472. Chemistry of the Interhalogen Compounds. Part II. Potassium Iodohexafluoride.

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Potassium fluoride combines with iodine pentafluoride to yield *potassium iodohexafluoride* (*hexafluoroiodate*), KIF_6. The structure of the $(IF_6)^-$ ion is discussed. The validity of Beck's claims (*Z. anorg. Chem.*, 1937, **235**, 77) to have prepared the compounds K_2ClF_7, K_2NOF_3, and $K_2N_2O_5F_2$ is questioned.

Indications of complex fluoride formation between potassium fluoride and iodine pentafluoride, analogous to that between potassium fluoride and bromine trifluoride, were mentioned in Part I (*J.*, 1948, 2135). Iodine pentafluoride is a much less vigorous fluorinating agent than bromine trifluoride, and at temperatures below its boiling point (97°) is without action on most metallic halides. It does, however, dissolve potassium fluoride, and removal of excess of the halogen fluoride by evaporation under 2—5 mm. pressure gives *potassium iodohexafluoride* (*hexafluoroiodate*), KIF_6.

Attention has so far been confined to the preparation of this salt, which is a white crystalline solid, sparingly soluble in cold, rather more soluble in hot, iodine pentafluoride. Water decomposes it, with evolution of heat, according to the equation

$$IF_6^- + 3H_2O = 6F^- + IO_3^- + 6H^+$$

Potassium iodohexafluoride is decomposed by heat, and the decomposition is rapid after it melts at *ca.* 200°; the residue is potassium fluoride. This general mode of decomposition of polyhalides, the most electronegative halogen remaining with the metal, is to be expected, since lattice energies in the alkali-metal halides decrease from fluoride to iodide, and formation of the fluoride (or, when fluorine is absent, the chloride) corresponds to the maximum decrease in energy. Carbon tetrachloride has no action on potassium iodohexafluoride, but dioxan produces slight decomposition. At low pressures (less than 1 mm.) the compound slowly loses iodine pentafluoride.

Potassium iodohexafluoride is the first reported well-defined polyhalide containing seven halogen atoms. Confirmation of its structure by *X*-ray analysis has not yet been possible, but its properties leave little room for doubt that it is to be formulated as $K^+(IF_6)^-$. Possible electronic and stereochemical configurations for such a complex fluoride ion are discussed below.

A claim to have prepared a compound formally similar to potassium iodohexafluoride has, however, been made by Beck (*loc. cit.*). The action of concentrated hydrofluoric acid on potassium chlorate was reported to yield the compound, K_2ClF_7 or $KF,KClF_6$; analytical data, but no other evidence, were quoted supporting this claim. By comparison with the new polyhalides described in Part I and here, it would be expected that a derivative of the as yet unknown chlorine pentafluoride would be a very unstable substance and would certainly be hydrolysed by 40% hydrofluoric acid. All attempts to repeat Beck's preparation have failed to yield anything but chlorate–fluoride mixtures, and it is believed that his claim is mistaken. In reaching this conclusion, account has been taken of other work described in the same paper, namely, the preparation of fluoronitrites, K_2NOF_3 and Na_3NF_6, and of the fluoronitrate $K_2N_2O_5F_2$, by the action of hydrofluoric acid on potassium nitrite, sodium nitrite, and potassium nitrate, respectively; and evidence for the production of a fluorocarbonate by the action of hydrofluoric acid on potassium carbonate. Beck's compound Na_3NF_6 has been shown by Zintl and Haucke (*Z. anorg. Chem.*, 1938, **237**, 45) to be sodium hydrogen fluoride; his K_2NOF_3 and $K_2N_2O_5F_2$ were found to be potassium acid fluorides, and a mixture of potassium acid fluoride and unchanged potassium nitrate, respectively; his evidence for fluorocarbonate formation is confined to a mistaken idea of the nature of calcium fluoride when precipitated in the cold. The subject is discussed in more detail below : it may be taken that solid polyhalides in which chlorine forms the central atom of a complex anion have not yet been prepared.

