consistent with the presence of $SiF_4 \cdot 2NH_3$[28] and NH_4HF_2.[28] Sulfur nitride was further identified by direct comparison of the X-ray film to a film prepared from a sample of pure S_4N_4.[29]

Reaction of SF_4 with NH_3.—Sulfur tetrafluoride (0.5815 g., 5.379 mmoles) and NH_3 (0.1467 g., 1.629 mmoles) were distilled into a reaction vessel, and upon allowing the vessel to warm from liquid nitrogen temperature, reaction was observed to occur while the reactants were still very cold. The infrared spectrum of the gas which was removed at room temperature showed the presence of SF_4[30] ($\sim$0.176 g.) and SOF_2.[20] Benzene was distilled into the multicolored solid remaining in the reactor. Evaporation of the filtered benzene solution yielded an orange solid, which was shown by infrared[26,27] and X-ray powder pattern examination to be S_4N_4. When the experiment was repeated using a large excess of NH_3, similar results were obtained, except that the volatile material at the conclusion of the reaction consisted only of unreacted NH_3.

It has been reported that SF_4 and NH_3 interact to give NSF[31]; however, only trace amounts were observed spectroscopically among the gaseous products of the reaction, and none of the pure material was isolated.[32] A more extensive examination of this reaction indicates that up to 70% yields of S_4N_4 may be obtained.[33]

Reaction of S_2F_{10} with $(CH_3)_2NH$.—Disulfur decafluoride (0.1320 g., 0.5195 mmole) and $(CH_3)_2NH$ (0.0235 g., 0.521 mmole) were heated in a 30-ml. borosilicate glass break-seal tube for 19 hr. at 160°. A nonvolatile yellow solid was deposited on the walls of the reaction vessel. Gas chromatographic separation of the volatile material showed the presence of S_2F_{10}, SiF_4, and SO_2, which were identified by their retention times and by their infrared spectra. All the $(CH_3)_2NH$ was consumed.

Reaction of S_2F_{10} with C_2H_4.—Disulfur decafluoride (0.2607 g., 1.026 mmoles) and C_2H_4 (2.9954 g., 106.98 mmoles) were vaporized in a 2-l. bulb and irradiated with ultraviolet light for a total period of 10 hr. The composition of the gaseous products was examined from time to time. A nonvolatile tarry material formed on the walls of the bulb. The volatile products which condensed in a trap held at −78° had an infrared spectrum similar to that found for hydrocarbons containing some SF_5 groups.[34] The molecular weight of the material ranged from 100 to 120. The infrared and mass spectra suggested that the material consisted primarily of short-chain hydrocarbons containing some SF_5 end groups.

Reaction of S_2F_{10} with NO.—A number of experiments were carried out in which S_2F_{10}, mixed with a large excess of NO, was either heated to temperatures up to 200° or exposed to ultraviolet light. Although reaction occurred and unidentified absorption bands were observed in the infrared spectra of the volatile products, no pure compound apart from SiF_4 and SOF_2 could be obtained. Extensive decomposition of many of the products appeared to take place when gas chromatographic separations were attempted.

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Difluorochlorates(I) of Cesium, Rubidium, and Potassium

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Received June 10, 1965

The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by the reaction of the corresponding fluorides with chlorine monofluoride or $NO^+ClF_2^-$. These white solids are the first known difluorochlorate(I) salts stable at 25°. They decompose exothermally at temperatures higher than 230°. Their composition and structure were established by elemental analysis, infrared, and X-ray studies. The salts are ionic and contain linear ClF_2^- anions. Attempts to prepare $LiClF_2$ and $Ca(ClF_2)_2$ failed, while $NaClF_2$, $Ba(ClF_2)_2$, and $Sr(ClF_2)_2$ may have formed to a very small extent.

