

the reaction mixture has carbonyl bands at 4.90 (vs) and 5.06 μ (vs). Attempts to isolate the product led to yellow crystals which decomposed as they were being purified.

N.m.r. Spectra.—The n.m.r. spectra were obtained using a Varian Associates 12-in. electromagnet and a frequency of 60

Mc. All samples were sealed in *vacuo* in 5 mm. o.d. glass sample tubes. They were studied at 30° as solutions in CDCl_3 . Chemical shifts, referred to external benzene, were obtained by the usual side-band technique using a Hewlett-Packard wide-range oscillator, Model 200CD.

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Solvolysis Reactions in Chlorine Trifluoride and Bromine Pentafluoride : Preparation of the Tetrafluorochlorates and Hexafluorobromates of Potassium, Rubidium, and Cesium¹

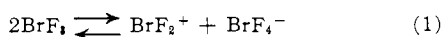
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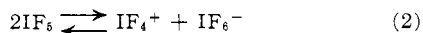
Solvolysis reactions of alkali metal fluorides in chlorine trifluoride and bromine pentafluoride at 100° resulted in the formation of the respective alkali metal tetrafluorochlorates and hexafluorobromates; the compounds KClF_4 , RbClF_4 , CsClF_4 , KBrF_6 , RbBrF_6 , and CsBrF_6 have been prepared. All of the above materials are powerful oxidizing agents, react violently with water, liberate iodine from aqueous iodide solutions, and interact explosively with common organic solvents.

Introduction

Halogen fluorides are a particularly interesting class of compounds from the standpoint of their unusual composition and great chemical reactivity. The fluorides are usually quite easy to prepare, their physical and chemical properties have been studied extensively, and several reviews on the subject have been published.³⁻⁷ Particular interest has been shown in the self-ionization of many of the halogen fluorides, and in the polyhalide salts resulting from the dissolution of metal halides in them. Indeed, many of the halogen fluorides act as solvents for the formation of a new class of acids and bases brought about *via* solvolysis reactions. Thus, bromine trifluoride and iodine pentafluoride have been shown by Emeléus and Woolf⁸ to act as ionizing solvents according to the following equilibria



and



Compounds containing the BrF_2^+ or IF_4^+ ions are thus considered as acids, whereas those containing BrF_4^- or IF_6^- ions are bases. Through solvolysis reactions in the above halogen fluorides, the bases KBrF_4 , AgBrF_4 , $\text{Ba}(\text{BrF}_4)_2$, and KIF_6 have been prepared.⁹⁻¹¹ No stable addition compounds of the type $\text{M}(\text{IF}_6)$ could be formed, however, when the alkali fluorides,

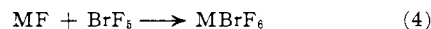
NaF , KF , or RbF , were mixed with iodine heptafluoride at room temperature.¹²

Although the tetrafluorohalates of cesium, rubidium, and potassium have been prepared through direct reaction of elementary fluorine with the corresponding alkali metal halides,¹³⁻¹⁷ there has been no report in the literature of bases of the type MClF_4 or MBrF_6 being formed as the result of solvolysis reactions in chlorine trifluoride or bromine pentafluoride, respectively.

In this paper are reported the results of solvolysis reactions between the fluorides of potassium, rubidium, and cesium, and the halogen fluorides, ClF_3 and BrF_5 , leading to the formation of the corresponding tetrafluorochlorates or hexafluorobromates, respectively. Our results can best be explained by the general reactions



and



To our knowledge this constitutes the first reported synthesis of bases containing the hexafluorobromate (BrF_6^-) ion, *i.e.*, compounds of the type MBrF_6 .

Experimental

Materials.—Anhydrous HF and 99% ClF_3 were obtained from the Matheson Co., Inc. Bromine pentafluoride and IF_5 were obtained from the General Chemical Division, Allied Chemical and Dye Corp. Prior to use, the halogen fluorides (except for IF_5) were allowed to distil under vacuum through a bed of NaF pellets maintained at 100° in a Monel pipe heated by means of a Fisher combustion tube furnace. In this manner HF impurities, and in the case of BrF_3 traces of BrF_5 , were removed. BrF_5 and ClF_3 were then fractionated under vacuum to remove traces of F_2 , and in the latter case Cl_2 and ClF if present. Fractionation was accomplished by a series of trap-to-trap distillations at -78°

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(3) A. G. Sharpe, *Quart. Rev.* (London), **4**, 115 (1950).

