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

The Reaction of Peroxydisulfuryl Difluoride with Sulfur Dioxide and with Fluorine

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Peroxydisulfuryl difluoride reacts with fluorine to give fluorine fluorosulfonate and with sulfur dioxide to give a compound of empirical formula $S_3O_8F_2$. The latter has been characterized.

Introduction

Peroxydisulfuryl difluoride, first prepared by Dudley and Cady,[2] has been shown to be a reactive molecule toward water, bases and iodide but further chemical reactions of this compound have not been reported. Since the peroxide bond is probably the weakest bond in this molecule, it should be possible to produce SO_3F radicals at high temperatures which could then combine with other molecules. Thus sulfur dioxide and peroxydisulfuryl difluoride may be expected to yield a compound of empirical composition $S_3O_8F_2$.

In 1953, Lehmann and Kolditz[3] prepared $S_3O_8F_2$ by saturating liquid sulfur trioxide with boron trifluoride and treating the solution with 70% sulfuric acid. Experimental details are lacking and only the density and boiling point were reported. The compound also was prepared by Muetterties and Coffman[4] by the same method.

It was the purpose of this investigation to study the reactions of peroxydisulfuryl difluoride with fluorine and with sulfur dioxide.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared by the method of Dudley and Cady[2] and identified by its physical properties. Sulfur dioxide, fluorine and nitrogen were used directly from cylinders of the compressed gases without further purification.

Reaction of $S_2O_6F_2$ with Fluorine.—Nitrogen gas was bubbled through the peroxide at room temperature and the gas stream allowed to mix at 250° with a fluorine stream in a straight one inch diameter nickel tube 18 inches long. The reaction products were collected at liquid oxygen temperature. The vapor pressure, molecular weight and other physical properties indicated that the product was entirely fluorine fluorosulfonate,[5] SO_3F_2.

Reaction of $S_2O_6F_2$ with Sulfur Dioxide.—Streams of sulfur dioxide and peroxydisulfuryl difluoride diluted with nitrogen were allowed to mix at 200° in the nickel tube and the products were collected in a trap at liquid oxygen temperature. Vacuum distillation showed that the major product was liquid at room temperature. This was purified by distillation and characterized.

Analysis.—Samples were vacuum distilled into small bulbs, sealed, weighed and the bulbs broken under 0.2 N NaOH. After digesting for 24 hr. on a steam plate, the solutions were titrated to the phenolphthalein end-point with standard acid. 7.0 to 7.5 milliequivalents of base had been consumed per millimole of compound which indicated that hydrolysis of the fluosulfonate ions was still incomplete. Separate aliquots were digested further and used for sulfur and fluoride analyses. Sulfur was determined by precipitation as barium sulfate; fluorine by precipitation as triphenyltin fluoride. Calcd. for $S_3O_8F_2$: S, 36.69; F, 14.49. Found: S, 36.74, 36.51; F, 13.9, 13.4.

Molecular Weight.—Molecular weight was determined by vapor density, ideal gas behavior being assumed. An average value of 262 ± 4 was found from eight determinations on three different preparations. The calculated value for $S_3O_8F_2$ is 262.18.

Density.—Densities were determined in a single capillary pycnometer of approximately 0.45-ml. capacity. The pycnometer had been calibrated with water and checked by measurements of carbon tetrachloride. Values found for $S_3O_8F_2$ at 15, 20, 25° were, respectively, 1.847, 1.840, 1.828 g./ml. These values differ slightly from the value 1.86 g./cm.[3] reported by Lehmann and Kolditz[3] for 25°.

Refractive Index.—The refractive index of $S_3O_8F_2$, measured with an Abbé refractometer at 25°, was found to be 1.3618 ± 0.0002. The Lorentz-Lorenz molar refraction was 31.80 ml.

Melting Point.—The melting point was determined by slowly warming the solid in an acetone-bath initially cooled with Dry Ice. The heating rate was approximately 1°/5 min. Liquid was first observed at −67.2° and all solid had disappeared at −66.5°. Attempts to determine the freezing point by cooling were unsuccessful due to the tendency of the compound to supercool as much as 40° even when being stirred.