The iodine atom in $(IF_6)^-$ should have a valency shell of fourteen electrons but only six-fold co-ordination; it thus differs from that in IF_7, and resembles rather the selenium and tellurium atoms in the ions $(SeCl_6)^{--}$, $(SeBr_6)^{--}$, and $(TeCl_6)^{--}$. In these (Engel, *Z. Krist.*, 1935, **90**, 341; Hoard and Dickinson, *ibid.*, 1933, **84**, 436) the configuration is octahedral, but, on the assumption that chlorine and bromine have their normal covalent radii, the octahedral radii of selenium and tellurium are unexpectedly large by 0·25 A., and it has been suggested by Beach (quoted by Pauling, " The Nature of the Chemical Bond," 1940) that the orbitals involved in bonding are, in the case of selenium, $4p^3 4d^2 5s$ hybridised orbitals and that the inert $4s$ orbital constitutes a separate energy level and is responsible for the long bond.

The necessity for d^2sp^3 bonding emerges from Kimball's systematic calculations of bond type and configuration (*J. Chem. Physics*, 1940, **8**, 194); no other combination of orbitals gives an octahedral structure. In the electrically neutral hexafluorides of selenium and tellurium, which have two valency electrons less than the complex halides, octahedral shape and almost normal bond length are satisfactorily reconciled with the obvious electronic configurations for the central atom : $4s^2 4p^6 4d^4$ for selenium, $5s^2 5p^6 5d^4$ for tellurium. For the iodine atom in $(IF_6)^-$ the expected electronic configuration is $5s^2 5p^6 5d^4 6s^2$ (unless the ion differs from all other known finite complex six-co-ordination ions by not being octahedral), and it may therefore be predicted that, unlike other polyhalide anions, in which the bond distances are the sums of the appropriate covalent radii (Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1100; Pauling, *ibid.*, 1925, **47**, 1561; Mooney, *Z. Krist.*, 1938, **98**, 324, 377), the $(IF_6)^-$ ion will have an abnormally large interhalogen distance. The structure of the covalent IF_7 molecule (b. p. +4°) must be considered on its own merits; here the outermost fourteen electrons round the iodine nucleus presumably form seven bonds, probably $5s5p^3 5d^3$ bonds arranged in a distorted octahedron, a structure already known in the ion $(ZrF_7)^{---}$ (Hampson and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 2702). There seems no reason to suggest an abnormal bond length in iodine heptafluoride.

If technical difficulties due to reactivity and difference in scattering power between the halogens can be overcome, structure determinations on these interhalogen ions and molecules should therefore provide useful experimental information about the relation between electronic configuration and stereochemical type.

EXPERIMENTAL.

Potassium Iodohexafluoride.—Quantities of up to 30 g. of iodine pentafluoride were conveniently prepared by passing fluorine over iodine in a quartz trap cooled by partial immersion in water and continuously shaken to prevent the formation of an inactive surface layer of the pentafluoride. The product was analysed by decomposition with sodium hydroxide, followed by determination of (i) iodine, by reduction with sulphurous acid and precipitation as silver iodide in the presence of dilute nitric acid, (ii) fluorine, by precipitation as calcium fluoride, (iii) oxidising power, by iodometric determination of the iodate formed (Found : I, 57·0; F, 42·2%; iodine liberation, 5·96 equivs. per mole. Calc. for IF_5 : I, 57·2; F, 42·8%; iodine liberation, 6·00 equivs. per mole).