(4) V. Gutmann, *Angew. Chem.*, **62**, 312 (1950).

(5) J. H. Simons, "Fluorine Chemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1954, p. 39.

(6) H. C. Clark, *Chem. Rev.*, **58**, 869 (1958).

(7) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 3, H. J. Emeléus and A. G. Sharpe, Ed., Academic Press, Inc., New York, N. Y., 1961, pp. 133-169.

(8) H. J. Emeléus and A. A. Woolf, *J. Chem. Soc.*, 2865 (1949).

(9) A. G. Sharpe and H. J. Emeléus, *ibid.*, 2135 (1948).

(10) A. G. Sharpe and H. J. Emeléus, *ibid.*, 2206 (1949).

(11) A. A. Woolf, *ibid.*, 3678 (1950).

(12) W. C. Schumb and M. A. Lynch, Jr., *Ind. Eng. Chem.*, **42**, 1383 (1950).

(13) H. Bode, *Naturwiss.*, **37**, 477 (1950).

(14) H. Bode and E. Klesper, *Z. anorg. allgem. Chem.*, **267**, 97 (1951).

(15) H. Bode and E. Klesper, *ibid.*, **313**, 161 (1961).

(16) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Am. Chem. Soc.*, **83**, 2955 (1961).

(17) D. H. Kelly, B. Post, and R. W. Mason, *ibid.*, **85**, 307 (1963).

followed by collection of the materials in a trap at 0°. Iodine pentafluoride was distilled before use.

Cesium and rubidium fluorides of high purity were obtained from the American Potash and Chemical Corp. Potassium and ammonium fluorides were ACS reagent grade materials. The fluorides were thoroughly dried before use.

Apparatus.—Due to the reactive nature of the compounds handled in this work experiments were conducted in a general purpose vacuum system in order to exclude air and moisture. The system consisted of both Pyrex and metal sections, the sections being joined by means of a copper to Pyrex No. 774 (Housekeeper) seal. The glass portion of the apparatus consisted of a nitrogen gas drying column, a mercury manometer, a three-way stopcock which was used for either pulling a vacuum on the system or introducing nitrogen into the apparatus, and a liquid nitrogen cooled trap. The trap served to protect the mercury manometer and Duo-Seal pump from accidental attack by halogen fluoride vapors. The metal portion of the equipment was constructed of 0.25-in. o.d. copper tubing, Hoke miniature forged Monel needle valves equipped with Teflon packing, and Monel traps. Silver-soldered connections were used on the traps and reactors, and flared connections in the rest of the apparatus. Steel tanks of HF and IF_5 were connected directly to this line, whereas cylinders containing ClF_3 and BrF_3 were attached to the system through the HF absorber. A thin layer of Teflon "T-Film" thread compound (Eco Engineering Co.) was used on all threaded connections. Pressures were measured on Helicoid gages equipped with stainless steel Bourdon tubes operating in the range 30 in. vacuum to 30 p.s.i. pressure. Each part of the apparatus was rigorously cleaned and carefully dried before assembly.

Synthesis reactions were conducted in 500-ml. nickel reactors fitted with threaded caps, Monel needle valves, and flared connections. Provision was made for removing the reactors from the vacuum system after introduction of the reactants. Heating and agitation of the reactants were accomplished by wrapping the reactors with heating tape and asbestos, and fastening the units to a laboratory shaker. Heating was controlled by means of a Brown Pyr-O-Vane temperature regulator.

