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

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

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

BY JOHN E. ROBERTS[1] AND GEORGE H. CADY

RECEIVED JULY 14, 1959

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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(1) University of Massachusetts, Amherst, Mass.

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Reaction of Peroxydisulfuryl Difluoride with Nitrogen Dioxide.—By the same technique used for the nitric oxide reaction, excess nitrogen dioxide was allowed to react with the peroxide. A white solid formed with the evolution of heat and the production of an uncondensable gas which was shown by gas density to be oxygen. A 0.8860-g. sample of peroxide yielded 1.281 g. of solid product and 0.0719 g. of oxygen. Calculated weights based on the following equation are 1.222 g. of solid and 0.716 g. of oxygen.

$$S_2O_6F_2 + 2NO_2 \longrightarrow NOSO_3F + NO_2SO_3F + {}^1/_2O_2$$

The solid mixture was analyzed. Calcd.: N, 10.22; S, 23.4; F, 13.8. Found: N, 10.12, 9.94; S, 23.77, 23.74; F, 11.17, 12.68.

Mercury(II) Fluorosulfonate.—An excess of peroxydisulfuryl difluoride was distilled into a bulb containing 1.67 mg. atoms of mercury. After all the mercury had reacted, the excess unchanged peroxide was distilled out leaving a white solid whose mass amounted to 1.68 mmoles of mercury(II) fluorosulfonate.

$$Hg + S_2O_6F_2 \longrightarrow Hg(SO_3F)_2$$

Mercury(II) fluorosulfonate has a density of 3.715 g./ml. at 25°. Kel-F oil was used as immersion liquid in Weld specific gravity bottles.

Hydrolysis of Mercury(II) Fluorosulfonate.—Water reacted immediately with mercury(II) fluorosulfonate with the separation of a finely divided yellow precipitate, leaving a colorless acidic solution. The yellow solid was separated and dissolved easily in 1:3 nitric acid. Titration of the mercury with standard thiocyanate indicated 78.2% Hg. (Calcd for $Hg_3F_4(OH)_2 \cdot 3H_2O$: 78.7% Hg.) The filtrate was titrated with standard base, boiling to ensure complete hydrolysis of the fluorosulfonate ion; 4.72 meq. of acid was found per mmole of mercury(II) fluorosulfonate (phenolphthalein end-point). The hydrolysis therefore proceeds according to the equation

$$3Hg(SO_3F)_2 + 11H_2O \longrightarrow Hg_3F_4(OH)_2 \cdot 3H_2O + 6H_2SO_4 + 2HF$$

giving the same basic fluoride that Ruff and Bahlau[10] found from the hydrolysis of mercuric fluoride.

Material of identical appearance and a mercury content nearly the same (79.1%) formed immediately when dilute sodium fluoride solution, slightly acidified with hydrofluoric acid, was added to 1 *M* mercuric nitrate solution.

Acknowledgment.—This work was supported in part by the Office of Naval Research.

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

Some Reactions of Fluorine Fluorosulfonate; Iodine Trifluoride Bisfluorosulfonate

BY JOHN E. ROBERTS[1] AND GEORGE H. CADY

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Fluorine fluorosulfonate reacts with sulfur dioxide to give pyrosulfuryl fluoride and with thionyl fluoride to give peroxydisulfuryl difluoride and thionyl tetrafluoride. With iodine, fluorine fluorosulfonate reacts to form iodine trifluoride bisfluorosulfonate, $IF_3(SO_3F)_2$. This new compound has been characterized. Chlorine does not react with fluorine fluorosulfonate.

Introduction

The reactive nature of fluorine fluorosulfonate, SO_3F_2, toward water, aqueous base and aqueous iodide has been established by Dudley, Cady and Eggers[2]; other reactions of this substance have not been investigated. The straightforward production of various fluorosulfonates from peroxydisulfuryl difluoride[3] suggested that similar reactions might occur with fluorine fluorosulfonate. A study of the reactions of this material with sulfur dioxide, thionyl fluoride, chlorine and iodine therefore was undertaken.

Experimental

Materials.—Fluorine fluorosulfonate was prepared by the method of Dudley, Cady and Eggers.[2] Thionyl fluoride was prepared by passing thionyl chloride over antimony trifluoride at 150° and subsequent purification by distillation. Chlorine and sulfur dioxide were used directly from cylinders of the compressed gases. Other materials were of reagent quality.

Analytical Methods.—Infrared spectra were measured in the range 2 to 15 μ using a Perkin–Elmer Model 21 Spectrometer with a sodium chloride prism. A 10 cm. nickel cell with silver chloride windows was used.

A Varian Associates 60 megacycle n.m.r. spectrometer was used for the nuclear magnetic resonance spectra.

Chemical analysis was carried out after long digestion of samples with excess base. Sulfur was determined as barium sulfate[4] and iodine by the Volhard method.[4]

Reaction of Fluorine Fluorosulfonate with Sulfur Dioxide.—The apparatus was the same as was used for the reaction of sulfur dioxide with peroxydisulfuryl difluoride.[3] Dry nitrogen was passed through SO_3F_2 at Dry Ice temperature and then into a nickel tube 18 inches long and 1 inch in diameter at 195°. Sulfur dioxide was introduced to give a 1:1 mole ratio of SO_3F_2 to SO_2. The collected products were fractionated by vacuum distillation and examined in the infrared spectrometer. The product consisted of pyrosulfuryl fluoride, $S_2O_5F_2$, together with unchanged reactants. Gas density measurements gave a molecular weight of 182, 188 for this material (calcd. for $S_2O_5F_2$: 182).

Reaction of Fluorine Fluorosulfonate with Thionyl Fluoride.—Fluorine fluorosulfonate and thionyl fluoride were admitted to a 1.7-l. nickel vessel in 1:1 mole ratio. Pressure changes were followed through a Booth–Cromer pressure transmitter as the temperature was increased slowly. Negative deviation from ideal behavior became apparent at 80° and was very marked at 130°. At this point the materials were distilled from the reactor and separated by vacuum distillation. Two distinct fractions were found, a liquid having appreciable vapor pressure at Dry Ice temperature and a solid melting at approximately −57°. Infrared spectra of the two fractions showed the volatile material to be thionyl tetrafluoride SOF_4 and the less volatile fraction to be peroxydisulfuryl difluoride $S_2O_6F_2$. The reaction must therefore have followed the equation

$$2SO_3F_2 + SOF_2 \longrightarrow S_2O_6F_2 + SOF_4$$

Fluorine Fluorosulfonate with Chlorine.—Chlorine gas was admitted to a bulb containing fluorine fluorosulfonate and the mixture allowed to warm to room temperature. No reaction was evident. Repeated experiments at tempera-

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[1] University of Massachusetts, Amherst, Mass.

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