430. *Chemistry of the Inter-halogen Compounds. Part I. The Reaction of Bromine Trifluoride with Metallic Halides.*

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Bromine trifluoride converts many metallic chlorides, bromides, and iodides into fluorides. Treated with excess of the reagent, the chlorides of potassium, silver, and barium yield the *bromofluorides* (*bromotetrafluorides*) $KBrF_4$, $AgBrF_4$, and $BaBr_2F_8$. Indications of the formation of other polyhalides of this type have been obtained.

Bromine trifluoride was first prepared more than forty years ago (Lebeau, *Compt. rend.*, 1905, **141**, 1015; Prideaux, *J.*, 1906, **89**, 316), but few details of its reactions with inorganic compounds have been published. A wide range of preliminary experiments with liquid bromine trifluoride showed that the compound was highly reactive. The study of its interaction with metallic halides is one of the simplest cases, particularly as the possibility of oxyfluoride formation can be excluded. The halides of lithium, sodium, potassium, rubidium, cæsium, copper, silver, calcium, strontium, barium, cadmium, aluminium, thallium, lead, uranous uranium, cobalt, and ferric iron have been examined.

The products of reaction, obtained in each case by treating the halide with excess of bromine trifluoride and pumping off the excess volatile material, were of several types. Cadmium iodide and lithium chloride, typical halides of elements of constant valency, gave the corresponding fluorides, which were not appreciably soluble in liquid bromine trifluoride. Anhydrous aluminium and ferric chlorides reacted similarly, but only very slowly and incompletely. Cuprous, thallous, plumbous, and cobaltous chlorides, and plumbous bromide, halides of elements of variable valency, gave mixtures of the lower and the higher fluorides, which were also not noticeably soluble in bromine trifluoride. Probably coating effects prevented complete conversion into the higher fluoride. Uranium tetrafluoride was completely converted into the volatile hexafluoride, and similar complete conversion will probably be found for halides of other elements, *e.g.*, vanadium, molybdenum, and tungsten, which form volatile highest fluorides. The chlorides of potassium, silver, and barium reacted with bromine trifluoride in the normal manner, free chlorine and bromine being formed (*e.g.*, $3KCl + BrF_3 = 3KF + Br + 3Cl$), but part of the excess bromine trifluoride was not removable in a high vacuum. Compounds having the respective empirical formulæ $KBrF_4$, $AgBrF_4$, and $Ba(BrF_4)_2$ were formed; their nature is discussed below.

Potassium bromofluoride (*bromotetrafluoride*), $KBrF_4$, the most closely studied of the new compounds, is a white crystalline solid which loses bromine trifluoride on heating, the more electronegative halogen remaining with the metal. This parallels the thermal decomposition of potassium iodochloride, $KICl_4$ (Caglioti and Centola, *Gazzetta*, 1933, **63**, 907), and rubidium monofluorotrichloroiodide, $RbFICl_3$ (Booth, Swinehart, and Morris, *J. Amer. Chem. Soc.*, 1932, **54**, 2561), to potassium chloride and rubidium fluoride, respectively. When heated in a platinum crucible, the crucible is attacked by potassium bromofluoride and addition of water to the solid product results in the deposition of the sparingly soluble potassium hexafluoroplatinate, a method of preparation which is probably more convenient than that of Schlesinger and Tapley (*ibid.*, 1924, **46**, 276) involving the action of the complex fluoride $3KF,HF,PbF_4$ on platinum, and the subsequent removal of lead.

With water, potassium bromofluoride decomposes rapidly, but much less violently than bromine trifluoride. The products are bromine, bromic acid, hydrofluoric acid, and oxygen. The first stage of the reaction is probably $BrF_4^- + 2H_2O \longrightarrow HBrO_2 + 3H^+ + 4F^-$ (cf. $BrF_3 + 2H_2O \longrightarrow HBrO_2 + 3H^+ + 3F$), followed by decomposition of the bromous acid to bromine, bromic acid, and oxygen. Further reactions of bromofluorides, expecially as fluorinating agents, are being studied in detail.

