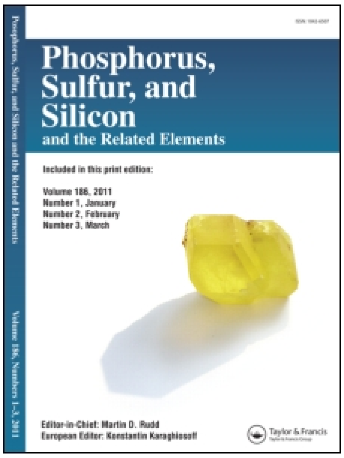

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THE REACTION OF SULFUR TETRAFLUORIDE WITH ANHYDROUS HYDROGEN HALIDES

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Communication to the Editor

The Reaction of Sulfur Tetrafluoride with Anhydrous Hydrogen Halides

ABSTRACT

Sulfur tetrafluoride is found to react with anhydrous hydrogen chloride/bromide/iodide at –78° in freon (II), CCl_3F, medium to yield sulfur dichloride, disulfur dibromide and sulphur diiodide.

It has been reported that sulfur tetrafluoride undergoes reduction with an excess of anhydrous hydrogen iodide at room temperature (25°) to give quantitative amounts of hydrogen sulphide and iodine.[1] This communication reports the isolation of the intermediate product of this reaction at low temperature as well as the products of reaction of sulfur tetrafluoride with anhydrous hydrogen chloride and hydrogen bromide.

Into a clear solution of sulfur tetrafluoride[2] (15 g) in 200 ml of freon (II), CCl_3F, maintained at –78° is passed anhydrous hydrogen chloride/bromide/iodide for 3 hours. At the end of this interval, the stream of hydrogen halide is stopped and the reaction products are examined for their contents:

a) In the case of hydrogen chloride a white precipitate is formed in the initial stages which disappears gradually. The colour of the solution turns brownish red during this interval. The contents of the reaction vessel are flushed with a slow stream of nitrogen to sweep off the gaseous contents. During this flushing the cold bath is removed and the reaction vessel is allowed to attain a temperature of 20° over a period of half an hour. The effluent gases are passed through an aqueous solution of potassium iodide. Considerable quantity of iodine is liberated during this process indicating the presence of free chlorine among the products of reaction. Hydrogen fluoride also could easily be detected in this gaseous stream. Any unreacted reactants are also swept off in the current of nitrogen. This operation was continued for an hour to expel all the gaseous contents in the solvent. The solvent freon is then distilled off at 30°. About 5 ml of red liquid is left behind which distilled at 59°C. The pure liquid gave an absorption band at 512 cm^{-1} corresponding to S–Cl stretching frequency in sulfur dichloride. The liquid could therefore be identified as sulfur dichloride. This could be confirmed by its hydrolytic reaction in which sulfide, sulfite, thiosulfate and elemental sulfur are formed.[3] Thus the reaction between sulfur tetrafluoride and hydrogen chloride could be represented by the equation,

$$SF_4 + 4HCl \rightarrow SCl_4 + 4HF;\ SCl_4 \rightarrow SCl_2 + Cl_2$$

It is rather difficult to isolate and characterize the intermediate product SCl_4 under these experimental conditions.

b) In the case of hydrogen bromide an orange brown solution is obtained. The reaction products are found to contain hydrogen fluoride and bromine. The liquid (4–5 ml) left behind after removing the solvent is found to boil at 48°/0.1 mm. It is not possible to identify the product by ir absorption as its absorption frequencies of S–Br are considerably lower than sulfur dichloride and are around 354 cm^{-1}. This liquid also on hydrolysis gives sulfur, sulfite, sulfide and thiosulfate. The elemental analysis after hydrolysis indicated an atomic ratio for sulfur to bromine 1:1. From these results, it could be inferred that disulfur dibromide is the final product of reaction between anhydrous hydrogen bromide and sulfur tetrafluoride. This is further confirmed by oxidation with chloramine-T and reduction with excess of anhydrous hydrogen iodide.[4] Ten equivalents of chloramine-T are consumed per mole of the product and six gram atoms of iodine are liberated for every mole of the sulfur bromide taken.

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

$$SF_4 + 4HBr \rightarrow SBr_4 + 4HF;\ SBr_4 \rightarrow SBr_2 + Br_2;$$
$$2SBr_2 \rightarrow S_2Br_2 + Br_2$$

It may be pointed out that the higher bromides of sulfur, i.e., SBr_4 and SBr_2 have so far not been isolated or characterized.

c) In the case of hydrogen iodide, a deep brownish purple precipitate is obtained, when the stream of anhydrous hydrogen iodide is passed through the sulfur tetrafluoride solution. The precipitate is filtered off at the pump at –78°, washed with cold (–78°) freon till no more iodine color appears in the filtrate. Then the precipitate is dried at the pump for 18 hours at –78°. The sample on analysis after hydrolytic reaction is

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[4] D. K. Padma and A. R. Vasudeva Murthy, *Zeit. Anorg. Allgem. Chem.*, **342**, 307 (1966).

found to contain sulfur and iodine in the ratio 1:2. So the molecular formula is SI_2. The overall reaction may be represented as:

$$SF_4 + 4HI \rightarrow SI_4 + 4HF\text{: } SI_4 \rightarrow SI_2 + I_2$$

It is important to mention that the intermediate SI_4 could not be isolated or characterized and that sulfur diiodide is very unstable above −40° and decomposes to sulfur and iodine. It is difficult from the above analytical data to say whether SI_2 is a monomer or a polymer. Molecular weight determinations have not been done as no suitable solvent could be found. The intense color of the solid makes raman spectroscopy less applicable. Low temperature ir below 400 cm^{-1} may throw some light on the structure of the molecule.

The following experimental facts bear evidence that it is a compound and not a mixture.

1) Iodine in the compound is not sublimable at −78° in vacuum, but if the compound is decomposed by raising the temperature to 20° and then held at −78° iodine sublimes out.

2) Iodine is soluble in all the solvents tried at low temperature but not the undecomposed compound.

3) Anhydrous hydrogen iodide is a well-known reductant for several sulfur compounds such as S_2Cl_2,[5] S_2Br_2,[4] SCl_2,[6] SF_4,[7] SOF_2,[8] S_4N_3Cl,[9] $PSCl_3$ [10] etc. In all cases the sulfur present in the compound is quantitatively reduced to hydrogen sulfide. Elemental sulfur does not undergo reduction under similar conditions. It has been found that the sulfur diiodide reacts with excess of anhydrous hydrogen iodide in freon medium at −78° in about 18 hours during which interval the reaction vessel attains a temperature of 20°, to yield quantitative amounts of hydrogen sulfide. On the other hand a decomposed sample if similarly treated gives very little hydrogen sulfide and sulfur is found floating.

These observations lend support for the inference.

It is interesting to point out that sulfur tetrafluoride has been reduced quantitatively to hydrogen sulfide by excess of anhydrous hydrogen iodide[7] at 25° whereas at low temperature (−78°), the intermediate product of the reaction could be isolated and then further reduced to hydrogen sulfide at a higher temperature.

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