to say definitely that PF_3 is a stronger acceptor molecule than PCl_3. Available data,[4,5] however, do permit the following ordering of acceptor ability toward $(CH_3)_3N$: $PCl_3 > PBr_3 \sim CH_3PCl_2 > (CH_3)_3P$.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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Preparation and Properties of N,N-Difluorohydroyxlamine-O-flourosulfonate, NF_2OSO_2F

BY MAX LUSTIG AND GEORGE H. CADY

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The preparation of the new compound, N,N-difluorohydroxylamine-O-fluorosulfonate, from tetrafluorohydrazine, N_2F_4, and peroxydisulfuryl difluoride, $S_2O_6F_2$, is reported, and some of its chemical and physical properties are given.

Introduction

Since the reported isolation of tetrafluorohydrazine by Colburn and Kennedy in 1958,[1] this compound has been a very useful free radical difluoraminating agent. The availability of $NF_2\cdot$ free radicals from tetrafluorohydrazine has been demonstrated by both ultraviolet spectrophotometric[2] and e.p.r. studies.[3] Its use as an intermediate in the preparation of NF_2 adducts with other free radicals also has been shown.[4-7]

The chemistry of peroxydisulfuryl difluoride strongly suggests that a free radical mechanism is available in its reactions. In the literature there are numerous examples of the homolytic cleavage of the oxygen–oxygen bond in the preparation of fluorosulfates by substitution[8] and addition reactions.[8-12] This information was used to predict the formation of NF_2OSO_2F from tetrafluorohydrazine and peroxydisulfuryldifluoride. The prediction has been found to be true. The chemical and physical evidence given below has confirmed the predicted structure.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared using a catalytic method of fluorinating sulfur trioxide.[12] The latter was obtained as "Sulfan B," a stabilized liquid, made by the General Chemical Division of the Allied Chemical Corp. Fluorine, obtained in a cylinder from the General Chemical Division, was passed through a flow meter and was controlled by a nickel diaphragm valve. A cylinder of tetrafluorohydrazine, obtained from E. I. du Pont de Nemours and Co., was surrounded by a protective 5/8-in. thick steel cylinder. The valve on the tank was operated from outside the steel shield by a key attached to the cylinder.

Preparation of N,N-Difluorohydroxylamine-O-fluorosulfonate.—The preparation was carried out using a Pyrex glass vacuum apparatus, the reactor being a 2-l. flask. This was filled with tetrafluorohydrazine at a pressure of 20 mm.; then an equal volume of $S_2O_6F_2$ vapor was added slowly. A mild reaction occurred at room temperature giving a gaseous product which was found by fractional codistillation[13] to be a single substance.

Chemical Analysis.—The compound was analyzed by allowing 0.273 g. (1.81 mmoles) of the gas to react at 70° in a glass flask with an excess of 0.1 *N* NaOH solution. Even at this temperature the reaction was slow. At room temperature the rate was too slow to be of practical value. The reaction occurred according to the equation

$$NF_2OSO_2F + 4OH^- \longrightarrow NO_2^- + SO_3F^- + 2H_2O + 2F^-$$

The solution was held at about 100° for 5 days to ensure complete hydrolysis of the fluorosulfate ion to sulfate. The nitrite then was determined volumetrically by titration with potassium permanganate solution using the method of Lunde. The sulfate was determined gravimetrically as $BaSO_4$ and the fluoride gravimetrically as triphenyltin fluoride.[14] *Anal.* Calcd.: N, 9.27; S, 21.18; F, 37.72. Found: N, 9.48; S, 20.9; F, 38.0. (Calcd. for the hydrolysis reaction: nitrite, 1.81 mmoles; sulfate, 1.79 mmoles; fluoride, 5.43 mmoles. Found: nitrite, 1.85 mmoles; sulfate, 1.79 mmoles; fluoride, 5.47 mmoles.)

Molecular Weight.—The average molecular weight, obtained from vapor density measurements assuming ideal gas behavior, was 150.8 g./g.m.v. (calcd. for NF_2OSO_2F, 151.1).

