

*Chloryl Fluoride and its Derivatives.*

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A new preparation of chloryl fluoride from alkali chlorates and bromine trifluoride is reported. The fluoride forms solid 1 : 1-compounds with boric and antimonie fluorides. These are regarded as chloronium ( $\text{ClO}_2^+$ ) salts. The preparation of other oxy-halogen cations is discussed.

THE presence of oxy-halogen cations has often been postulated in the halogen oxides and as intermediates in reaction mechanisms. The chloryl ion  $\text{ClO}_2^+$ , for example, might exist in the diamagnetic dimer of chlorine trioxide in the same way as the nitrosyl ion in nitrogen tetroxide. There should be interesting analogies between the chemistry of nitryl and chloryl ions and consequently a method of preparation of chloryl salts has been sought. A method, using bromine trifluoride, similar to that used in the preparation of nitrosyl and nitryl complex fluorides, proved unsuccessful, and it has been suggested that the chloryl ion can be displaced by  $\text{BrF}_2^+$  in this solvent (Woolf, *Chem. and Ind.*, 1954, 346). The preparation of a red solid,  $\text{Cl}_2\text{O}_5 \cdot 3\text{SO}_3$  (Lehmann and Krueger, *Z. anorg. Chem.*, 1953, 274, 141) provided a definite indication that the chloryl ion was capable of existence in salts. The compound may be of the same type as  $\text{N}_2\text{O}_5 \cdot 3\text{SO}_3$ , the structure of which has been recently established as  $(\text{NO}_2^+)_2\text{S}_3\text{O}_{10}^{2-}$  (Eriks and MacGillavry, *Acta Cryst.*, 1954, 7, 430). A direct reaction of chloryl fluorides with acceptor fluorides has therefore been attempted and has led to chloryl complex fluorides. During the course of this investigation a preliminary report of the preparation of the same complexes has appeared (Schmeisser and Ehenhöch, *Angew. Chem.*, 1954, 66, 230). These authors have improved the original preparation of chloryl fluoride (Schmitz and Schumacher, *Z. anorg. Chem.*, 1942, 249, 238) by the use of trichlorofluoromethane as a diluent. The complex fluorides,  $\text{ClO}_2\text{F} \cdot \text{BF}_3$ ,  $\text{ClO}_2\text{F} \cdot \text{AsF}_5$ , and  $\text{ClO}_2\text{F} \cdot \text{PF}_5$  were prepared by passage of the gaseous fluorides into chloryl fluoride solutions with the above solvent, and  $\text{ClO}_2\text{F} \cdot \text{SbF}_5$ ,  $\text{ClO}_2\text{F} \cdot \text{SO}_3$ , and  $2\text{ClO}_2\text{F} \cdot \text{SiF}_4$  by direct reaction. It seems that chloryl fluoride and complexes can only be prepared pure in quartz or metal apparatus. The products made in borosilicate glass apparatus, however, were sufficiently pure to enable us to establish their compositions.

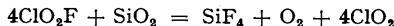
In an earlier investigation of the reaction of bromine trifluoride with halogenates (Emeléus and Woolf, *J.*, 1950, 164) it was found that the alkali salts were converted into tetrafluorobromites, but whereas in the reactions with bromates and iodates the oxygen was quantitatively displaced, with chlorates only one third of the oxygen was evolved as such. It was suggested that the rest of the oxygen was expelled as either chlorine dioxide or chlorine dioxide (chloryl fluoride).

