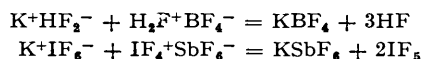**725.** *The Formation of Complex Fluorides. Part II. Reactions in Anhydrous Hydrogen Fluoride and Iodine Pentafluoride.*

By A. A. WOOLF.

The formation of complex fluorides by neutralization-type reactions in hydrogen fluoride and iodine pentafluoride has been demonstrated by the following reactions :

$$K^+HF_2^- + H_2F^+BF_4^- = KBF_4 + 3HF$$
$$K^+IF_6^- + IF_4^+SbF_6^- = KSbF_6 + 2IF_5$$

The conductivities of some fluorides and oxy-salts in iodine pentafluoride have been measured.

IN Part I (*J.*, 1950, 2200) the relationship between complex formation in solution and the conductivity of the solvents was considered. The use of anhydrous hydrogen fluoride and iodine pentafluoride as solvents is described below.

Neutralization reactions would be expected to occur in anhydrous hydrogen fluoride because of its high dielectric constant and consequent ability to bring about ionization. The alkali fluorides form conducting solutions from which " bases " containing the bifluoride ion HF_2^- can be isolated. The following " acids " have also been obtained, although no systematic measurements of their conductivities in hydrogen fluoride have as yet been made : $H_2F \cdot BF_4$, $H_2F \cdot ClO_4$ (Hantzsch, *Ber.*, 1930, **63**, 1789), H_2PO_3F, HPO_2F_2 (Lange and Livingston, *J. Amer. Chem. Soc.*, 1947, **69**, 1073; 1950, **72**, 1280), and HSO_3F (Ruff and Braun, *Ber.*, 1914, **47**, 646). These acids are of two types : the fluoroborate and the perchlorate appear to be ionic solids containing a solvated proton, whereas the remainder are probably covalent liquids limited in number by the covalency maxima of the elements concerned. Anhydrous fluorosilicic acid, for example, with eight-fold co-ordination is unknown although the di- and tetra-hydrates, which probably contain the hydroxonium ion, exist.

Reactions have been carried out with acids of both types to illustrate neutralizations in hydrogen fluoride solution. Boron trifluoride was passed into a solution of potassium hydrogen fluoride in hydrogen fluoride at temperatures as low as $-78°$ and the excess of solvent was subsequently removed in a stream of nitrogen. Pure potassium fluoroborate remained.

Similarly potassium fluorosulphonate was formed from equimolecular amounts of potassium hydrogen fluoride and fluorosulphonic acid. These reactions can be represented as follows :

$$K^+HF_2^- + H_2F^+BF_4^- = KBF_4 + 3HF$$
$$K^+HF_2^- + H_2F^+SO_3F^- = KSO_3F + 3HF$$
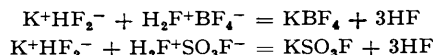
Further examples are provided by the formation of potassium hexafluoroantimonate from antimonic fluoride, and the recently described preparation of hexafluorophosphates from phosphorus pentachloride and metal halides in hydrogen fluoride (Woyski, *Inorg. Synth.*, Vol. III, p. 111). These reactions may well proceed by the intermediate formation of the " acids " $H_2F^+SbF_6^-$ and $H_2F^+PF_6^-$. Unsuccessful attempts to prepare polyhalides in hydrogen fluoride from iodine pentafluoride and chlorine trifluoride are described later.

There is also evidence for neutralization reactions in iodine pentafluoride although no pure products were obtained. Both potassium fluoride and antimonic fluoride dissolve and produce conducting solutions from which potassium hexafluoroiodate, KIF_6 (Eméleus and Sharpe, *J.*, 1949, 2206), and $SbF_5 \cdot IF_5$ can be isolated. The latter compound is the counterpart of the antimony " acid " $BrF_2^+SbF_6^-$ in bromine trifluoride (Woolf and Eméleus, *J.*, 1949, 2865). When these iodine pentafluoride solutions are mixed in equimolecular proportions and the solvent is removed under reduced pressure, a solid of composition $KSbF_6,0\cdot23IF_5$ remains. The presence of iodine pentafluoride in the product may be caused by solvolysis of the type demonstrated by Sharpe when bromine trifluoride was used as the solvent (*J.*, 1950, 2907). The neutralization process may be represented by the following equation, which assumes the existence, in iodine pentafluoride itself, of the ions IF_4^+ and IF_6^- :

