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.

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[10] O. Ruff and G. Bahlau, *Ber.*, **51**, 1752 (1918).

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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.

[2] F. B. Dudley, G. H. Cady and D. F. Eggers, THIS JOURNAL, **78**, 290 (1956).

[3] J. E. Roberts and G. H. Cady, *ibid.*, **81**, 4166 (1959).

[4] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 720 and 736.

tures up to 100° failed to give any new materials, the unchanged reactants always being recoverable.

Reaction of Fluorine Fluorosulfonate with Iodine.—Fluorine fluorosulfonate was admitted to a bulb containing iodine at room temperature. Reaction occurred immediately with the evolution of heat and the production of a black liquid. Further addition of the hypofluorite caused the liquid to become green, then yellow and finally very light yellow, almost colorless. The volatile material was removed by distillation and was found to contain fluorine fluorosulfonate and peroxydisulfuryl difluoride which were identified by molecular weight determinations after separation by distillation at Dry Ice temperature.

The non-volatile liquid residue amounted to 2.4392 g. from 0.8157 g. of iodine, which was 99.36% of the calculated 2.4548 g. of product for the composition $IF_3(SO_3F)_2$. This composition was established by analysis after long digestion with aqueous base. Aliquots for sulfur and fluorine were reduced with hydrazine to destroy the iodate prior to precipitation of barium sulfate; aliquots for iodine were reduced with sodium bisulfite prior to the Volhard determination. Calcd. for $IF_3(SO_3F)_2$: I, 33.2; S, 16.8. Found: I, 33.4, 33.2; S, 16.3, 16.2. From these data it is clear that the preparation reaction must have followed the equation

$$I_2 + 6SO_3F_2 \longrightarrow 2IF_3(SO_3F)_2 + S_2O_6F_2$$

Properties of Iodine Trifluoride Bisfluorosulfonate.—The pentavalent nature of the iodine in $IF_3(SO_3F_2)$ was established by hydrolysis of the compound. Reaction with water was violent and rapid producing iodate but only traces of iodine. Iodometric titration showed 5.88 and 5.90 oxidizing equivalents per mole. Titration of the hydrolysis solution after 3 days' digestion showed 10.51 and 10.48 (theory = 10.0) equivalents of acid per mole of original compound. These slightly high values are the result, at least in part, of action of the hot base on glass during the long digestion and the absorption of carbon dioxide. Hydrolysis evidently proceeds according to the equation

$$IF_3(SO_3F)_2 + 3H_2O \longrightarrow HIO_3 + 3HF + 2HSO_3F$$

with subsequent further hydrolysis of the HSO_3F.

The density of the $IF_3(SO_3F)_2$ was determined in a graduated straight tube 3 mm. in diameter which had been calibrated with water and mercury. At 25°, $IF_3(SO_3F)_2$ has a density of 2.63 g./ml. The nuclear magnetic resonance spectrum of $IF_3(SO_3F)_2$ showed two fluorine peaks with a separation of 31.8 p.p.m. The peak caused by SO_3F groups was quite sharp; that due to the other three fluorine atoms came at a higher field strength and was very broad. This clearly established the existence of two different environments for the fluorine atoms in the molecule. Areas under the curves, however, differed from the expected ratio of 3:2, approaching 4.5:2. The cause of this discrepancy was not apparent but in view of the synthetic and analytical data, it was considered not to constitute proof of a ratio truly different from 3:2. The simple nature of the n.m.r. spectrum indicated the sample to be a single substance rather than a mixture.

Attempts to crystallize the compound yielded only a glass; the freezing point is therefore unknown.

The measurement of the temperature dependence of vapor pressure was attempted but slow decomposition, becoming appreciable at 35 cm. and 123°, made accurate measurements impossible. Extrapolation from the data obtained, however, indicated a boiling point in the vicinity of 150°.

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[CONTRIBUTION FROM THE GENERAL ENGINEERING LABORATORY, GENERAL ELECTRIC CO.]

Reactions of Solid Alkaline Earth Oxides. II.[1] CaO and MgO

BY HANS J. BORCHARDT AND BARBARA A. THOMPSON

RECEIVED JULY 29, 1959

The reactions of salts of oxy-acids with CaO and MgO are re-examined. The supposed phenomenological similarity of the CaO reactions with those of BaO and SrO is not borne out by the data. The thesis that the "reactivity" is a function only of the oxide and the associated "reaction temperature" concept are shown to be invalid.

The reactions of BaO, SrO, CaO and MgO with salts of oxy-acids have been the subject of extensive investigation and speculation in the past, the results of which are recorded in most modern references on solid state chemistry.[2-5] The unusual rate behavior reported for these reactions is the subject of this series of communications.

According to Hedvall and co-workers,[2,6] the alkaline earth oxides begin to react rapidly with salts of oxy-acids at a temperature characteristic of the oxide only (see, for example, Table II, ref. 5). Furthermore, it was postulated that in each case the reaction occurs in the solid state.[2,7,8]

It was shown[1] previously that for BaO and SrO, the reaction phenomenon observed by Hedvall is due to the appearance of a liquid phase. At the so-called "reaction temperature," a barium (or strontium) hydroxide-containing eutectic melts and the reaction proceeds *via* this liquid phase. In these terms, the sudden "triggering-off" of the reaction at a temperature independent of the salt component and the substantial completion of reaction in a matter of seconds is readily understood.

The appearance of a liquid phase, however, cannot account for the behavior of CaO and MgO since the hydroxides of Ca and Mg decompose below the "reaction temperature." Indeed, this fact was used by Hedvall and co-workers to counter the criticism of contemporaries[9] who originally proposed that the reactivity of BaO and SrO is due to a hydroxide melt. The argument that Hedvall[2] and Jagitsch[10] present is as cited:

> In the case of CaO, the constancy of the "reaction temperature" cannot be due to the formation of a liquid phase. The reaction phenomenon is substantially the same for CaO as for BaO and SrO and a single explanation is required. Therefore, the behavior of BaO and SrO cannot be explained in terms of the formation of a liquid phase.

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[1] For part I, see H. J. Borchardt and B. A. Thompson, THIS JOURNAL, **81**, 4182 (1959).

[2] J. A. Hedvall, "Einfuhrung in die Festkorperchemie," Fr. Vieweg and Sons, Verlag, Braunschweig, 1952.

[3] K. Hauffe, "Reaktionen in und an Festen Stoffen," Springer Verlag, Berlin.

[4] W. E. Garner, "Chemistry of the Solid State," Butterworth Publishing Co., London, 1955.

[5] G. Cohen, *Chem. Revs.*, **42**, 527 (1948).

[6] J. A. Hedvall and J. Heuberger, *Z. anorg. Chem.*, **122**, 181 (1922); **128**, 1 (1923); **140**, 243 (1924).

[7] J. A. Hedvall, *ibid.*, **162**, 110 (1927).

[8] G. Tammann, *ibid.*, **160**, 101 (1927).

[9] D. Balarew, *ibid.*, **160**, 92 (1927).

[10] R. Jagitsch, *Arkiv Kemi, Mineral. Geol.*, **15A**, 1 (1942).