis of the hexafluorophosphate in the hot acid solution. The hexafluorophosphate was determined as the nitron salt [Found: Ba, 31·8; PF_6, 67·6%; equiv., 422. Calc. for $Ba(PF_6)_2$: Ba, 32·1; PF_6, 67·9%; equiv., 427]. *Silver hexafluorophosphate* was prepared similarly, silver being used in preference to its chloride since it reacted more rapidly. The hexafluorophosphate was determined as the nitron salt after removal of silver with an equivalent amount of potassium bromide (Found: Ag, 43·6; PF_6, 56·8; equiv., 248. $AgPF_6$ requires Ag, 42·7; PF_6, 57·3%; equiv., 253). The yellow-brown silver salt differed from other hexafluorophosphates in being soluble in bromine trifluoride. It was soluble in cold water, but when the solution was heated yellow silver phosphate was precipitated. The calcium salt could not be prepared by the reaction of calcium fluoride and phosphorus pentabromide, the product consisting of over 90% of calcium fluoride mixed with a little hexafluorophosphate.

Preparation of Hexafluoroarsenates.—Mixtures of certain metals or their halides and excess of arsenious oxide yielded these salts on treatment with bromine trifluoride. The potassium, *silver* and *barium* salts were prepared in this way. The compounds were analysed by fusion with sodium carbonate–sodium nitrate and precipitation of the arsenic as silver arsenate, which was dried at 250° and weighed. The fluoride was precipitated from a separate aliquot as calcium fluoride and any co-precipitated calcium arsenate was removed by subsequent extraction with dilute acetic acid [Found: As, 33·5; F, 49·4%; equiv., 232. Calc. for $KAsF_6$: As, 33·6; F, 50·0%; equiv., 228. Found: Ag, 35·6; As, 25·4%; equiv., 302. $AgAsF_6$ requires Ag, 36·4; As, 25·2%; equiv., 297. Found: Ba, 25·7; F, 43·9%; equiv., 518. $Ba(AsF_6)_2$ requires Ba, 26·7; F, 44·3%; equiv., 515]. The presence of the AsF_6^- ion was shown, in the case of the potassium salt, by precipitating and analysing the nitron salt (Found: C, 47·6; H, 3·5; N, 11·4. Calc. for $C_{20}H_{17}N_4F_6As$: C, 47·8; H, 3·4; N, 11·2%). The barium and silver salts, unlike the potassium salt, were soluble in bromine trifluoride.

Preparation of Fluoroantimonates.—The silver and barium salts have been described (Woolf and Emeléus, *J.*, 1949, 2865), although the latter, obtained at room temperature, was impure. When the temperature was raised to 120° all bromine trifluoride was removed and the pure salt resulted [Found: Ba, 22·3; SbF_6, 76·0; F, 36·9%; equiv., 615. $Ba(SbF_6)_2$ requires Ba, 22·6; SbF_6, 77·4; F, 37·4%; equiv., 609]. The SbF_6^- ion was determined as the nitron salt (Lange and Askitopoulos, *Z. anorg. Chem.*, 1935, **223**, 369). The *lithium* salt was prepared from lithium carbonate, antimonous oxide, and bromine trifluoride (Found: SbF_6, 96·6; equiv., 241. $LiSbF_6$ requires SbF_6, 97·2%; equiv., 243). The nitron salt was also analysed (Found: C, 44·3; H, 3·6; N, 10·0. Calc. for $C_{20}H_{17}N_4F_6Sb$: C, 43·7; H, 3·1; N, 10·2%). Calcium hexafluoroantimonate could not be prepared in a pure state. When a solution of the barium salt was boiled, a precipitate of barium fluoride was formed.

Formation of Fluorosilicates.—A mixture of potassium chloride and excess of silica when treated with bromine trifluoride left a product of equivalent weight 153 corresponding to a 1 : 1 mixture of potassium fluorosilicate and fluorobromite (Found : K, 25·8; F, 44·2. Calc. for 1 : 1 $KBrF_4 : K_2SiF_6$: K, 25·6; F, 45·2%).

This partial formation of fluorosilicate is significant since it means that all salts prepared by bromine trifluoride reactions in silica flasks will be contaminated to a greater or lesser degree. In most experiments, in which gram-quantities of the salts were made, the flask loss was only a few mg. and in these cases the contamination will not be more than a few parts per thousand. Losses of up to 100 mg. however were suffered in the preparation of nitronium compounds, no doubt owing to the corrosive nature of the excess of nitryl fluoride which was removed by heating the solution. Fortunately a blank experiment with silica, nitrogen dioxide, and bromine trifluoride showed that the yield of nitronium fluorosilicate was less than 2% and hence contamination of the other nitronium salts by the fluorosilicate would be negligible.

Reaction of Nitrates and Boric Oxide with Bromine Trifluoride.—Potassium nitrate was converted quantitatively by bromine trifluoride into the corresponding fluorobromite but, when the reaction was carried out in presence of excess of boric oxide, nitrogen was retained in the product. It was found by analysis to be a mixture of the metal fluoroborate and the compound *nitronium fluoroborate*, $(NO_2)BF_4$ (Found : K, 15·2; N, 5·6; F, 57·0%; equiv., 251. $KBF_4 + NO_2BF_4$ requires K, 15·2; N, 5·4; F, 58·7%; equiv., 258). The nitrogen was determined by reduction with Devarda's alloy and distillation of the ammonia into standard acid. The product from silver nitrate, boric oxide, and bromine trifluoride contained approx. 1% of bromine (Found : Ag, 33·3; equiv., 326. Calc. for $AgBF_4 + NO_2BF_4$: Ag, 32·9%; equiv., 328). The nitronium salt is hydrolysed by water to a mixture of nitric and fluoroboric acids. This was verified by precipitation of the mixed nitron salt from the hydrolysate [Found : C, 61·2; H, 4·3; N, 16·1. Calc. for $2(C_{20}H_{16}N_4HBF_4) + C_{20}H_{16}N_4HNO_3$: C, 61·2; H, 4·3; N, 15·5%].