$$K^+IF_6^- + IF_4^+SbF_6^- \rightleftharpoons KSbF_6 + 2IF_5$$
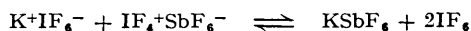
Boron trifluoride also increases the conductivity of iodine pentafluoride, and potassium fluoroborate was prepared by passing the gas into potassium fluoride in iodine pentafluoride. Attempts to isolate other acids failed. Stannic fluoride was insoluble, and although sulphur trioxide was freely soluble and increased the conductivity, only a constant-boiling mixture of the composition $IF_5,1\cdot17SO_3$ could be obtained from the solution. It is possible that this solution contains the " acid " $IF_4^+SO_3F^-$. The indirect method of demonstrating the presence of an acid by neutralizing a sulphur trioxide solution in iodine pentafluoride with potassium hexafluoroiodate was, however, a failure, since the product left after removal of solvent under reduced pressure was not the fluorosulphonate but contained approximately one molecule of iodine pentafluoride. This retention of solvent was observed with other oxy-salts such as potassium metaphosphate, perdisulphate, and iodate. The last salt was examined in some detail. It dissolved readily in cold iodine pentafluoride without evolution of oxygen, and since its equivalent conductivity decreased proportionally to the square root of its concentration in this solvent it behaved in the normal manner of a salt in aqueous solution. The pure iodate could not, however, be recovered from these solutions even after several hours' heating *in vacuo* at 200°; the products always contained appreciable amounts of iodine pentafluoride. The solid iodate itself absorbed iodine pentafluoride vapour at room temperature. In view of this retention of solvent by oxy-salts it is unjustifiable to ascribe to solvolysis the residual iodine pentafluoride content of the product from the attempted preparation of potassium fluorosulphonate. The pentafluoride may be retained attached to the cation as in the compounds $(KHF)H_2PO_4$ and $(KHF)_2S_2O_6$ described by Weinland and Alpha (*Z. anorg. Chem.*, 1899, 21, 60) rather than attached to the anion as in the salts $K_2SO_4BF_3$, $K_3PO_4,3BF_3$, and $K_4P_2O_7,4BF_3$ (Baumgarten and Hennig, *Ber.*, 1939, 72, 1743). The possibility of iodine pentafluoride behaving as a co-ordinate group, analogous to ammonia for example, needs further investigation.

In conclusion it can be seen that the preparation of complex fluorides in anhydrous fluoride solvents has limitations on account of both the low solubilities of many fluorides and the retention of solvent arising from solvolytic or co-ordination phenomena.

EXPERIMENTAL.

Reactions in anhydrous hydrogen fluoride.

Preparation of Potassium Tetrafluoroborate.—About 50 c.c. of hydrogen fluoride were condensed on 3 g. of dry potassium hydrogen fluoride in a nickel test-tube cooled at −78° in an alcohol–carbon dioxide bath. The copper inlet tube, fitted through a rubber bung, was connected to the nickel container in series with a 2-v. accumulator and milliammeter so that the circuit was completed when the liquid reached the base of the copper tube. The entry of atmospheric moisture was prevented by a drying-tube, packed with sodium fluoride and silica gel, fitted to the outlet tube. The inlet tube was then lowered into the liquid, and an excess of boron trifluoride passed into the solution which was shaken.

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The excess of solvent was removed by a stream of dry nitrogen first at room temperature, and then, when fuming practically ceased, at 70° for 1 hour. Potassium fluoroborate remained (Found : K, 31·3; BF_4, 68·0. Calc. for KBF_4 : K, 31·1; BF_4, 68·9%).

Preparation of Potassium Fluorosulphonate.—Potassium hydrogen fluoride (2·5 g.) and an equimolecular quantity of freshly distilled fluorosulphonic acid were treated as above, to give the fluorosulphonate (Found : K, 28·1; S, 23·4; F, 13·3. Calc. for KSO_3F : K, 28·3; S, 23·2; F, 13·7%). Potassium hydrogen fluoride and fluorosulphonic acid liberate hydrogen fluoride when mixed in the cold, but the reaction is complete only at higher temperatures. A mixture kept at 110° for 20 hours left only traces of hydrogen fluoride (Found : Equiv., calc. from KHF_2, 137·9; S, 23·2. Calc. for KSO_3F : Equiv., 138·2).

Preparation of Potassium Fluoroantimonate.—Equivalent quantities of potassium hydrogen fluoride and antimony pentafluoride yielded the fluoroantimonate when the above technique was used (Found : Sb, 43·5; F, 42·1. Calc. for $KSbF_6$: Sb, 44·3; F, 41·5%). The reaction between barium chloride and antimony pentachloride was incomplete under the same conditions. The residue contained only 23·0% of fluorine and large quantities of chlorine [Calc. for $Ba(SF_6)_2$: F, 37·4%].

