

Fig. 1.— B^{11} magnetic resonance spectrum (19.2 Mc.) of aqueous $Rb_2B_{10}H_{14}$ externally referenced to trimethyl borate. Possible assignments of peaks to specific boron environments of predicted $B_{10}H_{14}^{-2}$ structure are noted along with the BH spin-spin coupling constants. Position of collapse of individual boron resonance doublets and triplet on irradiation of H^1 at 60 Mc. is indicated at the top. As noted by a referee, an alternative scheme is simply the assignment of the 1,3 and 2,4 boron atoms to the high and low field doublets, respectively.

saturating 60 Mc. field, the multiplets of the B^{11} spectrum successively collapsed as noted in Fig. 1. Acidified solutions of $B_{10}H_{14}^{-2}$ have a B^{11} spectrum that consists of three peaks (146 c.p.s. separations at 19.2 Mc.) of unequal intensity. Exchange of hydrogen atoms may be rapid under these conditions. In any case, the spectrum sheds no light on the $B_{10}H_{14}^{-2}$ - $B_{10}H_{15}^{-}$ equilibrium⁷ nor on the $B_{10}H_{15}^{-}$ structure.

Experimental

Reagents and Equipment.—See paper V.¹

Synthesis of $B_{10}H_{14}^{-2}$.—To a stirred solution of 0.04 mole of KBH_4 in 200 ml. of distilled water was added 0.02 mole of decaborane. The outlet of the flask was connected to a wet test meter, and within 15–30 min. about 3–4 l. (~ 0.15 mole) of hydrogen evolved. At this stage, essentially all of the decaborane had dissolved. The solution was filtered, and saturated aqueous CsCl solution was added until no further precipitation was evident. The yield of crude $Cs_2B_{10}H_{14} \cdot CsCl$ (*vide infra*) averaged 0.144 mole (72%). Yields up to 90% were obtained by using 0.08 mole of KBH_4 instead of 0.04 mole.

Characterization of $B_{10}H_{14}^{-2}$ Salts.—The simple cesium and rubidium salts were prepared by adding a saturated cesium or rubidium fluoride solution to the reaction solution obtained from decaborane and KBH_4 . The tetraaminozinc salt was prepared in a similar fashion employing a concentrated solution of zinc chloride in ammonium hydroxide. The zinc salt was recrystallized from hot aqueous ammonium hydroxide, and the other salts were recrystallized from hot water.

Anal. Calcd. for $Cs_2B_{10}H_{14} \cdot 0.5H_2O$: Cs, 66.8; B, 27.2; H, 3.79. Found: Cs, 65.1; B, 27.7; H, 3.81.

Anal. Calcd. for $Cs_2B_{10}H_{14} \cdot CsCl$: Cs, 71.7; B, 19.5; H, 2.52; Cl, 6.37. Found: Cs, 70.6; B, 19.5; H, 2.87; Cl, 6.63.

Anal. Calcd. for $Zn(NH_3)_4B_{10}H_{14}$: Zn, 25.6; N, 21.9; B, 42.4; H, 10.3. Found: Zn, 25.2; N, 21.5; B, 42.1; H, 9.65.

Anal. Calcd. for $Rb_2B_{10}H_{14} \cdot 1.5H_2O$: Rb, 53.3; B, 33.7. Found: Rb, 53.7; B, 33.5.

Infrared Spectra.—The infrared spectra of Nujol mulls of the $B_{10}H_{14}^{-2}$ salts show the following major characteristics attribut-

able to the anion: 2460 cm^{-1} (vs), 2400 cm^{-1} (m), 2330 cm^{-1} (m), ~ 2000 cm^{-1} (vw), and 1200 cm^{-1} (s). From 1200 cm^{-1} down, the spectral details vary from salt to salt. In the case of $Cs_2B_{10}H_{14} \cdot 0.5H_2O$ and $Rb_2B_{10}H_{14} \cdot 1.5H_2O$, there are major absorptions at 1070 cm^{-1} (m), 1030 cm^{-1} (s), 775 cm^{-1} (m), and 726 cm^{-1} (m). Solutions of $Rb_2B_{10}H_{14}$ in water show the same BH stretching frequencies at 2460, 2400, and 2330 cm^{-1} as a mull of the solid. The absorptions at 2400 and 2330 cm^{-1} suggest that a BH_2 group is present, and the broad weak absorption at 2000 cm^{-1} may reflect a B–H–B grouping.

