decomposed over a wide range. Attempts to prepare an analytically pure sample have failed.

Addition to N-Trimethylborazine.—On attempting the reaction of N-trimethylborazine and bromine under vacuum, by condensing them together as solids and then warming to their melting point, an explosion resulted. However, if the reaction was carried out at atmospheric pressure as described for borazine, the N-trimethylborazine also reacted smoothly. For 0.90 g. of N-trimethylborazine (7.4 mmoles) plus 3 ml. of Br_2 (54 mmoles) at 0°, the yield of dried solid adduct was 4.04 g. or 91% of the theoretical based on three molecules of Br_2 adding to one of N-trimethylborazine. The adduct softened at 125°, m.p. 145° dec.

Purification of this intermediate was precluded by its ready hydrolysis, particularly in solution. Similar behavior has been noted[8] for other halocyclotriborazanes and they are normally allowed to react as soon as they are formed. Thus, B-hexachlorocyclotriborazane[7] prepared directly from HCl and B-trichloroborazine under vacuum conditions has been found to be hydrolyzed a few per cent.

Treatment, similar to the above, of B-trichloroborazine and hexamethylborazine with Br_2 produced no reaction as evidenced by the 95% recovery of the respective unreacted borazines.

Bromine Adduct Pyrolyses.—The orange-yellow solid adducts were pyrolyzed for several hours under vacuum at 80–140°. A white crystalline solid collected on a cold water condenser immediately above the hot zone and the more volatile materials traveled into a succeeding −196° trap. The volume of gas trapped at −196° (but volatile at −80°) was measured in calibrated bulbs on a vacuum system. The gas was identified as HBr by its infrared spectrum.[9] The solids were identified by their melting points and infrared spectra[10] as B-tribromoborazine (m.p. 126–128°; lit.[11] 128°) for the borazine adduct and B-tribromo-N-trimethylborazine (m.p. 143–146°; lit.[10] 143°) for the N-trimethylborazine adduct. The pyrolysis data are summarized in Table II.

Infrared Spectra.—Nujol mulls of all solids were prepared in a glove box and the spectra determined on a Perkin-Elmer Infracord spectrophotometer.

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[9] R. H. Pierson, A. N. Fletcher, and E. S. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

[10] I. M. Butcher, W. Gerrard, E. F. Mooney, R. A. Rothenbury, and H. A. Willis, *Spectrochim. Acta*, **18**, 1487 (1962).

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Reaction between Sulfur Hexafluoride and Hydrogen Iodide

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Sulfur hexafluoride is well known for its inert character. It is reported that this gas is not reactive under ordinary laboratory conditions.[1]

A variety of sulfur compounds are reduced by anhydrous hydrogen iodide, liberating hydrogen sulfide and iodine in quantitative yields.[2–4] It was of interest therefore to investigate the reaction between hydrogen iodide and sulfur hexafluoride. Preliminary studies indicated that this seemingly inert gas could be reduced easily at room temperature (30 ± 2°). The results of such an investigation are reported in this communication.

Experimental

Preparation of Sulfur Hexafluoride.—In the absence of a source for elemental fluorine, sulfur hexafluoride was prepared in the present investigation by the reaction between elemental sulfur and a metallic fluoride like cobalt(II) fluoride or antimony(III) fluoride, at elevated temperature under vacuum, although the yield of sulfur hexafluoride was very small under these conditions. The products of such a reaction are known to contain lower fluorides of sulfur (S_2F_2, SF_4, and traces of S_2F_{10}) and fluorides of silicon as well as a small quantity of sulfur hexafluoride.[1] The hexafluoride could be freed from these impurities in the following way. The gaseous products evolved from the reaction vessel were condensed in a trap cooled by liquid air. The condensate was later allowed to thaw in a current of nitrogen, and the issuing gases were passed through an aqueous solution of potassium hydroxide and then through an alcoholic solution of potassium hydroxide.[5] The unabsorbed gas was dried through a sulfuric acid bubbler and over phosphorus pentoxide and then frozen in a trap cooled by liquid air. The noncondensable gaseous impurity was removed by evacuation. The condensate was allowed to sublime into a gas measuring buret over mercury from which known volumes of the gas could easily be dispensed into the reaction vessel connected to a vacuum manifold. In this way it was possible to obtain 5–10 ml. of pure sulfur hexafluoride at a time.