Introduction

The existence of ionic complexes containing species such as ClF_2^+,[1-5] and ClF_4^-,[6-9] derived from chlorine trifluoride, is well-established. However, complexes containing such species as Cl^+ and ClF_2^-, formed from chlorine monofluoride, have not been investigated until recently. Schmeisser[10] isolated $Cl^+AsF_6^-$ and $Cl^+SbF_6^-$, prepared by the interaction of ClF with the corresponding Lewis acid, AsF_5 or SbF_5. We[11] have reported the existence of the ClF_2^- anion in the form of its nitrosyl salt, $NO^+ClF_2^-$. Nitrosyl difluorochlorate(I) was shown to be ionic in solution and in the solid state. The ClF_2^- anion was assigned a linear structure based on infrared investigation. Since NO^+-ClF_2^- is stable only at low temperature we have investigated the replacement of the NO^+ cation by an alkali or alkaline earth metal cation with the hope of

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obtaining more stable complex salts. This paper describes the results obtained from (1) the metathetical reaction shown by the equation

$$NO^+ClF_2^- + M^+F^- \longrightarrow M^+ClF_2^- + NOF \qquad (1)$$

and (2) the direct reaction shown by the equation

$$ClF + M^+F^- \longrightarrow M^+ClF_2^- \qquad (2)$$

where M^+ is an alkali metal cation.

Experimental

Materials and Apparatus.—The materials used in this work were manipulated in a standard Pyrex glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Reactions at over atmospheric pressure and elevated temperature were carried out in Monel containers equipped with a Monel pressure gauge and a Monel valve (Whitey, M6TS6). This valve could be connected to the glass vacuum line by Swagelock fittings and Kovar metal to graded glass seals. Chlorine monofluoride, nitrosyl fluoride (both from Ozark-Mahoning Co.), and hexafluoroacetone (Allied Chemical) were purified by several low-temperature vacuum distillations. The purity of the volatile starting materials was determined by measurement of their vapor pressures, molecular weights, and infrared spectra. Little etching of the vacuum line could be observed. The alkali and alkaline earth metal fluorides (CsF, 99.9%, and RbF, 99%, both from K & K Laboratories, Inc.) were used without further purification. Hygroscopic nonvolatile compounds were handled in the dry nitrogen atmosphere of a glove box.

Infrared Spectra.—Infrared spectra were recorded on a Beckman Model IR-9 grating spectrophotometer in the range 4000–420 $cm.^{-1}$. Screw cap metal cells equipped with neoprene O rings and AgCl windows were used for solid samples. The solids were either mulled with dry hexafluorobenzene or dry Nujol, or they were used directly as dry powders.

X-Ray Powder Data.—Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper $K\alpha$ radiation and a nickel filter. Samples were sealed in Lindeman glass tubes (~0.5 mm. o.d.).

Density Measurements.—Density measurements were carried out by the displacement method[8] using a perfluorinated cyclic ether to fill the pycnometer.

Differential Thermal Analysis.—A Perkin-Elmer differential scanning calorimeter Model DSC-1 was used to obtain the DTA of the new compounds. These were sealed in aluminum pans. A heating rate of 10°/min. and an argon purge of 30 ml./min. were used.

Elemental Analysis.—Products were analyzed for fluorine, chlorine, and alkali or alkaline earth metal. Fluorine was determined by direct alkaline hydrolysis or by Parr bomb fusion of the sample, each followed by titration with $ThNO_3$ using alizarine red as indicator. Chlorine was reduced to Cl^- either by Parr bomb fusion with Na_2O_2 or by direct alkaline hydrolysis of the sample followed by reduction with $TiSO_4$. Finally, the resultant Cl^- was potentiometrically titrated with $AgNO_3$. Both methods compared favorably, yielding results with negligible deviations. The alkali metal content was determined by direct aqueous hydrolysis of the sample followed by flame spectroscopy. Gravimetric analysis yielded the allaline earth metal content of a sample.

Preparation of the Alkali Metal Difluorochlorates(I).—Chlorine monofluoride and an alkali metal fluoride were mixed under different conditions at temperatures from 25 to 230° under autogenous pressures. In some reactions agitation and/or NOF (as a catalyst) were employed. Also, CsF was sometimes pretreated with CF_3COCF_3.