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The Synthesis of Difluoraminosulfur Pentafluoride¹

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Several monosubstituted derivatives of sulfur hexafluoride are known. These include SF_5Cl , SF_5OF , SF_5OSF_5 , SF_5OOSF_5 , and RSF_5 , where R is an alkyl, substituted alkyl, aryl, or perfluoroalkyl radical.² We wish to report the synthesis of difluoraminosulfur pentafluoride, SF_5NF_2 , a derivative of sulfur hexafluoride containing the previously unreported SF_5-N bond.

This compound has been obtained in a number of reactions, but the best method of preparation is the reaction of disulfur decafluoride with tetrafluorohydrazine at 150° in a stainless steel autoclave.

Difluoraminosulfur pentafluoride is a white solid at -186° and a colorless liquid below its boiling point, which is roughly estimated from vapor pressure data as -17° . It has been recovered unchanged after storage at room temperature for periods in excess of 1 month.

The structural assignment of this compound is based on molecular weight determinations, nuclear magnetic resonance, and infrared analysis, all of which are consistent with the structure SF_5NF_2 . The infrared spectrum is shown in Fig. 1. Attempts at obtaining consistent elemental analyses were not successful.

Besides SF_5NF_2 , the major product, several other compounds are isolated from the reaction mixture. These include SF_6 , SiF_4 , SOF_2 , SF_5OSF_5 , and a compound whose infrared spectrum is nearly identical with that of $SF_4(SO_2F)_2$.³ The oxygen- and silicon-containing compounds, however, are formed during transfer in the glass vacuum system. The last two compounds are present in only trace amounts.

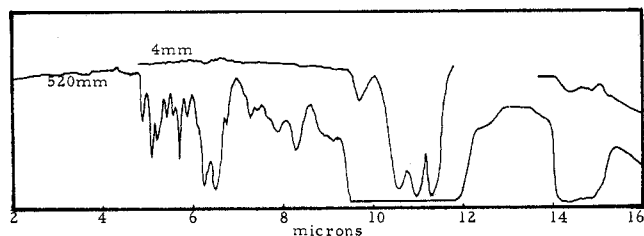
Optimum conversions are obtained at a reaction temperature of 150° after 3 hr. This was determined by

(1) This work was supported by the Department of the Navy under Contract NOrd 16640, Subcontract No. 16 with Allegany Ballistics Laboratory.

(2) H. L. Roberts, *Quart. Rev. (London)*, **16**, 30 (1961).

(3) J. M. Shreeve and G. H. Gady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

(7) J. A. Dupont and M. F. Hawthorne have reported the preparation of the $B_{10}H_{15}^{-}$ ion by reaction of $B_{10}H_{14}^{-2}$ and HCl in alcohol [*Chem. Ind. (London)*, 405 (1962)].

Fig. 1.—Infrared spectrum of SF₅NF₂.

monitoring a reaction using gas chromatographic analysis. Samples were taken at regular intervals over a 5-hr. period. The peak due to SF₅NF₂ gradually grew larger until the reaction mixture had been heated for 3 hr. After this time the peak size gradually diminished. Higher temperatures also gave decreased yields, possibly due to the tendency of S₂F₁₀ to decompose quite rapidly at 200° to SF₄ and SF₆.⁴

Difluoramino sulfur pentafluoride also has been obtained as a product of the electric discharge reaction of tetrafluorohydrazine with SF₄, SO₂, S₂F₁₀, and thiophosgene. It also is formed in the reaction of fluorine and thiourea.

Experimental

Disulfur decafluoride⁵ (5.08 g., 0.02 mole) and tetrafluorohydrazine⁶ (2.08 g., 0.02 mole) were condensed into an evacuated 300-ml. stainless steel autoclave and heated at 150° for 3 hr. The autoclave was cooled to -78° and the more volatile products (fraction A) were condensed into a cylinder in the vacuum line. The material (fraction B, 1.03 g.) remaining in the autoclave was separated by gas chromatography using a 40 ft. glass column (0.5 in. diameter) packed with the ethyl ester of Kel-F Acid 8114⁷ on Chromosorb (35 g. of ester/100 g. of Chromosorb). Helium at a flow rate of 125 cc./min. was used as the carrier gas. Good separation of the products was obtained by this method, although the first components to be eluted (SiF₄, SF₆, and unreacted N₂F₄) could not be obtained in pure state without additional separation. Other peaks, in order of their elution, were due to SOF₂, SF₂NF₂, SO₂, SF₅OSF₅, S₂F₁₀, and a compound whose infrared spectrum is very similar to SF₄(SO₂F)₂. A total of 0.88 g. of pure SF₅NF₂ was recovered.