Temperature Dependence of Vapor Pressure.—The vapor pressure of the $S_3O_8F_2$ was measured using previously described apparatus.[6] The results are shown in Table I including an interpolated value at 760. mm.

TABLE I

T, °K.	$P_{mm.}$	T, °K.	$P_{mm.}$
309.6	23.93	362.4	284.78
318.2	38.25	366.9	315.3
319.6	40.07	370.2	353.66
329.5	67.08	373.6	394.4
336.2	89.91	380.3	500.1
337.9	99.04	384.1	572.3
346.5	140.88	392.0	722.
352.1	179.11	(393.5)	(760.)
357.2	235.08	393.6	767.

These data are in good agreement with the boiling point of 120° reported by Lehmann and Kolditz and with the value 82° at 310 mm. reported by Muetterties and Coffman. Application of the Clapeyron equation to these data gave a heat of vaporization of 8640 cal. per mole. The Trouton constant is 21.9.

Infrared Spectrum.—The infrared spectrum in the range 2 to 15 μ was measured in the vapor phase at 2.5 to 8 mm. pressure using a Perkin-Elmer Model 21 Spectrometer with a sodium chloride prism. A nickel cell 10 cm. long with silver chloride windows was used.

The spectrum of $S_3O_8F_2$ strongl yresembles the spectra of other fluorine-oxygen-sulfur compounds. Strong absorption was observed at 1490, 1250, 1225, 872, 790 cm.$^{-1}$. A weak band at 1028 cm.$^{-1}$ was attributable to silicon tetrafluoride and was distinctly less intense on freshly distilled samples than on older material. By analogy with the spectra reported for peroxydisulfuryl difluoride[2] and other similar fluorine compounds studied in these laboratories, the bands at 1490, 1250 and 1225 cm.$^{-1}$ may be associated with the S-O bonds and those at 872 and 790 cm.$^{-1}$ are characteristic of S-F bonds.

Nuclear Magnetic Resonance Spectrum.—A Varian Associates 60 megacycle n.m.r. spectrometer was used to determine the nuclear magnetic resonance spectrum of the

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[2] F. B. Dudley and G. H. Cady, THIS JOURNAL, **79**, 513 (1957).

[3] H. A. Lehmann and L. Kolditz, *Z. anorg. allgem. Chem.*, **272**, 73 (1953).

[4] E. L. Muetterties and D. D. Coffman, THIS JOURNAL, **80**, 5914 (1958).

[5] F. B. Dudley, G. H. Cady and D. F. Eggers, *ibid.*, **78**, 290 (1956).

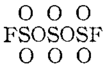
[6] K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

compound. Perfluorocyclopentane was used as a reference material with a field strength of 15,020 gauss. The $S_3O_8F_2$ showed a single peak at a negative shift of 31.7 p.p.m. from the reference sample. Comparison of areas under the curves corrected for different densities gave approximately a 5:1 ratio for the number of fluorine atoms per molecule. These data show that the compound $S_3O_8F_2$ has two fluorine atoms per molecule, both having the same chemical environment.

Mass Spectra.—Mass spectra were obtained with a Consolidated Electrodynamics Corp. Mass Spectrometer, Model 21-103C with an ionizing current of 10.5 μamp. and an ionizing potential at 70 volts. The butane sensitivity was 27.7 divisions per micron. Spectra were obtained for $S_3O_8F_2$ as well as for $S_2O_5F_2$ and $S_2O_6F_2$ for comparison. The $S_3O_8F_2$ spectrum showed major peaks corresponding to SO_2F^+, SOF^+, SO_2^+, SO_3^+ and numerous minor peaks. The parent peak at mass number 262 was missing in all spectra. Persistent peaks at mass numbers 182 and 184 corresponding to $S_2O_5F_2^+$ could not be explained, comparsion with the spectrum of S_2O_5F, showed marked similarities even though all other tests showed the absence of $S_2O_5F_2$ in the $S_3O_8F_2$ sample. It is probable, therefore, that the $S_3O_8F_2$ molecule is extensively disintegrated in the mass spectrometer or in the line for admitting the gas to the spectrometer, with the production of $S_2O_5F_2$.