The gas formed in the reaction with potassium chlorate has now been examined. It was too reactive to be handled in a normal vacuum-system since it attacked both tap greases and mercury. It could be studied in simple borosilicate glass apparatus provided that the gas was not kept in contact with glass for too long at room temperatures. The gas was identified chemically after hydrolysis with excess of alkali. The solution contained practically all its chlorine in the form of chlorate. Perchlorate was absent, but there were traces of halide ions and of positive chloride ions. The latter was below 5% of the total

chloride as judged by the liberation of iodine from hydriodic acid. The total chlorine, determined after reduction with sulphurous acid, was equivalent to that in the potassium chlorate used to liberate the gas, and the chlorine : fluorine ratio was near to unity. A molecular weight of 88 was found from the weight ratio of gas to potassium chlorate, and approximately two equivalents of alkali were required for each molecule of gas. Thus the formation and hydrolysis are represented by :



The liquefied gas was pale red at  $-95^\circ$  and it seems likely that the impurities were chlorine dioxide, which itself forms a red liquid and solid, silicon tetrafluoride, and possibly some bromine. The colour was intensified after further exposure to glass at room temperatures. Chlorine dioxide could be produced from the reaction :



The preparation of chloryl complex fluorides was attempted by methods analogous to those used for nitronium and nitrosonium complexes. It has been shown that mixtures of silver nitrate and antimonite (1 : 1) were converted by bromine trifluoride into mixtures of nitronium and silver hexafluoroantimonates (Woolf and Emel us, *J.*, 1950, 1050). The product from a silver chlorate-antimonite mixture was free from chlorine, and appeared from analysis to be a mixture of difluorobromosonium and silver hexafluoroantimonates,  $\text{BrF}_2\text{SbF}_6$ , and  $\text{AgSbF}_6$ . This showed that the chloryl ion was unstable in bromine trifluoride. However, by the direct reaction of excess of chloryl fluoride with antimonite a white solid of composition  $\text{ClO}_2\text{F}, \text{SbF}_6$  was formed which was involatile *in vacuo* at room temperatures. A solid was also formed on reaction with boric fluoride, but this was volatile *in vacuo*. It could be isolated almost quantitatively by mixing the components at  $-78^\circ$  and distilling off the excess of boric fluoride into a trap at  $-190^\circ$ . In view of the tendency of antimonite and boric fluorides to form complex anions with fluorides it seems feasible that these compounds are chloronium salts  $\text{ClO}_2^+\text{SbF}_6^-$  and  $\text{ClO}_2^+\text{BF}_4^-$ .

Chloryl fluoride also reacts with sulphur trioxide to form a 1 : 1 compound isolated as a red liquid at room temperature. This froze to a red solid and changed to a pale yellow solid as the temperature was reduced to that of liquid air. This also may be  $\text{ClO}_2^+\text{SO}_3\text{F}^-$  in the solid form. The possibility of formation of oxychlorine cations in fluorosulphonic acid solution will be discussed in a forthcoming publication.

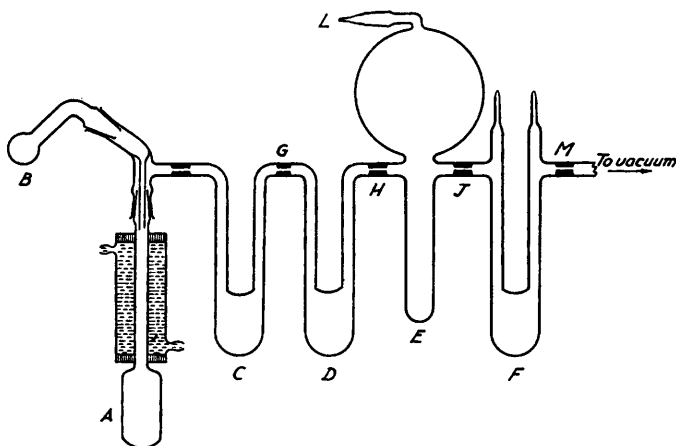
The stability of the chloryl ion is less than that of the alkali-metal and oxy-nitrogen cations when compared by displacement reactions in bromine trifluoride (Woolf, *J.*, 1950, 1053). The order of stability  $\text{K}^+ > \text{NO}^+ > \text{BrF}_2^+ > \text{ClO}_2^+$  is suggested by the fact that the cation of the fluoroantimonate is displaced by the cation of the tetrafluorobromite next highest in the series (*e.g.*,  $\text{NOSbF}_6 + \text{KBrF}_4 \longrightarrow \text{KSbF}_6$ ;  $\text{ClO}_2\text{SbF}_6 + \text{BrF}_2\text{BrF}_4 \longrightarrow \text{BrF}_2\text{SbF}_6$ ). Such data as are available confirm that the stability of  $\text{ClO}_2^+$  is lower than that of  $\text{NO}^+$ , when the energetics of complex formation of their salts, with the same cation, are compared in the manner described for  $\text{CN}^+$  and  $\text{NO}^+$  (Woolf, *J.*, 1954, 253). The terms considered are the dissociation energy of chloryl fluoride, the ionization potential of  $\text{ClO}_2$ , and the lattice energy of the salt. The last term is especially significant since the ionic radius expected for  $\text{ClO}_2^+$  is  $0.3 \text{ \AA}$  greater than for  $\text{NO}^+$ . (The  $\text{ClO}_2^+$  ion is isoelectronic with sulphur dioxide and hence the S-O bond length of  $1.43 \text{ \AA}$  in the latter should be close to the ionic radius of the former.)