In a typical experiment, CsF (0.204 mole) was introduced into a 300-ml. Monel cylinder having NPT openings (0.5-in.) on both ends to facilitate removal of solid products. One end of the cylinder was capped with a Swagelock fitting and the other end was connected by Monel high-pressure tubing to a Monel pressure gauge (0–2000 p.s.i.) and a Monel control valve (Whitey, M6TS6). The cylinder was connected to the vacuum system and CF_3COCF_3 (0.350 mole) was condensed into it. The mixture was vigorously shaken for 12 hr. at 25° under autogenous pressure, after which all volatile material was removed by vacuum pumping on the cylinder (warmed to 150°) for 2 hr. Now, excess ClF (0.700 mole) was condensed at −196° over the CsF. The mixture was heated for 48 hr. at 175° in an electric tube furnace equipped with an automatic temperature control. An internal pressure of 800 p.s.i. developed. After cooling to 25°, the volatile material was similarly removed (except in this case the cylinder was warmed only to 100°). The nonvolatile, white, crystalline product was removed from the cylinder and the increase in weight of the starting material (CsF) was determined (Table I).

Results and Discussion

Synthesis.—The difluorochlorates(I) of cesium, rubidium, and potassium were successfully prepared by (1) metathetical reaction or (2) direct interaction of ClF with the corresponding fluoride. Table I lists the results of several experiments. A 100% conversion of starting material to the difluorochlorate(I) was never achieved. After reaction at elevated temperature and pressure, the product usually was a fused solid and was difficult to remove from the reactor. The temperature of reaction could not be increased much higher than 230° due to the limited thermal stability of the products and interaction of the compounds with the Monel reactor, resulting in the formation of some dark red alkali metal hexafluoronickelate(IV). This impurity was easily identified by its known X-ray diffraction pattern[12–15] and by analysis of the product for nickel.

No difficulties were expected for the metathetical reaction. The low thermal stability[11] of $NO^+ClF_2^-$ assured the complete removal of the complex from the product. Since NOF is regenerated during the reaction (eq. 1), only catalytic amounts are required. Generally, the use of NOF resulted in higher conversions of the starting material; however, analyses indicated too low a chlorine content compared with the alkali metal and fluorine content and the per cent conversion found from the weight increase of starting material. Therefore, the reaction of CsF with NOF in the absence of ClF was investigated. A weight increase was obtained; however, the analytical results were inconclusive. The X-ray pattern showed only alkali metal bifluoride and starting material. No $CsNO_3$ was found in the product. Impurities in or decomposition of NOF to nitrogen oxides could have produced this nitrate. Therefore, no conclusions can presently be made concerning the type of interaction observed. In several experiments the CsF was pretreated with excess CF_3COCF_3. However, no significant activation effect was observed. On this basis, the direct reaction of ClF with the corresponding alkali metal fluoride seems to be the preferred method for preparing the difluorochlorate(I) salts.

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TABLE I

SYNTHESIS OF $CsClF_2$, $RbClF_2$, AND $KClF_2$[a]

Reactants, moles			Reaction temp., °C.	Reaction time, hr.	Reaction press., p.s.i.	Conversion to ClF_2^- salt, %[b]	Calcd., %[c]			Found, %		
Fluoride	ClF	NOF					Metal	Cl	F	Metal	Cl	F
CsF							Cs					
0.200[d]	0.700	...	175	48	800	55	74.8	9.4	15.8	73.6	9.1	16.0
0.035	0.210	0.012	175	48	1100	80	69.0	13.7	17.2	69.5	8.7	17.4
RbF							Rb					
0.047[e]	0.200	0.047	25	24	1100	49	68.1	10.9	21.0	68.1	10.8	20.7
0.036	0.220	...	230	60	1300	73	61.4	16.3	22.4	60.6	15.0	22.3
0.028[f]	0.240	0.015	230	60	1580	87	57.4	19.4	23.2	58.2	8.2	22.4
KF							K					
0.069	0.390	0.031	150	14	2200	27	58.5	8.5	33.0	58.2	8.5	33.7

[a] All reactions were done in 30-ml. Monel cylinders, except the first row reaction (done in a 300-ml. Monel cylinder). [b] Based on weight increase of starting material. [c] Calculated from the weight increase of the starting material assuming the product to be a mixture of metal fluorides and metal difluorochlorates(I) only. [d] CsF was pretreated with excess CF_3COCF_3 at 25°. [e] This mixture was vigorously agitated. [f] A small amount of Rb_2NiF_6 impurity caused the product to have a slight pink color.