Boiling iodine pentafluoride did not react with sodium, potassium, or silver chloride. Argentous and barium fluorides were almost insoluble in the reagent, but potassium fluoride dissolved (about 1 g. per 100 g. at the b. p.) and white crystals were formed on cooling this solution. Attempts to remove the solvent at low pressures (<1 mm.) in a simple vacuum system gave products of varying composition ($KF,0·6IF_5$ to $KF,0·9IF_5$), which continued to lose iodine pentafluoride slowly. Iodine pentafluoride forms a compound with dioxan (Scott and Bunnett, *J. Amer. Chem. Soc.*, 1942, **64**, 2727), and the possibility of removing the uncombined halogen fluoride with dioxan was studied, without, however, obtaining even a moderately pure product. This was finally obtained by removal of the iodine pentafluoride at 15—20° under a pressure of 2—5 mm. of mercury; under these conditions, the vapour pressure of the solvent is sufficient for its removal before dissociation of the deposited solute is appreciable. The whole preparation was conducted in quartz apparatus, and a constant weight was attained. Analysis by determination of potassium as sulphate, and of iodine, fluorine, and equivalent weight as an oxidising agent by the method used for iodine pentafluoride, established the identity of the product as moderately pure *potassium iodohexafluoride* (Found : K, 14·7; I, 43·6; F, 40·1%; equiv., 48·4. KIF_6 requires K, 13·9; I, 45·4; F, 40·7%; equiv., 46·7). Discrepancy with calculated results corresponds to the presence of 4% (molar) of potassium fluoride, arising from the method of preparation. Properties of potassium iodohexafluoride have been described above.

Reactions of 40% Hydrofluoric Acid with Some Oxy-salts.—Several attempts to prepare K_2ClF_7 by three times evaporating potassium chlorate with the acid (Beck, *loc. cit.*) yielded products containing K, 31—33; Cl, 14—23; F, 6—21% (Calc. for K_2ClF_7 : K, 31·7; Cl, 14·4; F, 53·8%). Water had no action on these products except to dissolve them without evolution of heat. Rapid recrystallisation of potassium chlorate from the boiling acid resulted in its recovery almost unchanged (Found : Cl, 25·4; F, 3·0. Calc. for $KClO_3$: Cl, 28·9%); repeated evaporation with the acid produced complete decomposition to fluoride, all the chlorine being removed. There is thus no evidence for an intermediate compound, and the reaction is gradual replacement of chlorate by fluoride.

Potassium bromate was completely and rapidly decomposed to the fluoride by warm hydrofluoric acid;

the iodate gave potassium difluoroiodate, KIO_2F_2 (Helmholtz and Rogers, *J. Amer. Chem. Soc.*, 1940, **62**, 1537).

The conditions described by Beck for the production of Na_3NF_6 and K_2NOF_3 (evaporation of nitrites with hydrofluoric acid) brought about elimination of all the nitrogen; the reactions which he quoted for the $(NOF_3)^{--}$ ion, erroneously stated to be iso-electronic with the sulphate ion, are in fact characteristic of fluorides. When potassium nitrate is heated with hydrofluoric acid, fluoride is substituted for nitrate and not for oxygen. Beck found that after three evaporations with hydrofluoric acid, the product contained: K, 35·8; F, 15·1%; no nitrogen determination was made on this or on his other products (Calc. for $K_2N_2O_5F_2$: K, 34·8; F, 16·0; N, 12·0%). We found on repetition of Beck's preparation: K, 38·8; F, 17·2; N, 9·4%. This indicates partial replacement of the nitrate. Beck actually observed that on further treatment the fluorine content of the product increased, but he attributed this to formation of fluorinated nitrates intermediate between potassium nitrate and (the highly unlikely) KNF_6.

Potassium carbonate and hydrofluoric acid were admitted to produce a vigorous evolution of carbon dioxide, but it was said (*loc. cit.*) that alcohol precipitated a substance which, dissolved in ice-cold water, gave only an opalescence with calcium chloride solution, warming being necessary for production of a precipitate. The character of the calcium fluoride precipitate is, however, well known, and since normal and acid potassium fluorides are all insoluble in alcohol, the evidence for the existence of a fluorocarbonate may be dismissed without further comment.

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