Preparation of Anhydrous Hydrogen Iodide.—Hydrogen iodide was prepared by the hydrolysis of phosphorus triiodide formed by the action of iodine and red phosphorus.[6] The hydrogen iodide liberated was swept off by a stream of dry hydrogen or nitrogen and passed through U tubes cooled to −16 and −60° to remove moisture and iodine.[7] The gas was then solidified in a trap cooled by liquid air. The carrier gas was pumped off, and pure anhydrous hydrogen iodide was sublimed into the reaction vessel. The hydrogen iodide taken for the reaction was in 50- to 100-fold excess over the amount of sulfur hexafluoride.

The reaction between sulfur hexafluoride and hydrogen iodide started immediately when the two gases were allowed to mix with each other in the reaction vessel. This was indicated by the color of the liberated iodine, the intensity of which increased gradually with time. After 4–6 hr., the products of the reaction were analyzed in the following way. A stream of nitrogen was passed (for 1 hr.) through the vessel to sweep off the products through traps containing chilled carbon tetrachloride (−16°) followed by sodium hydroxide (4 *N*) holding a cadmium hydroxide suspension. The carbon tetrachloride dissolved and retained iodine vapors present in the gaseous stream while hydrogen sulfide and hydrogen fluoride were absorbed by the alkali. Cadmium sulfide was separated by filtration and estimated iodometrically.

Fluorine was estimated in the filtrate by a modified method of Willard and Winter.[8] Iodine retained in carbon tetrachloride and in the reaction vessel was extracted with an aqueous solution of potassium iodide (10%) and titrated against a standard solution of thiosulfate to determine the iodine content.

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[1] J. H. Simons, "Fluorine Chemistry," Volume I, Academic Press, Inc., New York, N. Y., 1950, p. 90.

[2] A. R. V. Murthy, *Proc. Indian Acad. Sci.*, **36**, 425, 537 (1952).

[3] A. R. V. Murthy, *ibid.*, **37**, 11, 17, 23 (1953).

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[5] J. W. Mellor, "Supplement to the Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Supplement I, Longmans, Green and Co., London, 1956, p. 57.

[6] J. N. Friend, "A Text Book of Inorganic Chemistry," Vol. VIII, Charles Griffin and Co., Ltd., London, 1915, p. 210.

[7] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., London, 1922, p. 172.

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The analytical results of a few representative experiments indicated that the sulfur hexafluoride taken was quantitatively reduced to hydrogen sulfide, and corresponding amounts of hydrogen fluoride as well as iodine were liberated. While the ratio of iodine produced to sulfur hexafluoride taken was found to be eight, the quantity of hydrogen fluoride produced was found to be six times that of sulfur hexafluoride.

The reaction may be visualized to take place in terms of the equation

$$SF_6 + 8HI \longrightarrow H_2S + 6HF + 4I_2$$

Such a reaction is to be expected from thermochemical data[9] ($\Delta H^\circ = -177.8$ kcal.) and the differences in electronegativities of the elements involved in this process.

Although the end products of the reduction are hydrogen sulfide, hydrogen fluoride, and iodine, it is likely that the reaction proceeds through several intermediate stages involving sulfur and iodine compounds.

From the foregoing observations it is possible to make use of the reaction between hydrogen iodide and sulfur hexafluoride for purposes of analyzing sulfur hexafluoride under the usual laboratory experimental conditions.

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(9) S. Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Co., Inc., 10th Ed., New York, N. Y., 1958, pp. 506-508.