The proposed formulation of the polyhalide as $K^+(BrF_4)^-$ is supported by analogy with $KICl_4$, shown by Mooney (*Z. Krist.*, 1938, **98**, 377) to contain K^+ and planar ICl_4^- ions. Powder *X*-ray photographs of $KBrF_4$ show no lines due to potassium fluoride, but instead an entirely different set of lines. There are great differences in reactivity between potassium bromofluoride and bromine trifluoride. The latter, for example, reacts vigorously with carbon tetrachloride and explodes with acetone or dioxan, whereas the potassium compound neither reacts nor dissolves. Even boiling bromine trifluoride (b. p. 128°) has no action on platinum, which the potassium compound attacks readily on heating. The reactivity of the silver and barium compounds is rather greater, perhaps because the bromine trifluoride dissociation pressures of these compounds are greater than that of the potassium salt. They do not react with carbon tetrachloride, but ignite ethyl ether, acetone, dioxan, and petrol. The existence of a silver polyhalide but not of a corresponding thallous compound is interesting in that the existence of silver tri-iodide (Schmidt, *Z. anorg. Chem.*, 1895, **9**, 418) is rather doubtful, whereas thallous tri-iodide (Wells and Penfield, *Z. anorg. Chem.* 1894, **6**, 312) is well characterised, being isomorphous with the tri-iodides of rubidium and cæsium. The final point supporting the existence of the bromofluoride ion $(BrF_4)^-$ is the combination of two such units with the invariably bivalent barium ion.

The $(BrF_4)^-$ ion may also be invoked to explain the electrical conductivity observed in pure liquid bromine trifluoride (unpublished observations by A. A. Banks and A. Woolf). The specific conductivity is 8×10^{-3} at 25°, and may perhaps be explained by the existence in the solid and liquid of ions BrF_2^+ and BrF_4^-. Chlorine trifluoride, which apparently does not form polyhalides analogous to $KBrF_4$ and $KICl_4$, has zero conductivity in the liquid state; iodine pentafluoride has a much lower conductivity (κ = approx. 10^{-5} at 25°). Solutions of potassium fluoride in bromine trifluoride are better conductors than the pure solvent.

If it is assumed that the BrF_4^- ion has a configuration similar to that of ICl_4^-, and the covalent radii for bromine and fluorine are 1·14 A. and 0·64 A., respectively, the Br–F distance should be 1·8 A. and the ion would therefore be considerably smaller than the ICl_4^- ion, in which the I–Cl distance is 2·34 A.

The existence of bromofluorides other than those of potassium, silver, and barium is extremely likely, but the possibility of isolating them in a pure state by the technique of pumping off bromine trifluoride will depend on the dissociation pressures of the compounds; and no solvent suitable for the recrystallisation of bromofluorides or for the separation of mixtures of fluoride and bromofluoride has yet been found. The chlorides of sodium, rubidium, cæsium, calcium, and strontium are rapidly converted by bromine trifluoride into fluorides, soluble, like those of potassium, silver, and barium, in excess of the reagent; and although the ratios of bromine trifluoride to metallic fluoride in the solid products obtained are other than 1 : 1 and 2 : 1, there is ample evidence for some sort of compound formation. Formation of lattice compounds containing fluoride and bromofluoride ions, as well as of mixtures, is possible, and a further study of these products by *X*-ray methods and the measurement of dissociation pressures may elucidate this point.

Iodine pentafluoride is a much less vigorous fluorinating agent than the bromine compound, but preliminary experiments have shown that it dissolves potassium fluoride and probably forms a compound KIF_6. Chlorine trifluoride, on the other hand, converts other halides into fluorides only, *e.g.*, potassium bromide and silver chloride yield potassium fluoride and silver bifluoride respectively, and no evidence for compound formation between chlorine trifluoride and metallic fluorides has been obtained.