The difluorochlorates(I) of lithium and calcium could not be prepared at 25 and 150° even using high autogenous ClF pressures (~2000 p.s.i.). No weight increase of the starting material was observed and the X-ray diffraction pattern showed no new products. Similarly, the reaction of NaF with ClF at 25° yielded negative results. Increasing the reaction temperature to 150° and using NOF as a catalyst resulted in a slight weight increase of the starting material. However, analysis indicated no chlorine in the product. From similar observations, SrF_2 and BaF_2 reacted with a mixture of ClF and NOF at 25 and 150° to an equally small extent. Again, no chlorine was found in the product. The greater tendency of CsF, RbF, and KF to form stable complex salts compared with the other alkali and alkaline earth metal fluorides was also observed in the case of tetrafluorochlorates(III)[6-8] and salts containing the CF_3O^- anion.[16]

Properties of Cesium, Rubidium, and Potassium Difluorochlorates(I).[17]—The compounds are white solids having good thermal stability. Differential thermal analysis indicated exothermic decompositions at 262, 248, and 237°, respectively. This stability order, $CsClF_2 > RbClF_2 > KClF_2$, follows the same sequence found for the ClF_4^- [8] and CF_3O^- [16] alkali salts. The decrease in cation size and the increase in polarizing power from Cs^+ to Li^+ [18] (in group Ia of the periodic table of elements) probably accounts for this order of stability. By comparison, the difluorochlorates(I) have lower oxidizing power and are somewhat less stable than the corresponding tetrafluorochlorates(III).[6-8] This is in agreement with the reported stabilities of $NO^+ClF_2^-$ and $NO^+ClF_4^-$.[11]

Structure of Cesium, Rubidium, and Potassium Difluorochlorates(I).—The infrared spectrum of $CsClF_2$ in the range 4000 to 420 cm.$^{-1}$ showed its strongest absorption at 636 cm.$^{-1}$, in agreement with the 635 cm.$^{-1}$ value found for the asymmetric stretching of the ClF_2^- anion in $NO^+ClF_2^-$.[11] Based on the suggested linearity of the ClF_2^- anion in $NO^+ClF_2^-$, a similar structure is assumed for the ClF_2^- anion in the alkali metal difluorochlorates(I).

The X-ray diffraction patterns of the products were of low intensity and resembled strongly those reported for the α modifications of the corresponding alkali metal bifluorides.[19,20] Since the found unit cell dimensions were nearly identical with those reported for the corresponding bifluorides, density measurements on the products were carried out. The large deviations between the found and calculated densities (for mixtures of metal fluoride and metal difluorochlorate(I)) indicated that the observed patterns are probably due to small amounts of the corresponding bifluoride as impurity, the difluorochlorate(I) salts being either amorphous or exhibiting only very low-intensity X-ray patterns.

The linear configuration of the ClF_2^- anion, supported by infrared analysis, may be explained by either of the following models: (i) a hybridization model,[21] assuming mainly sp^3d hybridization of the orbitals of the chlorine atom resulting in a trigonal bipyramid with the two fluorine atoms at the apexes, the chlorine atom at the center, and the three free electron pairs at the remaining corners or, perhaps more probably, (ii) a semi-empirical molecular orbital model[21] involving mainly $p\sigma$ atomic orbitals for the formation of semi-ionic bonds.

Acknowledgment.—We thank Dr. A. E. Pavlath for helpful discussions. This work was supported by the Advanced Research Projects Agency and the Office of Naval Research.

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