Reactions with Halogen Fluorides.—Equimolecular amounts of iodine pentafluoride and potassium hydrogen fluoride were dissolved in hydrogen fluoride. The residue after passage of nitrogen for 3 hours at room temperature was still liquid. A further 3 hours at 70° left a fuming white solid which by its rapid action with glass showed the presence of free hydrogen fluoride (Found : K, 10·3; I, 38·3; F, 52·0. Calc. for KIF_6 : K, 14·0; I, 45·3; F, 40·7. Calc. for KHF_2: K, 50·6; F, 48·7%). The analysis alone is insufficient to fix the composition of the residue, since even if a complex fluoride of HF and IF_5 could be isolated it could ionize as either $H_2F^+IF_6^-$ or $IF_4^+HF_2^-$ and thus give rise to different products in a neutralization reaction. Such a complex could not be prepared by passing nitrogen at 20° through a solution of iodine pentafluoride in hydrogen fluoride in order to remove free hydrogen fluoride. Iodine pentafluoride remained (Found : I, 57·3. Calc. for IF_5 : I, 57·2%).

Chlorine trifluoride, in contrast to the above, did not react with potassium hydrogen fluoride in hydrogen fluoride. The residue after removal of solvent at room temperature was free from chlorine.

Reactions in iodine pentafluoride.

Reaction with Antimonic Fluoride.—Antimony pentafluoride dissolved readily in hot iodine pentafluoride. The products after removal of excess of solvent at 5 mm. or in a higher vacuum were identical although in the latter instance some of the product distilled off. The substance was analysed for iodine by reducing its aqueous solution with sulphurous acid and precipitating silver iodide in dilute nitric acid solution. The oxidising power was found iodometrically after addition of potassium iodide and hydrochloric acid in the cold. The antimony was precipitated as sulphide and, after dissolution in hydrochloric acid, was titrated with potassium bromate. The fluoride was determined in the filtrate as calcium fluoride after decomposition with aqueous sodium carbonate. The *product* reached a constant weight after evacuation at 5 mm. for 3 hours and did not alter after a further 3 hours (Found : Sb, 27·9; I, 29·3; F, 42·7%; Equiv., 438; I liberated, 5·98 equivs./mol. $SbIF_{10}$ requires Sb, 27·8; I, 28·9; F, 43·2%; Equiv., 439; I liberated, 6·00 equivs./mol.). The product left after 4 hours in a high vacuum had an equiv. wt. of 395 (Found : Sb, 27·9; I, 29·1%; I liberated 6·02 equivs./mol.).

The hygroscopic white solid melted sharply at 103° with slight decomposition to a blue liquid. The solid reacted immediately with acetone in the cold, liberating iodine and producing charring, but had no effect on carbon tetrachloride. On warming, however, the compound dissolved with effervescence and the pungent fluorochlorocarbon smell was noted.

Reaction with Sulphur Trioxide.—Mixtures of iodine pentafluoride and sulphur trioxide were distilled in a small one-piece silica apparatus. Fractions were collected when the temperature reached a maximum at 145—147°/759 mm. The identity of the fractions obtained from different mixtures (see data below) indicated a constant-boiling mixture. The iodine was analysed iodometrically, fluorine by the Willard–Winter method, and sulphur by precipitation as barium sulphate after the solution had been reduced with hydrazine hydrochloride.

Mol. ratio IF_5/SO_3.	Fraction (b. p. 145—147°).	Analyses, %.		
		I.	S.	F.
1·11	1	40·2	11·7	29·2
	3	40·4	11·8	29·4
2·64	1	40·3	11·8	29·0
	3	40·3	11·9	29·3
Calc. for $IF_5,1·17SO_3$	—	40·2	11·9	30·0

Preparation of Potassium Fluoroantimonate.—Approx. 0·01 g.-mol. each of potassium and antimonic fluorides were heated under reflux in iodine pentafluoride (25 c.c.). Removal of the solvent at 8 mm. at room temperature gave the fluoroantimonate (Found : Sb, 37·0; F, 41·0; I, 8·9%; Equiv., 327. Calc. for $KSbF_6,0·23IF_5$: Sb, 37·2; F, 41·5; I, 8·9%; Equiv., 327).