Analysis. (a) **Molecular Weight.**⁸—Calcd. for SF₇N: 179.0 Found: 178.2 (average of 7 determinations on 3 separate samples).

(b) **Nuclear Magnetic Resonance.**⁹—The n.m.r. spectrum showed three peaks as described below.

Peak	Chemical shift, p.p.m.	Pattern and splitting	Rel. area	Assignment
A	-144.8	Broad triplet	1.00	NF ₂
B	-127.0	Multiplet	0.5	SF
C	-115.0	Multiplet	1.92	SF ₄

The spectrum for the SF₅ group was analyzed according to the methods of Merrill, Williamson, Cady, and Eggers.¹⁰ The pat-

(4) W. R. Trost and R. L. McIntosh, *Can. J. Chem.*, **29**, 508 (1951).

(5) A sample of this compound was generously supplied by Dr. James W. Dale, Monsanto Research Corp., Everett, Mass.

(6) 99% purity, obtained from E. I. du Pont de Nemours and Co., Wilmington, Del.

(7) Kel-F Acid 8114 was obtained from 3M Co., St. Paul, Minn.

(8) Determined by the vapor density method.

(9) These spectral results were obtained on a Varian High-Resolution nuclear magnetic resonance spectrometer Model V-4300-2, provided with field homogeneity control, magnet insulation, and superstabilizer. Chemical shifts were determined by side-bands applied with an audio oscillator for which the frequency is continuously monitored by an electronic counter. A tube of CF₃COOH was used as a reference. The frequency was 56.4 Mc.

terns were much as expected for this group. In addition, the four basal fluorines are coupled by 19 c.p.s. to the two fluorine atoms in the NF₂ group, and the apex atom is coupled by 4.5 ± 0.3 c.p.s. It will be noted that the apex fluorine atom is downfield from the basal atoms, which is the same relationship as that found¹¹ when the SF₅ substituent contains carbon attached to sulfur, and opposite to that usually found for oxygen attached to the sulfur atom.

(c) **Infrared.**—The infrared spectrum of SF₅NF₂ (Fig. 1) shows peaks at 9.72 (s), 10.58 (vs), 10.99 (vs), and 11.33 (vs) μ. Although no specific assignments have been made, the peaks are in the general region usually assigned to N-F and S-F absorptions.

(10) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, **1**, 215 (1962).

(11) N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1043 (1957).

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The Dissociation Constants of α-Oxyhyponitrous Acid¹

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Sodium α-oxyhyponitrite, Na₂N₂O₃, has been titrated with HCl at 1°. Experimental values of pK₁ and pK₂ have been extrapolated to infinite dilution to give the thermodynamic values, pK₁ = 2.51 and pK₂ = 9.70. These data have been interpreted as excluding the structure HO-NON-OH for α-oxyhyponitrous acid.

Experimental

Sodium α-oxyhyponitrite was prepared as previously described² by a modification of the procedure of Addison, *et al.*³ Baker analyzed reagent potassium chloride was used to adjust the ionic strength.

The titration was carried out at 1° under a nitrogen atmosphere using a Beckman Model G pH meter standardized against NBS buffers of pH values of 4.01 and 6.97 at 1°. The pH meter and temperature compensator were calibrated against a Leeds and Northrup Type K-2 potentiometer.

The weighed sample of sodium α-oxyhyponitrite was introduced and dissolved under a nitrogen atmosphere. In most experiments 1 ml. of 1 N NaOH (carbonate-free) was introduced before the titration with 1 N HCl. In the later experiments the titrant was changed to 0.01 N HCl just on the alkaline side of the end point for the titration of N₂O₃⁻² to HN₂O₃⁻. This allowed increased accuracy in evaluation of the fraction titrated just past this end point.

The values of pK₂ were obtained from the titration data by interpolation of the point where N₂O₃⁻² was half-titrated to HN₂O₃⁻.

Values of pK₁ were calculated at each point past the end point by the procedure outlined below. The average number of

(1) Presented in part before the Division of Physical Chemistry at the 141st National Meeting of the American Chemical Society, March, 1962, in Washington, D. C.

(2) H. R. Hunt, Jr., J. R. Cox, Jr., and J. D. Ray, *Inorg. Chem.*, **1**, 938 (1962).

(3) C. C. Addison, G. A. Gamlen, and R. T. Thompson, *J. Chem. Soc.*, 338 (1952).