EXPERIMENTAL.

Bromine trifluoride was prepared by a method similar to that of Ruff and Braida (*Z. anorg. Chem.*, 1932, **206**, 62). Reaction between bromine vapour, carried in a stream of nitrogen, and fluorine took place in a copper T-tube; the product was collected in a copper trap cooled by immersion in water. The crude bromine trifluoride was purified by distillation in a steel retort, the fraction boiling at 126—128° being collected separately and stored in a steel bottle stoppered by a screw-on steel cap. Immediately before use, the reagent was redistilled in quartz under reduced pressure at room temperature in order to free it from small quantities of ferric fluoride produced by slight attack on the containing vessel.

Reactions were carried out by slow addition of a large excess of bromine trifluoride to the halide in a quartz flask. When the reaction (if any) had subsided, the flask and its contents were heated to approx. 120° for a few minutes, and allowed to cool. The flask was then connected by a quartz trap cooled in liquid air to a simple vacuum line. The excess of bromine trifluoride was pumped off in a vacuum, without external heating, and condensed in the trap; distillation was continued until a very nearly constant weight was attained. In such a series of operations the loss in weight of the quartz reaction vessel was negligibly small (about 0·01%—a few mg. on 30 g.) so long as the apparatus was quite dry, and the formation of hydrogen fluoride thereby avoided. As a lubricant for ground joints, a very thin film of silicone vacuum grease was used; in bulk, this reacts explosively with bromine trifluoride, and the amount used was kept at the absolute minimum consistent with maintenance of a vacuum.

Potassium Bromofluoride (*Bromotetrafluoride*).—Approx. 0·5 g. of dried A.R. potassium chloride was caused to react as described above; chlorine was evolved. Values obtained for the conversion factor KCl : product indicated an equivalent weight of 193 ($KBrF_4$ requires 195). The product was analysed for (i) potassium, by exposure to moist air, followed by conversion into sulphate; (ii) bromine, by decomposition in a stoppered bottle with dilute ammonia, reduction with sulphur dioxide, and precipitation as silver bromide; (iii) fluorine, by decomposition with dilute ammonia and estimation as calcium fluoride (Treadwell and Hall, " Analytical Chemistry," Vol. II, 9th English edtn., p. 397) (Found : K, 20·7; Br, 39·5; F, 39·7. $KBrF_4$ requires K, 20·0; Br, 41·0; F, 39·0%). Discrepancy with calculated results is attributed to the presence of about 2% of potassium fluoride in the product. The *compound* was also prepared by direct combination of potassium fluoride and bromine trifluoride; the simple halide dissolved with no sign of reaction beyond a slight evolution of heat. The ratios found for KF : BrF_3 in two preparations were 1·00 : 0·98 and 1·00 : 0·99. With potassium bromide and iodide vigorous reactions took place, clouds of bromine being evolved in the former reaction; most of the iodine from the iodide appeared to be fluorinated before it escaped. In each case the product was qualitatively identical with that obtained from the chloride or fluoride, but the reactions were too violent, and attack on the reaction vessel too marked, for quantitative study.

Silver Bromofluoride (*Bromotetrafluoride*).—This ***compound*** was prepared by treating either argentous fluoride or chloride with bromine trifluoride. The fluoride dissolved without any sign of reaction; chlorine was liberated from the chloride. The product after excess of reagent had been pumped off was white, and could therefore have contained no significant quantity of argentic fluoride, which is black. Gravimetric conversion factors from argentous fluoride and chloride indicated equivalent weights of 259 and 262 respectively ($AgBrF_4$ requires 264).