Melting Point.—Due to the supercooling effect of the liquid compound, the freezing point was not obtained. The liquid phase could be observed at temperatures as low as −183°. Prolonged exposure to this temperature resulted in freezing. The melting point was obtained by freezing the sample in a 5 mm. o.d. Pyrex glass tube. As the tube warmed at a rate of about 0.2°/min. in a pentane bath the solid was observed to melt within a 0.5° range, the last solid disappearing at −128.8 ± 0.5°.

Vapor Pressure and Boiling Point.—The vapor pressures were measured in a Pyrex glass apparatus similar to that described by Kellogg and Cady.[15] In this method a sample of the liquid was boiled under a variety of constant and measured pressures while the vapor was condensed in a reflux condenser and returned to the pot as a stream of liquid. The temperature corresponding to

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equilibrium between liquid and vapor was measured by a thermocouple located about 2 cm. above the boiling liquid. Vapor pressures are shown in Table I. For pressures above 60 mm. the data can be expressed by the equation

$$\log P\ (\text{mm.}) = -1.287 \times 10^3/T + 7.6461$$

The molar heat of vaporization at −2.5° calculated using the Clausius–Clapeyron Equation is 5.89 kcal. and the Trouton constant is 21.7 e.u. The boiling point, calculated from the above equation, is −2.5 ± 0.5°.

TABLE I

VAPOR PRESSURE OF NF_2OSO_2F

P, mm.	T, °K.	P, mm.	T, °K.
18.5	206.2	282.5	248.6
60.0	219.0	330.3	251.5
83.7	226.1	450.8	257.3
113.4	231.6	520.7	261.5
124.9	232.8	520.9	261.7
152.2	236.3	606.8	265.2
155.6	237.1	642.9	266.6
205.9	241.2	715.3	269.1
228.6	244.2	794.2	272.0
250.5	245.4		

Liquid Density.—The densities of liquid NF_2OSO_2F as a function of temperature were measured with a cathetometer by the observation of the position of the meniscus in a 1-mm. capillary attached to a measured bulb containing the sample. This device was placed in a bath at various fixed temperatures. The densities at different temperatures are shown in Table II. The interpolated density at 25° is 1.498 g./cc. and the volume coefficient of expansion, calculated from the data, is 2.12×10^{-3} per degree at 25°. The temperature dependence of the density, σ_t, is given by the equation

$$\sigma_t = -3.17 \times 10^{-3}t + 1.577$$

where t is °C.

TABLE II

DENSITY DATA

T, °C.	Density, g./cc.	T, °C.	Density, g./cc.
25.8	1.494	0.4	1.576
20.3	1.512	0.0	1.578
17.2	1.522	−2.3	1.586
9.0	1.549	−5.8	1.595
5.9	1.559	−10.6	1.610

Infrared Spectrum.—The infrared spectrum shown in Fig. 1 was taken at 6 and 12 mm. pressure using a Perkin-Elmer Model 21 spectrometer with a sodium chloride prism. A nickel cell equipped with silver chloride windows and having a length of 10 cm. and an inside diameter of 3 cm. was used. Strong absorptions at 1492 and 1250 cm.$^{-1}$ were attributed, respectively, to the asymmetric and symmetric S=O stretching vibrations of the sulfuryl group. These frequencies are close to those which have been reported for the sulfuryl group in SO_3F_2,[16] $S_2O_6F_2$,[16] and SO_2F_2.[17] Absorptions at 1032 and 913 cm.$^{-1}$ were attributed to N–F stretching because NF_3 has such bands at 1030 and 910 cm.$^{-1}$,[18,19] and N_2F_4 has a broad complex band between 1015 and 970 cm.$^{-1}$. The band at 840 cm.$^{-1}$ was assigned to S–F stretching because this mode occurs at 848 cm.$^{-1}$ for SO_2F_2, at 852 cm.$^{-1}$ for SO_3F_2,[16] and at 848 cm.$^{-1}$ for $S_2O_6F_2$.[16] The absorption at 778 cm.$^{-1}$ probably was due to S–O stretch in the S–O–X group. This mode is considered to give frequencies close to this value.[20] It had been assigned at 789 cm.$^{-1}$ in SO_3F_2 and at 787 cm.$^{-1}$ in CH_3OSO_2F.[21]