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Rare Earth Compounds. II. The Series $YbLn_2S_4$[1]

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When ytterbium sesquisulfide is heated under vacuum to a sufficiently high temperature, sulfur (and a small amount of ytterbium) is lost through volatilization and an ytterbium-deficient monosulfide phase is formed. Magnetic susceptibility measurements indicate that the ytterbium is converted from a trivalent to a divalent species in the process, the amount of trivalent character remaining being dependent upon the deviation from the ideal stoichiometry of YbS.[3] In view of the reducibility demonstrated by ytterbium sesquisulfide, we thought it might be possible to heat, under vacuum, mixtures of trivalent ytterbium with other rare earth metal sulfides to obtain double sulfides with the ytterbium present in the divalent state. By this procedure we have prepared for the first time and subsequently identified the X-ray powder diffraction spectra of a series of compounds with the nominal stoichiometry $Yb^{II}Ln_2S_4$ for Ln = La, Pr, Y, Ho, Er, and Tm. The known, analogous compound $Yb^{II}Yb^{III}{}_2S_4$ was also prepared.

Experimental

The starting compounds were the "polysulfides" of La and Pr and the sesquisulfides of Y, Ho, Er, and Tm, prepared as previously reported.[4] The starting ytterbium sulfide was prepared in a similar manner from the elements at 700° and consisted of a mixture of low temperature phases of over-all stoichiometry $YbS_{1.51}$.[5]

Mixtures of the appropriate sulfides were intimately ground in a mortar and then pressed at 50,000 p.s.i. A 2.5% excess of ytterbium sulfide was used to compensate for volatilization loss of ytterbium during the subsequent vacuum heating step. Pieces of a pressed mixture were placed in a molybdenum crucible which, in turn, was placed in an induction furnace connected to a vacuum line. The system was evacuated to 10^{-5} torr before heating. The temperature was raised over the course of 1.5–2 hr. and then maintained at 1500–1515° for an additional hour. For the preparation of YbY_2S_4 the temperature was maintained at 1485°. The bulk of the excess sulfur present in the mixtures was evolved rapidly at temperatures below 1200°. Loss of ytterbium became appreciable at about 1450°, as evidenced by the appearance of a glow discharge when the temperature was raised too rapidly. The cooling rate was moderately rapid, taking about 3 min. to cool from the reaction temperature to below 800°.

The ytterbium sulfide sample was pressed and fired in a manner similar to that used for the mixed rare earth samples except that the firing was carried out in an atmosphere of argon and held at 1520° for 0.5 hr.

X-Ray diffraction spectra were obtained from powdered specimens on a diffractometer employing nickel-filtered, copper Kα radiation. Room temperature magnetic susceptibilities were measured on powders contained in fused silica tubes by the Gouy technique.

Results and Conclusions

The X-ray diffraction peaks obtained from the ternary compositions containing La, Pr, Y, and Ho were all indexed on the basis of the body-centered cubic Th_3P_4 structure. The data and cell parameters deduced therefrom are presented in Table I. The columns labeled P/P_0 contain the relative peak heights, on the scale of 1 to 20, as measured directly from the diffractometer strip-chart record. The unmixed ytterbium compound and those containing Er and Tm exhibited a series of homologous spectra, all the peaks of which were indexed on the basis of the orthorhombic Yb_3S_4 structure.[3] The data for these three compounds are presented in Table II. In this case the values in the P/P_0 column refer to all three compounds. The fourth significant figure for the a and b cell parameters and the third figure for the c parameter cannot be considered precise because the available indices allowed calculations up to a Bragg angle of only 47° (2θ).

To provide a check on the stoichiometry produced by the vacuum heating, the $YbTm_2S_4$ product was analyzed for all three elements and found to contain them in the atomic ratio 1.00:2.00:3.97. Results of an analysis on the Yb_3S_4 product gave the elemental ratio 3.00:4.08.

None of the compounds produced melted at the firing temperatures, although the sesquisulfides of Er and Tm do melt under similar conditions. The ternaries with Th_3P_4 structures fired to hard, black products and gave black powders on grinding. Those products having the Yb_3S_4 structure could be crushed to yield

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(1) This work was done under the Lockheed Independent Research Program.

(2) Correspondence concerning this paper should be addressed to Melvin Tecotzky.

(3) J. Flahaut, L. Domange, M. Guittard, and J. Loriers, *Bull. soc. chim. France*, **28**, 102 (1961).

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(5) To be published.