Decomposition with sulphurous acid reduced all the bromine to bromide, and after addition of a slight excess of silver nitrate solution and acidification with nitric acid, silver bromide equivalent to bromine in the compound was filtered off and weighed. For the determination of silver and fluorine, a fresh sample was decomposed with sodium carbonate solution containing a little potassium bromide; the solution was made weakly acid with nitric acid, and silver bromide, this time equivalent to silver, was filtered off; fluoride was determined in the filtrate by the method cited above. The use of sulphur dioxide was avoided in order to prevent co-precipitation of calcium sulphate with calcium fluoride (Found: Ag, 40·6; Br, 30·0; F, 27·3. $AgBrF_4$ requires Ag, 40·9; Br, 30·3; F, 28·0%).

Barium Bromofluoride (*Bromotetrafluoride*).—This salt was prepared in the same way, by treating anhydrous barium chloride with bromine trifluoride. The weight equivalent to $BaCl_2$ was 445 (duplicate) ($BaBr_2F_8$ requires 449). Barium was determined by conversion into fluoride and then into sulphate by heating to constant weight with concentrated sulphuric acid. Decomposition with sodium carbonate solution, removal of all barium as carbonate, and reduction by sulphur dioxide solution was followed by precipitation of the bromine as silver bromide. Barium fluoride is somewhat soluble in water, and for the determination of fluorine the barium bromofluoride was decomposed by dilute ammonia, and then sufficient water was added to dissolve all the barium fluoride; barium was precipitated as carbonate, and fluoride estimated (as above) in the filtrate (Found: Ba, 32·1; Br, 35·2; F, 31·2. $BaBr_2F_8$ requires Ba, 30·5; Br, 35·7; F, 33·9%). Attempts to prepare ***barium bromofluoride*** from barium fluoride gave products of approximate composition $BaF_2,0{\cdot}9BrF_3$ and $BaF_2,1{\cdot}1BrF_3$ in successive experiments; their nature is still being investigated; it is considered most likely that they are mixtures of roughly equal quantities of BaF_2 and $Ba(BrF_4)_2$.

Reaction of Bromine Trifluoride with Other Metal Halides.—Lithium chloride gave lithium fluoride, containing only a trace of chlorine or bromine. Lithium fluoride was not appreciably soluble in bromine trifluoride and was recovered unchanged in weight and free from bromine. Cadmium iodide yielded pure cadmium fluoride. When sodium chloride was treated in a platinum crucible, and excess of the reagent removed by gentle heating, the residue was sodium fluoride (Found: Na, 54·4; F, 44·8; Cl, Br, nil; equiv., 41·8. Calc. for NaF: Na, 54·7; F, 45·3%; equiv., 42·0). When, however, the reaction was carried out as in the preparation of potassium bromofluoride, products of widely variable composition containing sodium, bromine, and fluorine resulted. Sodium bromide and iodide reacted similarly. Sodium fluoride dissolved in bromine trifluoride and a product $NaF,0{\cdot}97BrF_3$ was obtained. This was probably impure sodium bromofluoride, $NaBrF_4$. It was insoluble in, and did not react with, organic solvents; it oxidised potassium iodide solution with the formation of considerably less than the expected quantity of free iodine. This compound was rapidly decomposed to sodium fluoride and bromine trifluoride at 80°. Comparison of the % losses in weight by the sodium and potassium compounds on heating 0·5-g. samples for 5 mins. at 200° illustrates the much lower stability of the former: the potassium compound lost only 30% by weight, but the sodium compound was completely decomposed into sodium fluoride. Calcium, cæsium, and rubidium chlorides, and calcium and strontium fluorides, gave ill-defined products, the bromine content of which varied with the temperature and time of evacuation. Here again it is highly probable that unstable compounds were formed, and that retention of bromine trifluoride was not mechanical, for though stoicheiometrically indefinite, the products possessed the same degree of reactivity as the definite bromofluorides. The high reactivity of bromine trifluoride and the considerable reactivity of the polyhalides make the quantitative study of loss of bromine trifluoride from them rather complicated, but suitable techniques are being developed. The indications so far are that bromofluorides of varying stability are formed only by the alkali metals (excluding lithium), the alkaline earths, and silver. This is borne out by further tests with other metal halides, which are described briefly below.