Procedure.—Purified halogen fluorides were condensed in a calibrated Pyrex tube attached to the vacuum system by means of a Housekeeper seal. The amount of halogen fluoride obtained in this way was determined from the measured volume and the density of the material. We have observed, along with Banks and Rudge,¹⁸ that ClF_3 and BrF_3 , when free of hydrogen fluoride, do not etch Pyrex glass.¹⁹ The halogen fluorides were then distilled into the nickel reactor containing the alkali metal fluorides; the reactor was closed, removed from the vacuum line, then heated and agitated for approximately 1 hr. At the conclusion of the experiment the reactor was returned to the vacuum line, excess halogen fluoride distilled off, and the reaction product subjected to reduced pressure at room temperature until a constant weight was obtained. Unreacted chlorine trifluoride or bromine pentafluoride, after condensation in a Monel trap, was identified by means of vapor pressure measurements at several temperatures. The extent of conversion of the metal fluoride to the corresponding polyfluorohalate was determined from the increase in weight of the starting material. The reactors were always opened and the reaction products removed and handled in a drybox which had been previously purged with dry nitrogen.

The polyfluorohalate salts were analyzed for total fluoride and total bromide or chloride by Parr bomb fusion with sodium peroxide, followed by standard analytical techniques. In spite of the fact that both the tetrafluorochlorate and hexafluorobromate salts react readily with water, simply analyzing solutions of these salts after hydrolysis for the corresponding halide ion was not satisfactory. Indeed, Asprey, *et al.*,¹⁶ have shown that hydrolysis of the tetrafluorochlorate salt yields primarily the chlorate, rather than the chloride ion. Presumably the hexafluorobromates form primarily bromates upon hydrolysis.

(18) A. A. Banks and A. J. Rudge, *J. Chem. Soc.*, 191 (1950).

(19) It is of interest to mention, however, that when attempts were made to treat alkali metal fluorides with ClF_3 or BrF_3 in Pyrex reactors an immediate and vigorous attack on the reactor walls took place resulting in the formation of white precipitates. X-Ray diffraction analysis revealed the precipitates to be the corresponding alkali metal hexafluorosilicates. The reaction was due, no doubt, to the increased self-ionization of the halogen fluorides brought about by the presence of the metal fluorides.

Densities of the polyfluorohalate salts were determined by means of the displacement method. Fluorochemical FC-75, a completely fluorinated cyclic ether with the empirical formula $\text{C}_8\text{F}_{16}\text{O}$,²⁰ was used to fill the pycnometer after introduction of the salt. Fortunately none of the compounds synthesized reacts with or is soluble in this material.

Results and Discussion

The results of the synthesis experiments are summarized in Tables I and II. In Table III are listed the measured densities of the polyfluorohalate salts. The reaction products are crystalline solids, powerful fluorinating agents, are violently reactive with water,

TABLE I
SOLVOLYSIS OF ALKALI METAL FLUORIDES IN CHLORINE TRIFLUORIDE AT 100°

Metal fluoride	Mole ratio ClF_3/MF	Analysis of product		Remarks
		% Cl	% F	
LiF	8	No reaction		
NaF	8	No reaction		
KF	8	14.7	46.7	White crystalline solid, 56.5% conversion of KF to KClF_4 . Theoretical for $\text{KClF}_4 \cdot 0.8\text{KF}$: Cl, 18.2; F, 46.5%
RbF	7	15.4	37.3	Pink crystalline solid, ^a 85.2% conversion of RbF to RbClF_4 . Theoretical for $\text{RbClF}_4 \cdot 0.2\text{RbF}$: Cl, 16.5; F, 36.9%
CsF	8	14.4	30.8	Pink crystalline solid, ^a 91.0% conversion of CsF to CsClF_4 . Theoretical for $\text{CsClF}_4 \cdot 0.1\text{CsF}$: Cl, 13.7; F, 30.0%

^a Pink color may be due to presence of red-colored complex fluorides Rb_2NiF_6 or Cs_2NiF_6 .

