[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON AND THE UNIVERSITY OF MASSACHUSETTS]

Halogen Fluorosulfonates $BrSO_3F$, $Br(SO_3F)_3$ and $I(SO_3F)_3$

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Bromine(I) fluorosulfonate, bromine(III) fluorosulfonate and iodine(III) fluorosulfonate have been prepared by treating peroxydisulfuryl difluoride with the appropriate halogen. These compounds have been characterized. Chlorine does not react with peroxydisulfuryl difluoride. Attempts to prepare lower fluorosulfonates of iodine have given inconsistent results.

Introduction

The existence of the stable compound fluorine fluorosulfonate, first prepared by Dudley and Cady,[2] and its preparation from peroxydisulfuryl difluoride and fluorine[3] suggested that other halogen fluorosulfonates might be stable and preparable via the same route. The known formal positive character of bromine[4-6] and iodine[7,8] in salt-like compounds supported this hypothesis. It was the purpose of this research, therefore, to study the reactions of peroxydisulfuryl difluoride with chlorine, bromine and iodine and to characterize the reaction products.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared by Dudley and Cady's method.[2] By increasing the proportion of sulfur trioxide to fluorine the amount of fluorine fluorosulfonate produced was kept at a minimum and it finally was separated by distillation at Dry Ice temperature. Other materials were of ordinary reagent quality.

General Methods.—Where possible, quantitative synthesis was used to prepare the compounds under vacuum. When analyses were necessary halogens were determined by the Volhard method or iodometrically, and sulfur gravimetrically as barium sulfate. Densities were determined with single-capillary pycnometers, straight graduated tubes or with Weld specific gravity bottles. Vapor pressures were determined using the apparatus described by Cady and Kellogg.[9]

Bromine(III) Fluorosulfonate.—When an excess of peroxydisulfuryl difluoride was distilled onto 5.135 mmoles of Br_2 and the mixture allowed to warm to room temperature, reaction occurred according to the equation $Br_2 + 3S_2O_6F_2 \rightarrow 2Br(SO_3F)_3$. After distilling off the excess peroxide, 3.8441 g. of product was left corresponding to 10.20 mmoles of $Br(SO_3F)_3$ (calcd.: 10.27 mmoles). By reaction with sodium bisulfite solution the bromine was converted to bromide and determined by the Volhard method. Calcd.: 21.2. Found: 21.0, 21.5.

Properties of Bromine(III) Fluorosulfonate.—Bromine (III) fluorosulfonate is an orange crystalline solid which melts at 59.0 ± 0.2° under vacuum. Attempts to determine its optical properties and its density by immersion methods failed due to the extreme hygroscopic nature of the compound and the lack of an inert immersion liquid. Even Kel-F oil is attacked by the compound.

Bromine(III) fluorosulfonate reacted violently and exothermally with water.

$$4Br(SO_3F)_3 + 6H_2O \longrightarrow 2Br_2 + 3O_2 + 12HSO_3F$$

The bromine produced was determined iodometrically, the oxygen by direct weighing and molecular weight (gas density). Moles calcd. per mole of $Br(SO_3F)_3$: Br_2, 0.50; O_2, 0.75. Found: Br_2, 0.49; O_2, 0.80 (mol. wt. 32.2).

Bromine(III) fluorosulfonate reacted readily with dry carbon tetrachloride to produce bromine. The other products were not identified.

When 3.27 mmoles of bromine were distilled onto an excess of bromine(III) fluorosulfonate a homogeneous red liquid formed. By vacuum distillation a dark reddish black liquid distillate was collected and later identified as bromine (I) fluorosulfonate; the residue was unchanged bromine(III) fluorosulfonate; 3.33 mmoles of $Br(SO_3F)_3$ had been consumed. The reaction must therefore have followed the equation

$$Br(SO_3F)_3 + Br_2 \longrightarrow 3BrSO_3F$$

Bromine(I) Fluorosulfonate.—The action of excess bromine on peroxydisulfuryl difluoride at room temperature produced a reddish black liquid, much less volatile than either of the two reactants from which it was readily separated. This liquid was identical with that formed by treating bromine with bromine(III) fluorosulfonate. Samples were caused to react with sodium bisulfite solution and bromide was determined by the Volhard method. Calcd. for $BrSO_3F$: Br, 44.7. Found: Br, 45.2. Further samples were allowed to react with potassium iodide solution and the oxidizing equivalence found to be 0.968 equivalent per mole. These data are consistent with the formula $BrSO_3F$.