Cuprous chloride reacted vigorously to give a reagent-insoluble mixture of cuprous and cupric fluorides; in one experiment 70% of the copper was shown by an iodometric determination to be in the cupric state. Thallous chloride was converted into an insoluble mixture of thallous and thallic fluorides, analysis showing 80—90% of thallium in the product to be in the tervalent state. Lead fluoride, chloride, and bromide gave products containing up to 20% of the tetrafluoride (von Wartenburg, *Z. anorg. Chem.*, 1940, **244**, 337). A similar result was obtained with cobaltous chloride, the product consisting mainly of cobaltic fluoride. Aluminium and ferric chlorides were converted slowly into their respective fluorides; there was no evidence of bromine trifluoride retention. In all these instances the insolubility of the fluorides presumably restricted the conversion, for uranous fluoride was rapidly and quantitatively converted into the hexafluoride (which volatilised as it was formed), and no visible residue remained. Ammonium fluoride and chloride both reacted explosively with bromine trifluoride.

Reactions of Potassium, Silver, and Barium Bromofluorides.—The dissociation pressure of potassium bromofluoride at room temperature is very small, for a 1·1-g. sample kept in a silica flask connected to a vacuum line lost only 0·5% by weight in 6 hours. Decomposition is rapid only above 280°. In contact with glass, the compound is slowly decomposed with the liberation of bromine. Potassium bromofluoride decomposes rapidly with water, but the reaction is not violent like that of bromine trifluoride. Shaken with potassium iodide solution, it liberates iodine immediately, but neither in neutral nor in acid solution does the iodine liberation correspond with the expected 4 equivs. per g.-mol. of the salt; the values obtained varied from 2·5 to 3·5. Since both fluorine and bromine are recovered quantitatively in the analysis of potassium bromofluoride involving its initial decomposition by water, this loss of oxidising power cannot be due to the formation of fluorine monoxide and must be due to the liberation of oxygen. This has been confirmed qualitatively. Free bromine, as well as oxygen, is formed on treating the bromofluoride with water, and a stable bromine oxyacid which is not reduced by ammonia (bromic acid) remains in solution; it is suggested that these are all decomposition products of bromous acid. The reactions of silver and barium bromofluorides with water were shown to be qualitatively similar to that of the potassium compound.

X-Ray powder photographs of samples of several preparations of potassium bromofluoride sealed in Pyrex tubes were taken, Cu-$K\alpha$ radiation being used. The salt showed slight local decomposition in the *X*-ray beam, but lines due to potassium fluoride were completely absent from the photographs. The method is being applied to the more detailed study of the bromofluorides prepared, as well as to the elucidation of the nature of the more complex products referred to above.

When the potassium compound was heated to *ca.* 280° in a platinum crucible, the metal was strongly attacked with the formation of a brown product. Taking the loss in weight of the crucible as a measure of the platinum used, quantitative figures obtained are consistent with the conversion of platinum into the tetrafluoride and decomposition of the bromofluoride to fluoride; the solid reaction products contained no bromine. 1·507 G. of $KBrF_4$ reacted with 0·579 g. of Pt, equivalent to 0·804 g. of PtF_4. The total weight of solid products was 1·253 g., hence the weight of KF was 1·253 − 0·804 = 0·449 g. The weight, assuming conversion of $KBrF_4$ into KF, should be 0·448 g. The reaction product was left in contact with water for a week, during which time potassium fluoroplatinate crystallised. After recrystallisation from boiling water this was analysed for platinum by heating to constant weight at 1400° (Schlesinger and Tapley, *loc. cit.*) (Found: Pt, 50·4, 49·9. Calc. for K_2PtF_6: Pt, 50·2%). The observations of Schlesinger and Tapley on the impossibility of quantitatively reducing platinum compounds in fluoride-containing solution were extended by an unsuccessful attempt to determine the metal by reduction with magnesium ribbon (Found: Pt 46·8%).

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