Preparation of Nitronium Tetrafluoroborate.—Dinitrogen tetroxide, prepared by heating lead nitrate previously dried at 120° in a nickel vessel, was purified by trap-to-trap distillation in a stream of dry oxygen and stored in contact with phosphoric oxide at 0°. The liquid was distilled into a weighing-tube directly before use. A two-fold excess of dinitrogen tetroxide was added to boric oxide in a silica flask, and bromine was added to moderate the reaction, followed by a moderate excess of bromine trifluoride. *Nitronium fluoroborate* separated as a white crystalline material when the reaction mixture was cooled. It was soluble in hot bromine trifluoride. The yield was 88% calculated on the boric oxide used. Nitrogen was determined by reduction to ammonia after decomposition of the solid with water in a stoppered bottle. Fluorine was determined by extracting the product from a sodium carbonate fusion with water and precipitating calcium fluoride [Found : N, 10·3; F, 56·2. $(NO_2)BF_4$ requires N, 10·5; F, 57·2. $(NO)BF_4$ requires N, 12·0; F, 65·0%]. Titration of the hydrolysed product with alkali (methyl-red) showed that 2·12 equivalents of acid were produced, the high result being due to hydrolysis of the BF_4^- ion.

Preparation of Nitronium Hexafluorostannate.—In the first attempt to prepare this compound stannous chloride was dissolved in bromine trifluoride, and dinitrogen tetroxide and bromine were added. Incomplete reaction occurred because of incomplete mixing of the two layers. If, however, stannic fluoride was isolated in the reaction vessel by removing bromine trifluoride at 200° (Woolf and Emeléus, *loc. cit.*) before addition of the nitrogen oxide and bromine, the conversion into *nitronium fluorostannate* was complete. The excess of solvent was removed by heating to 40° in vacuum Nitrogen and fluorine were determined as above and the tin iodometrically after reduction with aluminium [Found : N, 8·3; Sn, 36·2; F, 35·1. $(NO_2)_2SnF_6$ requires N, 8·4; Sn, 36·5; F, 35·0. $(NO)_2SnF_6$ requires N, 9·6; Sn, 40·6; F, 39·0%].

Preparation of Nitronium Hexafluorophosphate.—Red phosphorus was converted by bromine into the pentabromide, and dinitrogen tetroxide added, followed by bromine trifluoride. The yield of *nitronium hexafluorophosphate* in duplicate experiments was 77 and 82%, based on the phosphorus used. Nitrogen was determined as above and also by the method of Pelouze (Kolthoff and Sandell, *J. Amer. Chem. Soc.*, 1933, **55**, 1454). The results were concordant. Phosphorus and fluorine were determined on the aqueous extract of a sodium carbonate fusion, the former by precipitating ammonium phosphomolybdate and converting it into magnesium pyrophosphate and the latter by the Willard–Winter method after distillation as fluorosilicic acid (Found : N, 7·25; P, 15·9; F, 59·8. NO_2PF_6 requires N, 7·34; P, 16·2; F, 59·7%).

Preparation of Nitronium Hexafluoroarsenate.—Arsenious oxide and excess of nitrogen dioxide when treated with bromine trifluoride gave a quantitative yield of *nitronium hexafluoroarsenate*, NO_2AsF_6, which was analysed by the methods described for other fluoroarsenates. Fluorine was determined after distillation of hydrofluorosilicic acid (Found : N, 6·0; As, 32·1; F, 48·2%; equiv., 239. NO_2AsF_6 requires N, 6·0; As, 32·2; F, 49·0%; equiv., 233).

Preparation of Nitronium Hexafluoroantimonate.—Antimonic fluoride or antimonous oxide treated with dinitrogen tetroxide and bromine trifluoride yielded this *salt*, which was soluble in hot bromine trifluoride but insoluble in the cold. Fluorine was determined as calcium fluoride in the filtrate after decomposition of the solid with aqueous sodium carbonate. Antimony was determined by precipitation of the sulphide and titration of a hydrochloric acid solution with potassium bromate (Found : N, 5·1; Sb, 42·8; F, 39·8; equiv., 291. NO_2SbF_6 requires N, 5·0; Sb, 43·2; F, 40·4%; equiv., 282).

Preparation of Nitronium Tetrafluoroaurate.—Gold and dinitrogen tetroxide reacted with bromine trifluoride, yielding a solvent-soluble product, which was light yellow but became brown in air. Gold was determined by reduction with alkaline formaldehyde, and filtering off the metal. Fluorine in the filtrate was determined as calcium fluoride (Found : N, 4·3; Au, 61·0; F, 23·0%; equiv., 322. NO_2AuF_4 requires N, 4·4; Au, 61·8; F, 23·8%; equiv., 319). The solid *product* did not react with boiling carbon tetrachloride but was immediately reduced to gold by ether in the cold.

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