Properties of Bromine(I) Fluorosulfonate.—Bromine(I) fluorosulfonate is a red-black liquid of density 2.60 g./ml. at 25°. Its melting point is unknown since all attempts to crystallize it result only in a glass. The compound boils at 120.5° (760 mm.) and the temperature dependence of its vapor pressure is shown in Table I. From the Clausius–Clapeyron equation the molar heat of vaporization is 8.67 kcal. The Trouton constant is 22.05. The plot of log P *vs.* $1/T$ for this compound is curved at the lower temperatures which may indicate association in the liquid.

TABLE I

VAPOR PRESSURE—$BrSO_3F$

T, °K.	P, mm.	T, °K.	P, mm.
331.2	53.9	367.9	327
337.5	77.0	370.8	365
342.3	98.1	373.9	410
347.2	128.8	375.0	450
347.8	130.8	377.4	456
352.3	163.2	383.2	564
354.0	182.5	387.6	623
357.8	209.5	388.1	662
359.6	221.0	391.6	695
362.6	263.5	391.9	743
367.2	315.5	(393.7)	(760)

Iodine(III) Fluorosulfonate.—An excess of peroxydisulfuryl difluoride was distilled into a bulb containing 0.3038 g. of solid iodine and the mixture allowed to warm to room temperature. Heat was evolved and a dark green liquid formed. On continued reaction the liquid became light yellow. Distillation of the excess peroxide left a residue of 0.991 g. (Calcd. for $I(SO_3F)_3$: 1.011 g.) which was very viscous. Freezing in liquid oxygen produced crystals which remained solid at room temperature.

$$I_2 + 3S_2O_6F_2 \longrightarrow 2I(SO_3F)_3$$

The solid was analyzed by reaction with water, extraction of iodine with carbon tetrachloride and titration iodometrically. The water phase contained iodate which also was determined iodometrically.

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$$5I(SO_3F)_3 + 9H_2O \longrightarrow I_2 + 3HIO_3 + 15HSO_3F$$

0.9474 mmole of $I(SO_3F)_3$ yielded 0.1835 mmole of I_2 and 0.571 mmole of HIO_3; calcd.: 0.1895 mmole I_2 and 0.569 mmole HIO_3.

Properties of Iodine(III) Fluorosulfonate.—Iodine(III) fluorosulfonate crystallizes in yellow hemihedral orthorhombic pinacoids showing negative elongation; one refractive index is slightly greater than 1.40. Further optical data could not be obtained readily due to lack of an unreactive immersion medium. The crystals melt at 32.2°. When heated to 114° at 3 cm. pressure the liquid boils with decomposition to volatile peroxydisulfuryl difluoride and a nonvolatile green liquid which approximates ISO_3F in composition. Supercooled liquid iodine(III) fluorosulfonate has a density of 2.40 g./ml. at 25°.

Attempts to Prepare Lower Fluorosulfonates of Iodine.—The addition of peroxydisulfuryl difluoride to an excess of iodine produced dark green to black liquids and brown solids from which the excess iodine was vaporized only with difficulty and was not extractable by perfluoromethylcyclohexane even when the mole ratio of I_2 to $S_2O_6F_2$ was initially as high as 25.9. Consistent results were not obtained either on synthesis or analysis. While some results suggested the existence of ISO_3F as well as I_3SO_3F, pure materials were not obtained and the existence of lower fluorosulfonates of iodine was not established definitely.