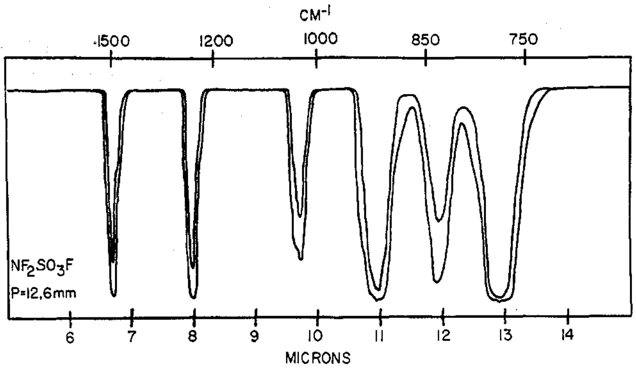

Fig. 1.—Infrared spectrum of NF_2SO_3F.

Mass Spectrum.—A Consolidated Engineering Corp. Type 21–103 with a heated inlet system and an ionization voltage of 66 volts was used to obtain the mass spectrum. Table III shows the relative intensities for the species in the region between 14 and 85 mass numbers. A higher mass number spectrum revealed no parent peak. Peaks corresponding to SO_3F^+, NSO_3F^+, and $NFSO_3F^+$ were very weak.

TABLE III

MASS SPECTRUM OF NF_2OSO_2F

Mass number	Species	Relative intensity
14	N^+	9.7
15	NO^{++}	1.2
16	O^+	7.3
19	F^+	7.6
24	SO^{++}	1.7
30	NO^+	41.3
32	SO_2^{++}, S^+	14.4
33	$^{34}SO_2^{++}$, NF^+	62.4
34	$^{34}S^+$	1.8
48	SO^+	70.6
49	NOF^+	46.9
50	$^{34}SO^+$	3.2
52	NF_2^+	100.0
64	SO_2^+	70.9
66	$^{34}SO_2^+$	3.7
67	SOF^+	16.6
68	NF_2O^+	5.1
69	$^{34}SOF^+$	0.7
80	SO_3^+	3.5
83	SO_2F^+	40.0
85	$^{34}SO_2F^+$	2.1

N.m.r. Spectrum.—A Varian Associates high resolution 40 Mc. nuclear magnetic resonance spectrometer with a Model No. V-4311 fixed frequency radiofrequency transmitter was used to obtain fluorine resonance spectra. The sample to be analyzed was placed in a 5-mm. o.d. glass tube.

The spectrum contained a sharply defined 1:2:1 triplet due to the fluorine atom in the fluorosulfate group, and a broad band barely resolvable into a multiplet caused by the fluorine atoms of the NF_2 group split by nitrogen. The area of the broad band was (1.9 ± 0.2) times the total area of the sharp triplet and the chemical shift between the two was 43.5 p.p.m. with the sharp triplet at the higher magnetic field. A spacing of 4.6 c.p.s. in the sharp triplet indicated this to be the spin–spin coupling constant between the two types of fluorine atoms in the

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F–N–O–S–F bond and space system. A somewhat related system, F–C–O–S–F, in $C_2F_5OSF_5$ has been studied by Merrill and co-workers,[22] who found coupling constants to be 3 and 10 c.p.s. between the $-CF_2-$ group fluorines and the A and B fluorines, respectively, of the pentafluorosulfur group.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research.