TABLE II
SOLVOLYSIS OF ALKALI METAL FLUORIDES IN BROMINE PENTAFLUORIDE AT 100°

Metal fluoride	Mole ratio BrF_5/MF	Analysis of product		Remarks
		% Br	% F	
LiF	10	No reaction		
NaF	10			In one experiment it was observed that NaF reacted with BrF_5 to form (presumably) a polyfluorohalate at 140°, but the conversion, at most, was less than 5%
KF	10	25.2	43.5	White crystalline solid, 49.4% conversion of KF to KBrF_6 . Theoretical for $\text{KBrF}_6 \cdot \text{KF}$: Br, 27.3; F, 45.4%
RbF	10	27.3	39.8	White crystalline solid, 90.0% conversion of RbF, to RbBrF_6 . Theoretical for $\text{RbBrF}_6 \cdot 0.1\text{RbF}$: Br, 27.6; F, 40.8%
CsF	10	24.4	34.8	White crystalline solid, 100% conversion of CsF to CsBrF_6 . Theoretical for CsBrF_6 : Br, 24.4; F, 34.8%

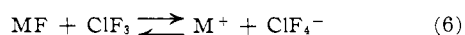
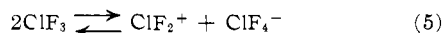
TABLE III
DENSITIES OF POLYFLUOROHALATE SALTS AT 25°

Salt	Density, g./cm. ³
$\text{CsClF}_4 \cdot 0.1\text{CsF}$	3.40
$\text{KClF}_4 \cdot 0.8\text{KF}$	2.58
CsBrF_6	3.68
$\text{RbBrF}_6 \cdot 0.1\text{RbF}$	3.59

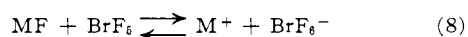
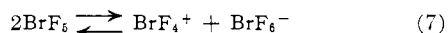
(20) FC-75 Technical Data Sheet No. 1, Minnesota Mining and Manufacturing Co., Saint Paul, Minn., April 1, 1957.

and liberate iodine from iodide solutions. They charred wood and ignited paper on contact.

It is postulated that the successful synthesis of the alkali metal tetrafluorochlorates and hexafluorobromates was brought about *via* solvolysis reactions in which the normal anion and cation concentrations of the solvent were changed by the presence of the metal fluorides, the systems being analogous to the solvolysis of metal fluorides in the ionizing solvents, BrF_3 and IF_5 . The self-ionization and solvolysis of metal fluorides in ClF_3 and BrF_5 may be expressed as



and



where $\text{M} = \text{K}, \text{Rb}, \text{or Cs}$. The relative ease of conversion of alkali metal fluorides into the polyfluorohalates was found to be the same irrespective of the halogen fluoride employed as the solvent, *i.e.*, for both ClF_3 and BrF_5 , $\text{CsF} > \text{RbF} > \text{KF}$. These observations are in accord with the general rule for stability in polyhalides as discussed by Wiebenga, *et al.*,⁷ in that the stability of the crystalline polyhalide depends upon the nature of its cation. The stability of the polyhalide is greater when the cation is larger and more symmetrical. Likewise, it has been shown²¹ that in the case of the solubility of alkali metal fluorides in BrF_3 the solubility of the fluoride increases as the size of the cation increases. Thermal decomposition studies on cesium tetrafluorochlorate and cesium hexafluorobromate revealed both these materials to be unusually stable as compared to alkali metal polyhalide compounds in general. Both $\text{CsClF}_4 \cdot 0.1\text{CsF}$ and CsBrF_6 could be heated to 300° for several hours without decomposition taking place. $\text{KClF}_4 \cdot 0.77\text{KF}$, however, started to decompose at approximately 200° .

The above observations are thus in agreement with the general conclusions of Cramer and Duncan²² that factors favoring the stability of a polyhalide are: (a) symmetry, (b) a cation of large molecular volume, (c) presence of a large electropositive atom at the center of the anion, and (d) that other atoms in the anion should be light electronegative atoms. Item c may explain why in the case of CsF and RbF higher conversions to the polyhalide were obtained with BrF_5 as the ionizing solvent than with ClF_3 . The latter halogen fluoride gave a higher conversion to the corresponding polyhalide with KF , however.

As can be seen from Tables I and II, the tetrafluorochlorates and hexafluorobromates of lithium and sodium were not obtained although presumably a small amount of NaBrF_6 may have been formed between NaF and BrF_5 at 140° . These observations are in agreement with the results of Asprey,¹⁶ who found the potassium salts more difficult to prepare than either the cesium or rubidium fluorohalates, and Kelly,¹⁷ who was unsuccessful in preparing either LiClF_4 or NaClF_4 by

(21) I. Sheft, H. H. Hyman, and J. J. Katz, *J. Am. Chem. Soc.*, **75**, 5221 (1953).