There are no other authenticated examples of oxyhalogen cations. It is therefore of interest to indicate possible preparations of new oxyhalogen cations. The chlorosonium ion ( $\text{ClO}^+$ ) should be at least as stable as the  $\text{ClO}_2^+$  ion, and the formation of complex fluorides by reaction of chlorosyl fluoride with higher fluorides seems feasible. Ruff and Krug (*Z. anorg. Chem.*, 1930, **190**, 270) may have prepared chlorosyl fluoride by the hydrolysis of chlorine trifluoride. Another possible preparation is by the reaction of bromine trifluoride with anhydrous hypochlorites. The thermal decomposition of ether complexes is unlikely to succeed on account of the reactivity of chlorine trifluoride.

Perfluoro-ethers would be unlikely to co-ordinate with chlorine trifluoride. The possibility of producing a fluorosonium ion ( $\text{FO}^+$ ) seems remote. It would require a positive trivalent fluorine atom. However, univalent fluorine exists in hypofluorites (Cady, *Chem. Eng. News*, 1950, **28**, 1478) and the F-O bond strength is not high enough to preclude any possibility of reaction between fluorine monoxide and higher fluorides.

#### EXPERIMENTAL

*Preparation of Chloryl Fluoride.*—Potassium chlorate (1–2 g.) was placed in the long-necked silica flask *A* and bromine trifluoride (4–5 ml.) frozen in *B* (see Figure). A pressure of 40–50 cm. of dry nitrogen was maintained in the apparatus. The traps and bulb (250 ml.) had been previously thoroughly dried *in vacuo*. With *A* cooled in liquid air the contents of *B* were added in one portion. *A* was warmed, and after the initial reaction ceased the contents were heated under reflux for a few min. The vapours were collected in *C*. *A* and *C* were then held at  $-78^\circ$  and *D* at  $-190^\circ$  and the apparatus evacuated. Seal *G* was closed after distillation and the contents of *D* were distilled from  $-78^\circ$  to *E* (at  $-190^\circ$ ). The bulb was finally sealed at *H* and *J* and weighed. A tap funnel containing excess of 0.1N-alkali was attached by rubber tubing at *L*, and with the tube of *E* cooled the glass was snapped inside the rubber and the bulb



partly filled with alkali. In a typical run 1.26 g. of potassium chlorate gave 0.906 g. of gas. Hence the equivalent weight was 87.8 (Calc. for  $\text{ClO}_2\text{F}$ : 86.5). Total chloride found was 370 mg. (Calc. for  $\text{ClO}_2\text{F}$ : 366 mg.). Fluoride found was 207 mg. (Calc. for  $\text{ClO}_2\text{F}$ : 196 mg.). Ratio Cl : F 0.96. Ratio of equiv. of alkali required per calc. equiv. for  $\text{ClO}_2\text{F}$ , 2.05.