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CONTRIBUTION FROM THE ORGANICS DIVISION,
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Chemistry of Decaborane–Phosphorus Compounds. II. Synthesis and Reactions of Diphenylphosphinodecaborane-14[1]

BY HANSJUERGEN SCHROEDER

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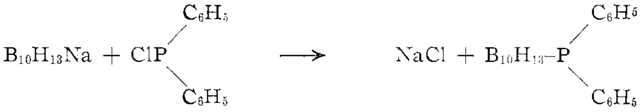
Decaboranyl sodium and diphenylchlorophosphine reacted in ether solution to form diphenylphosphinodecaborane-14 ($(C_6H_5)_2P-B_{10}H_{13}$), the first phosphine substituted decaborane-14 with trivalent phosphorus. B^{11} n.m.r. spectral investigation proved the substituent to be at the 6-position. Unlike monomeric phosphinoboranes (R_2P-BR_2), it is unreactive toward Lewis acids, oxidation, and quaternization, but undergoes partial degradation with alcohols to form $B_9H_{13}-((C_6H_5)_2PH)$. Its reactions with amines and phosphines resulting in salts containing the $(C_6H_5)_2PB_{10}H_{12}$ anion are described.

The original instance of the formation of a decaborane–phosphine compound occurred when decaborane-14 was found to react with triphenylphosphine to form bis-(triphenylphosphine)-decaborane,[2] a compound of the $B_{10}H_{12}$(ligand)$_2$ type in which the ligands donate electrons to the $B_{10}H_{12}$ units. Recently two other such compounds with pentavalent phosphorus, bis-(tri-*n*-butylphosphine)-decaborane and bis-(diethylphosphine)-decaborane, have been reported.[3] The present investigation was undertaken with the objective of synthesizing phosphinodecaboranes ($R_2P-B_{10}H_{13}$) with trivalent phosphorus, to study their properties, and thus to gain additional insight into the character of phosphorus–borane bonding. No examples of higher phosphinoboranes had been reported, and only a few monomeric phosphinoboranes (R_2P-BR_2) have been described.[4]

To this end, decaborane-14 was treated with diphenylphosphine, diphenylchlorophosphine, and ethyl diphenylphosphinite. Substitution involving the elimination of hydrogen, hydrogen chloride, or ethanol, respectively, did not occur; rather the corresponding $B_{10}H_{12}((C_6H_5)_2P\cdot R)_2$ compounds were obtained: bis-(diphenylphosphine)-decaborane (I), bis-(chlorodiphenylphosphine)-decaborane (II), and bis-(ethoxydiphenylphosphine)-decaborane (III). $B_{10}H_{12}((C_6H_5)_2P\cdot Cl)_2$ was the subject of a comprehensive study of nucleophilic chlorine substitution, also the ligands of II and III were proved to be attached at the 6,9 positions of the decaborane nucleus.[1]

More promising for the desired purpose appeared to be the application of an established reaction for the preparation of substituted decaboranes, namely, the interaction of a metallodecaborane and a halogenide as exemplified by the synthesis of benzyldecaborane from decaboranyl sodium[5] or decaboranyl magnesium chloride[6] and benzyl bromide (or chloride). Treatment of $B_{10}H_{13}Na$ with diphenylchlorophosphine in ether solution resulted in the desired substitution; diphenylphosphinodecaborane (IV, m.p. 147°) was recovered in 56.5% yield.[6a] Compound IV is readily soluble in organic solvents except petroleum ether. It was of particular interest to determine whether the lone pair of electrons would be available for additional reaction.



$$B_{10}H_{13}Na + ClP(C_6H_5)_2 \longrightarrow NaCl + B_{10}H_{13}-P(C_6H_5)_2$$

IV

Appropriate reactions were attempted, but $B_{10}H_{13}-P(C_6H_5)_2$ was found not to form adducts with Lewis acids such as borine (from diborane), trimethylborane, boron trifluoride, or boron trichloride, it could not be oxidized (*e.g.*, with sulfur in hot benzene), and quaternization attempted with methyl (and ethyl) iodide in ether as well as in benzene solution did not occur. This markedly contrasts the behavior of tertiary phosphines or monomeric phosphinoboranes, and clearly indicates that the unshared electron pair at the phosphorus atom has been absorbed into the electron-deficient decaborane nucleus.

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[6a] NOTE ADDED IN PROOF.—After this paper was accepted for publication, E. L. Muetterties and V. D. Aftandilian reported the reaction between $B_{10}H_{13}MgI$ and $(C_6H_5)PCl$ to give $B_{10}H_{13}P(C_6H_5)_2$, m.p. 136–137° (*Inorg. Chem.*, **1**, 731 (1961)).