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SILICON TETRAFLUORIDE : PREPARATION AND REDUCTION WITH LITHIUM ALUMINIUM HYDRIDE

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SUMMARY

Pure silicon tetrafluoride can be prepared in 66% yield from silicon tetrachloride by refluxing with lead fluoride in acetonitrile. The gas can be reduced to pure silane by lithium aluminium hydride in diethyl ether.

INTRODUCTION

It has been shown that lead fluoride partially fluorinates sulphuryl chloride in boiling acetonitrile to sulphuryl-chloride fluoride leaving behind lead chloride fluoride [1]. It was of interest to investigate whether such partial fluorination takes place with silicon tetrachloride under similar experimental conditions. It is observed that in the case of silicon tetrachloride complete fluorination takes place giving silicon tetrafluoride in good yield.

It may be mentioned that silicon tetrachloride undergoes complete fluorination by sodium fluoride in acetonitrile [2].

EXPERIMENTAL

A. Preparation of silicon tetrafluoride

50 g. of finely powdered and dried lead fluoride is suspended in 60 ml of pure, dry acetonitrile in a three-necked flask

fitted with a magnetic stirrer and ice water-cooled condenser. The assembly is protected from moisture by using intensely dried apparatus and appropriate guard tubes. The entire operation is carried out in a slow stream of dry nitrogen . To the gently refluxing acetonitrile is added 5 ml of silicon tetrachloride (purity - 99.9%) over a period of 30 minutes by means of a dropping funnel. The SiF_4 formed is swept into two traps - the first maintained at -70°C and the second at liquid nitrogen temperature (-197°C). Any unreacted $SiCl_4$ and the acetonitrile coming over with the SiF_4 are condensed in the first trap and the SiF_4 is condensed in the second trap. After the completion of the addition of $SiCl_4$, the solvent is allowed to reflux for a further period of 30 minutes. The uncondensed gases are removed from the SiF_4 trap while the trap is cooled to -197°C and the SiF_4 is allowed to sublime into a previously evacuated glass globe from a -60°C bath.

The IR spectrum of the gaseous sample shows the presence of hydrogen chloride contaminating the SiF_4. The gas sample is purified by absorbing the HCl in ether in which HCl is soluble and SiF_4 practically insoluble. The ether is removed by dissolving in benzene. Thus the following procedure is adopted for obtaining a pure sample of silicon tetrafluoride.

The impure gas is condensed into dry distilled ether (15 ml) in a trap and then warmed to room temperature. This is allowed to stand for one hour, when the ether absorbs the HCl. The remaining gas (SiF_4 and ether) is condensed into dry distilled benzene (25 ml). The trap is warmed to room temperature and is allowed to stand for one hour, when the benzene absorbs the ether vapours. After cooling to -197°C, the liquid nitrogen bath is withdrawn and replaced with a slush bath at -80°C and the subliming SiF_4 is collected in a glass globe. The IR spectrum of the gaseous sample recorded on a UR-10 (Carl Zeiss) spectrophotometer shows only the characteristic band (1030 cm^{-1}) of silicon tetrafluoride and complete absence of impurities. The purity of the SiF_4 sample is over 99.8% (chemical analysis).

The average yield of SiF_4 is 66% as observed in 4 preparations and is based on $SiCl_4$ used.

The residue in the fluorination flask contains PbClF and the excess PbF_2. The fluorination reaction may be represented by the equation

$$4\ PbF_2 + SiCl_4 \longrightarrow SiF_4 + 4\ PbClF$$

B. Reduction of silicon tetrafluoride by lithim aluminium hydride

Lithium aluminium hydride reduces silicon tetrafluoride-amine adducts at elevated temperatures giving rise to aminofluoro-silanes, $SiF_{4-n}(NR_2)_n$[3]. It has been found in the present work that SiF_4 itself will undergo reduction in ether to give silane.

In a reaction vessel fitted with appropriate ground glass joints and stopcocks, a small amount (200 mg) of lithium aluminium hydride in dry ether (20 ml) is taken. SiF_4 gas (100 mg) is condensed into the reaction vessel at -196.7°C and the reactants are brought to room temperature. The product gas is freed from ether using benzene as described in section A. The IR spectrum of the gaseous sample shows only the characteristic bands of silane (974.0, 2190.0, 914.0 cm^{-1}). No other band is observed to indicate the presence of any impurity.

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