Peroxydisulfuryl Difluoride with Chlorine.—Attempts to prepare chlorine fluorosulfonates from chlorine and the peroxide were unsuccessful even at elevated temperatures, the unchanged reactants being recovered in all cases. The high bond energy of the chlorine molecule could make such reactions energetically unfavorable.

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The Preparation of Mercury(II), Nitrosyl and Nitronium Fluorosulfonates from Peroxydisulfuryl Difluoride

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Peroxydisulfuryl difluoride reacts with nitric oxide to give nitrosyl fluorosulfonate and with mercury to give mercury(II) fluorosulfonate. With nitrogen dioxide an equimolar mixture of nitrosyl and nitronium fluorosulfonates is produced. The reaction products have been characterized.

Introduction

The reaction of peroxydisulfuryl difluoride with sulfur dioxide[2] suggests that the reaction may proceed by rupture of the peroxide bond forming two SO_3F radicals which are the reactive species. If this hypothesis is correct, reaction should occur readily with odd-electron molecules. Nitric oxide and nitrogen dioxide may therefore be expected to react readily with the peroxide. This has been found to be the case.

Nitrosyl fluorosulfonate has been prepared by Woolf[3] from solution of nitronium pyrosulfate in bromine trifluoride and by Lange[4] from dinitrogen trioxide and fluorosulfonic acid. The latter product was contaminated with nitrosyl bisulfate.

Nitronium fluorosulfonate was prepared and characterized by Goddard, Hughes and Ingold[5] by treating dinitrogen pentoxide with fluorosulfonic acid in nitromethane, and its crystal structure has been studied by Millen[6] who found an ionic lattice of NO_2^+ and SO_3F^- ions.

During the present study the mercury in the manometer was observed to be strongly attacked by the peroxide. This reaction was investigated quantitatively.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared by the method of Dudley and Cady[7] and separated from the accompanying fluorine fluorosulfonate by distillation at Dry Ice temperature. Nitric oxide and nitrogen dioxide were used directly from cylinders of the compressed gases. Other materials were of reagent quality.

Analytical Methods.—Weighed samples were treated with aqueous sodium hydroxide containing hydrogen peroxide to ensure conversion of nitrogen compounds to nitrate. Nitrogen[8] was determined by the Devarda method, sulfur[8] as barium sulfate and fluorine[9] as triphenyltin fluoride.

Reaction of Peroxydisulfuryl Difluoride with Nitric Oxide.—An excess of nitric oxide was admitted to a 125-ml. bulb containing 1.213 g. of the peroxide at room temperature. Heat was evolved and a white solid formed immediately. After removal of excess nitric oxide 1.558 g. of solid remained which was 98.7% of the 1.581 g. required by the equation

$$2NO + S_2O_6F_2 \longrightarrow 2NOSO_3F$$

Properties of Nitrosyl Fluorosulfonate.—The density of nitrosyl fluorosulfonate was determined by preparing small amounts of the compound in Weld specific gravity bottles and immersing the solid in bromobenzene. A value of 1.96 g./ml. at 25° was found. The solid was also observed to sink slowly in Kel-F oil of density 1.925 g./ml. at 25°, thus providing a check on the pycnometric value.

The melting point was determined by slow heating (1°/min.) in capillaries and in 6 mm. tubes. Reproducible values of 156–157° were obtained. This is higher than the value of 140° reported by Lange[4] whose sample was contaminated with nitrosyl bisulfate; Woolf[3] did not report a melting point.

Immersed in Kel-F oil under the microscope, nitrosyl fluorosulfonate as prepared above consists of anisotropic grains with only an occasional face large enough to show oblique symmetry. All refractive indices were greater than 1.406. In the absence of suitable solvents for recrystallization, a more detailed study was not attempted.

Nitrosyl fluorosulfonate is extremely hygroscopic. Reaction with water follows the equation

$$NOSO_3F + H_2O \longrightarrow HSO_3F + HNO_2$$

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