(22) H. W. Cramer and D. R. Duncan, *J. Chem. Soc.*, 2243 (1931).

treating the corresponding chlorides with elemental F_2 at elevated pressures and temperatures.

It has been observed²³ that chlorine trifluoride dissolves in both iodine pentafluoride and bromine trifluoride and is not evolved upon heating the resulting solutions to $60\text{--}70^\circ$, although chlorine trifluoride itself boils at 12° . This phenomenon is logically explained through the assumption of mutual ionization of the constituents in the above halogen fluoride solutions. The effect of such complex ionization on the solvolysis of alkali metal fluorides in mixtures of ClF_3 and BrF_5 , and ClF_3 and IF_5 is shown in Table IV. The recovery of rubidium and cesium hexafluorobromates from the mixed solvents is not surprising in view of the apparent ease of preparation of the above materials as compared to the corresponding tetrafluorochlorate salts. The preferential formation of potassium tetrafluorochlorate at 25 and 100° is again difficult to explain, and indeed appears to be analogous to the unusually low solubility of potassium perchlorate in water.

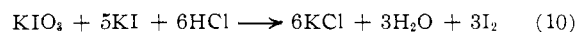
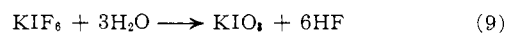
TABLE IV

SOLVOLYTIC REACTIONS EMPLOYING MIXTURES OF CHLORINE TRIFLUORIDE AND BROMINE PENTAFLUORIDE OR IODINE PENTAFLUORIDE AS SOLVENTS

Metal fluoride	Solvent, ClF_3^a	Temperature, $^\circ\text{C}$.	Product
KF	BrF_5	25	$\text{KClF}_4 \cdot \text{KF}$
KF	BrF_5	100	$\text{KClF}_4 \cdot 0.7\text{KF}$
RbF	BrF_5	25	$\text{RbBrF}_6 \cdot 0.5\text{RbF}$
CsF	BrF_5	25	$\text{CsBrF}_6 \cdot 0.1\text{CsF}$
KF	IF_5	100	KIF_6

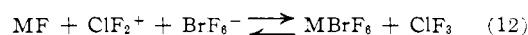
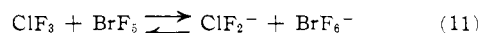
^a 1:1 molar solutions.

Identification of KIF_6 was based upon the percentage of iodine in the product and the "oxidizing power" of the material. The latter was measured as equivalents of I_2 per gram of sample, and was based upon the reactions

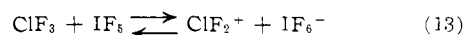


Potassium hexafluoroiodate was first prepared by Emel us and Sharpe.¹⁰

The data appearing in Table IV are interesting examples of the relative acidities of the halogen fluorides, the stronger acid coordinating a fluoride ion to form ions of the type XF_n^- . From the last three experiments listed in Table IV it would appear that BrF_5 and IF_5 are both stronger acids than is ClF_3 as indicated by the reactions

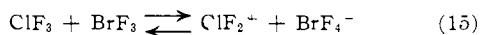


where $\text{M} = \text{Rb}$ or Cs , and



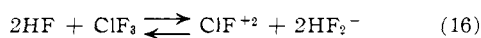
(23) R. N. Haszeldine, *ibid.*, 3037 (1950).

Indeed, studies on the isotopic exchange reaction of fluorine between ClF_3 and BrF_3 have shown²⁴ that chlorine trifluoride acts as a base in bromine trifluoride solution, the exchange reaction proceeding through the equilibrium

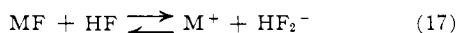


The results with potassium fluoride are again exceptional. In a mixture of ClF_3 and BrF_3 , potassium tetrafluorochlorate was obtained at both 25 and 100° whereas potassium hexafluorobromate had been expected.