*Reaction with Antimonic Fluoride.*—An ampoule of the pentafluoride (1 g.) and a magnetic hammer were enclosed in a tube attached to *F*. After preparation of an excess of chloryl fluoride (from 1.5 g. of  $\text{KClO}_3$ ) and distillation to *E* as before, the pentafluoride was distilled into *F*, and the ampoule tube and contents were sealed and removed. The chloryl fluoride was condensed into *F*. On allowing it to warm an exothermic reaction occurred with the separation of a white solid. (A white solid also formed when excess of the pentafluoride was used.) After a few min. at room temperature the excess of gas was pumped off through *L*, and the solid product sealed in trap *F*. This was weighed and the contents were subsequently hydrolysed with water. Aliquot portions of the hydrolysate were analysed for chloride (precipitated as silver chloride after reduction with sulphurous acid), fluoride (as calcium fluoride after decomposition with sodium carbonate), and antimony (iodometrically after precipitation as sulphide and dissolution in hydrochloric acid) [Found: equiv. (relative to  $\text{SbF}_5$ ), 298; Cl, 10.7; Sb, 40.7; F, 37.5.  $\text{ClO}_2\text{SbF}_6$  requires equiv., 303; Cl, 11.7; Sb, 40.2; F, 37.7%].

*Reaction with Tantalum Pentafluoride.*—The product contained only 0.48 mole of chloryl fluoride per mole of pentafluoride. The reaction is therefore slow at room temperature.

*Reaction with Boric Fluoride.*—A 500-ml. bulb was used. The chloryl fluoride from 0.8 g. of  $\text{KClO}_3$  was collected finally in *F*. Boric fluoride (400 ml., approx.) was condensed into *F* and the apparatus sealed at *H* and *M*. The contents were allowed to warm and then kept at  $-78^\circ$ . The excess of gas was condensed into *E* (at  $-190^\circ$ ), and trap *F* removed by sealing at *J*. A pale

yellow solid remained at room temperature. This was hydrolysed with alkali and the presence of the tetrafluoroborate ion shown by precipitation with nitron (chlorate ions were removed with sulphurous acid). In one experiment 0.80 g. of  $\text{KClO}_3$  was converted into 0.94 g. of *product* equivalent to a 93% yield of  $\text{ClO}_2\text{BF}_4$ . The ratio F : Cl was found for two specimens (Found : F/Cl, 4.08, 3.98.  $\text{ClO}_2\text{BF}_4$  requires F/Cl, 4.00). Reaction with phosphoric fluoride was performed in a similar manner and the product had a F/Cl ratio of 5.82.

*Reaction with Sulphur Trioxide.*—This was carried out as was the antimonious fluoride reaction, with sulphur trioxide in a sealed ampoule. The reaction was violent and some product sprayed into *E*. The excess of gas was distilled into *E* with *F* at room temperature. The equivalent weight of *product* in trap *F* (calculated from the weight of sulphur trioxide) was 154 (Found : Cl/S/F, 1.04/0.985/1.00.  $\text{SO}_3\text{ClO}_2\text{F}$  requires equiv., 166.5; S/Cl/F, 1.00/1.00/1.00). The residue was hydrolysed violently in water.

*Reactions with Bromine Trifluoride.*—Silver chlorate and antimonious oxide (1 : 1) were caused to react with the trifluoride, and the excess of solvent was removed *in vacuo*. The product was free from chlorine [Found : equiv., 701; Ag, 15.3; Br, 11.9. Calc. for  $(\text{AgSbF}_6 + \text{SbBrF}_6)$  : equiv., 698; Ag, 15.5; Br, 11.5%]. Similarly, all chlorine was eliminated from  $\text{ClO}_2\text{SbF}_6$ . The product was  $\text{BrF}_2\text{SbF}_6$  (Found : Br, 22.9. Calc. : Br, 22.6%).

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