Preparation of Potassium Fluoroborate.—Boron trifluoride was passed into a suspension of potassium fluoride (0·27 g.) in iodine pentafluoride (25 c.c.) with shaking. After a short period of heating most of the solvent was removed at 20°/8 mm. and then in a high vacuum at 180°. The residue, analysed by precipitation of nitron fluoroborate, consisted of KBF_4 45% and KF 55%. The nitron salt was identified by analysis (Found : C, 60·0; H, 4·5; N, 14·3. Calc. for $C_{20}H_{17}N_4F_4B$: C, 60·0; H, 4·3; N, 14·0%).

Reactions with oxy-salts.

Potassium Metaphosphate.—The solid was incompletely soluble in iodine pentafluoride but the residue after evacuation contained iodine pentafluoride. Since it gave no precipitate with nitron

acetate it was free from KPF_6 and KPO_2F_2 (Found : Equiv., 629; I, 47·0%. Calc. for $KPO_3,2·3IF_5$: Equiv., 629; I, 46·4%).

Potassium Persulphate.—This compound was also insoluble in iodine pentafluoride but the residue contained about one mole of the pentafluoride (Found : Equiv., 498; I, 25·1. Calc. for $K_2S_2O_8,1·02IF_5$: Equiv., 498; I, 26·0%). The latter was determined as silver iodide since the persulphate itself slowly liberates iodine from potassium iodide. The slow production of a nitron precipitate could not be taken as indicative of fluorosulphonate formation since hydrolysis of $K_2S_2O_8$ and IF_5 would produce enough fluorosulphonate ion to give a positive test.

Potassium Iodate.—This was readily soluble in iodine pentafluoride, but no oxygen was evolved. The residues left after evacuation even at high temperatures retained upwards of half a molecule of pentafluoride.

Potassium iodate and iodine pentafluoride were kept for a fortnight in separate platinum crucibles in a desiccator. The iodate absorbed nearly its own weight of pentafluoride. The residue was not homogeneous, however. The failure of iodine pentafluoride to displace oxygen from potassium iodate is surprising in view of the formation of the difluoroiodate when it is treated with aqueous hydrogen fluoride.

Conductivities in iodine pentafluoride.

A re-determination of the solvent conductivity at 25·0°, an all-silica apparatus being used for purification, gave a lower value ($1·53 \times 10^{-5}$ ohm^{-1}cm.$^{-1}$) than has been obtained previously (Banks, Eméleus, and Woolf, *J.*, 1949, 2861).

Antimonic fluoride (0·045 g.-mol./1000 g. of solvent) increased the conductivity to 114×10^{-5} at 25° and 93×10^{-5} at 12·5°. A solution saturated with boron trifluoride had a conductivity of $3·55 \times 10^{-5}$ at 25°, and a sulphur trioxide solution (1·71 g.-mol./1000 g.) gave a value $8·50 \times 10^{-5}$. Heating of solutions was avoided in order to avoid spurious increases resulting from attack on the cell.

Conductivity of KIO_3 in IF_5 at 25°.
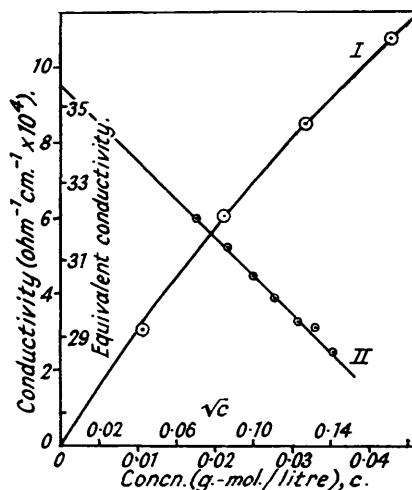
The following values obtained for potassium iodate solutions are plotted against concentration in curve I :

Mol. KIO_3/l. IF_5	0·0107	0·0212	0·0318	0·0428
Conductivity of solution–solvent at 25°	3·07	6·07	8·52	10·75

The following values, obtained from this curve, are plotted in curve II :

Mols. KIO_3/l. IF_5 (c).	$c^{\frac{1}{2}}$.	Equiv. conductivity.	Mols. KIO_3/l. IF_5 (c).	$c^{\frac{1}{2}}$.	Equiv. conductivity.
0·0050	0·071	32·0	0·0150	0·123	29·3
0·0075	0·087	31·3	0·0175	0·132	29·1
0·0100	0·100	30·5	0·0200	0·141	28·5
0·0125	0·112	29·9			

The extrapolated value for the equivalent conductivity at infinite dilution is 35·5.

On electrolysis solutions of potassium iodate liberate iodine at the cathode, and direct current measurements show that Ohm's law is not obeyed.

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