During some preliminary investigations, several experiments were conducted in which chlorine trifluoride was added to solutions of LiF , NaF , KF , and CsF in anhydrous HF at room temperature. The mole fractions of the metal fluorides in HF were adjusted so as to assure complete solution of the metal fluoride. With LiF and NaF only the bifluorides were obtained, whereas for fluorides containing larger cations, *i.e.*, KF and CsF , solvated bifluorides were obtained. In no instance was any chlorine found in the above products. The above results not only are consistent with the observation that HF forms a complex with ClF_3 ^{24,25} but also substantiate the observation of Nikolaw and Malyukov²⁶ that ClF_3 behaves as a very strong base when dissolved in HF , *i.e.*



as do the alkali metal fluorides (M = alkali metal atom)



It is not surprising, therefore, that no chlorine-containing polyfluorohalate salt could be obtained under these conditions. The extent of solution of the alkali metal fluorides as deduced from this work is in agreement with the relative solubilities of the fluorides in HF ,²⁷ *i.e.*, $\text{CsF} > \text{RbF} > \text{KF} > \text{NaF} > \text{LiF}$.

Finally, it is of interest to mention some experiments performed in an attempt to synthesize some ammonium polyhalides. Dry crystalline NH_4F was placed in Pyrex tubes and the halogen fluoride allowed to

distil into the tube by condensation of the latter at liquid nitrogen temperatures. The -196° bath was then removed and the reaction mixture allowed to warm slowly in air at room temperature. Experiments were conducted with ammonium fluoride and with ClF_3 , BrF_3 , BrF_5 , and IF_5 . The results are summarized in Table V.

TABLE V

REACTION BETWEEN AMMONIUM FLUORIDE AND SOME HALOGEN FLUORIDES

Halogen fluoride	Results
ClF_3	Mixture exploded at $T < 0^\circ$, NH_4ClF_4 presumably produced
BrF_3	White solid product, NH_4BrF_4 presumably produced
BrF_5	White solid which decomposed at $T > 0^\circ$, NH_4BrF_6 presumably produced
IF_5	White solid product, NH_4IF_6 presumably produced

None of the above NH_4F -halogen fluoride complexes was further characterized. The observation that reacting mixtures of liquid ClF_3 and crystalline NH_4F nearly always explode on warming to temperatures slightly below 0° has been made by Gardner, Knipe, and Mackley²⁸ in their studies on the preparation of chlorodifluoramine. The order of stability of the ammonium polyfluorohalates probably is NH_4BrF_4 (NH_4IF_6) $>$ NH_4BrF_6 $>$ NH_4ClF_4 .

Sheft, Martin, and Katz²⁹ have discussed the use of bromine trifluoride addition compounds, *i.e.*, KBrF_4 and BrF_2SbF_6 , for the high temperature fluorination of inorganic substances not readily attacked by liquid BrF_3 . Because of their low dissociation pressures the above addition compounds can be employed in reactions at up to 500° in closed systems without developing high pressures. The use of bromine trifluoride under similar conditions would involve considerably more complex apparatus and more difficult experimental operations. By analogy it is suggested that because of their stability up to $\sim 300^\circ$, both rubidium and cesium hexafluorobromates, and the corresponding tetrafluorochlorates, may be employed as convenient laboratory sources of fluorine in high temperature reactions where the use of liquid bromine pentafluoride or chlorine trifluoride would be inconvenient.

(24) M. T. Rogers and J. J. Katz, *J. Am. Chem. Soc.*, **74**, 1375 (1952).

(25) J. P. Pemsler and D. F. Smith, *J. Chem. Phys.*, **22**, 1834 (1954).

(26) N. S. Nikolaw and I. M. Malyukov, *Zh. Neorgan. Khim.*, **2**, 1587 (1957).

(27) A. W. Jache and G. H. Cady, *J. Phys. Chem.*, **56**, 1106 (1952).

(28) D. M. Gardner, W. W. Knipe, and C. J. Mackley, *Inorg. Chem.*, **2**, 413 (1963).

(29) I. Sheft, A. F. Martin, and J. J. Katz, *J. Am. Chem. Soc.*, **78**, 1557 (1956).