Preparation from SO_3 and BF_3.—Following the method of Lehmann and Kolditz[3] a compound was isolated which had a molecular weight of 267 as determined by gas density. The melting point, infrared spectrum and mass spectrum were identical with those found for the product obtained from the reaction of sulfur dioxide with peroxydisulfuryl difluoride. A second product of this reaction was identified as pyrosulfuryl fluoride, $S_2O_5F_2$.

Structure.—From the fact that one mole of $S_3O_8F_2$ reacts with a solution of potassium hydroxide to give approximately two moles of SO_3F^- and one of SO_4^{--}, Lehmann and Kolditz proposed the structure



$$\begin{array}{c}\mathrm{O\ O\ O}\\ \mathrm{FSOSOSF}\\ \mathrm{O\ O\ O}\end{array}$$

This structure is consistent with the nuclear magnetic resonance spectrum which indicates only one type of fluorine atom, but it is not consistent with a mass spectrum containing a $S_2O_5F_2^+$ peak. The writers are of the opinion that the above structure is correct and that the $S_2O_5F_2^+$ peak in the mass spectrum is probably due to $S_2O_5F_2$ as indicated earlier.

The name trisulfuryl fluoride was assigned to $S_3O_8F_2$ by the discoverers. If the above structure is correct the name sulfuryl fluorosulfonate is equally good.

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Evidence for the Existence of Peroxyuranic Acid[1]

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Uranium trioxide was treated with aqueous hydrogen peroxide to form a hydrated uranium peroxide compound identical to that precipitated from aqueous uranyl nitrate solution by the addition of hydrogen peroxide. The stoichiometric compound, $UO_4 \cdot 2H_2O$, was shown to react with alcoholic potassium hydroxide to form hydrated monobasic ($KHUO_5 \cdot xH_2O$) and dibasic ($K_2UO_5 \cdot xH_2O$) potassium salts. A hydrated peroxyuranic acid structure ($H_2UO_5 \cdot H_2O$) was concluded to best represent a compound of the stoichiometry $UO_4 \cdot 2H_2O$. This structure was supported by the infrared absorption spectrum and reactions with a strong base of the uranium peroxide compound.

Introduction

Since Fairley[2] first prepared hydrated uranium peroxide by the precipitation of uranium from weakly acidic aqueous solutions of uranyl nitrate or uranyl acetate with hydrogen peroxide, a controversy has existed regarding its structure. Despite the controversy regarding its structure, the stoichiometric compound $UO_4 \cdot 2H_2O$ readily can be prepared with a high degree of purity.

Previous experimental efforts to define the structure of this uranium peroxide compound were based on its reactions in aqueous solution, its stepwise thermal decomposition to U_3O_8 and/or infrared spectral studies. As a result of these experiments the following structures have been postulated for the compounds: $UO_4 \cdot 2H_2O$,[3] $UO_2(O_2) \cdot 2H_2O$,[4] $UO_3 \cdot H_2O_2 \cdot H_2O$,[5] $H_2UO_5 \cdot H_2O$[6] and H_4UO_6.[7]

In light of the recent work by Gentile, Talley and Collopy,[8] further substantiating the acidic character of hydrated uranium trioxide by its reaction with the weak base urea to form urea uranate, additional study of the reactions of the peroxyuranium hydrate compounds was warranted.

Preliminary tests employing uranium peroxide hydrates and aqueous or alcoholic solutions of urea failed to produce sufficient quantities of a compound corresponding to urea peroxyuranate. A solid material corresponding to urea peroxyuranate was precipitated, however, from a concentrated solution of diaquotetraureadioxouranium(VI) nitrate by the addition of hydrogen peroxide. This precipitate, after continued contact with water, hydrolyzed to a peroxyuranic acid hydrate.

In view of the above results and the generally diminished acidity of peroxyacids as compared with fundamental oxygen acids of the same system, a series of tests was conducted with the strong base potassium hydroxide in alcoholic media to demonstrate the acidic character of uranium peroxide hydrates. These experiments were supplemented with infrared spectral data to determine the presence of the uranyl group, hydrate water and hydroxyl groups. X-Ray diffraction patterns were

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(1) This paper is based on work performed for the Atomic Energy Commission by the National Lead Company of Ohio at Cincinnati, Ohio.

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