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Fluorine chemistry synthesis

Preparation of hexafluorodisilane

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Abstract

Hexachlorodisilane (formed by reacting ferrosilicon and chlorine) was fluorinated with antimony trifluoride to synthesize hexafluorodisilane. Improvements in synthesis and purification of Si_2F_6 were reported. © 1997 Elsevier Science S.A.

Keywords: Hexafluorodisilane; Fluorination; Synthesis; Purification; Hexachlorodisilane; Ferrosilicon; Chlorine; Antimony trifluoride

1. Introduction

Owing to recent progress in the study of silicon isotope separation by means of laser radiation [1,2], technologies which facilitate mass production of silicone isotopes [3] have been realized. It has been demonstrated that hexafluorodisilane Si_2F_6 (b.p. −18.5 °C, m.p. −18.7 °C) is a suitable material for this process. When Si_2F_6 gas is irradiated with a CO_2 TEA laser at 10.6 μm band, multiple photon dissociation occurs as $Si_2F_6 + nh\nu \rightarrow SiF_4 + (SiF_2)_n$ and a silicon isotope, either ^{29}Si or ^{30}Si, is enriched in the SiF_4 produced. In these studies, more than 1 kg of Si_2F_6 was required. Furthermore, high-purity Si_2F_6 was also required for various related scientific studies such as the measurement of the vibrational spectrum [4] and infrared multiple photon absorption [5,6] of Si_2F_6 molecules, and the determination of the isotopic shift. In order to meet these requirements, we developed methods for synthesis and purification of Si_2F_6.

From among the few Si_2F_6 synthetic methods already proposed [7–9], we adopted and improved the method of obtaining Si_2F_6 by fluorination of Si_2Cl_6 (formed by reacting ferrosilicon and chlorine) with antimony trifluoride (SbF_3).

2. Experimental

2.1. Preparation of Si_2Cl_6

The reaction of ferrosilicon with chlorine gives mainly Si_2Cl_6 and a small amount of higher polysilicon chlorides. Although percentage yields of these products differ with the reaction temperature, this method is considered to be suitable for mass production of Si_2Cl_6 as compared with the other methods [10,11]. The apparatus used for Si_2Cl_6 synthesis is shown in Fig. 1. 60 g of ferrosilicon powder (43% Si, 57% Fe. Yamaishi Metals Co.) and 12 g of ammonium chloride with the purity > 99.0% (Kanto Chemicals Co.) as catalyst were mixed thoroughly and packed in a Pyrex reaction tube (outer diameter, 30 mm; length, 600 mm). Since there was a risk that the ferric chloride produced through the reaction of ferrosilicon with chlorine would choke the reaction tube, ferrosilicon powder was packed loosely leaving one-third of the tube empty. The tube was inclined at an angle of about 10°; its exit was connected to a distillation flask via a condenser.

Before starting the reaction, nitrogen (dehydrated by passing through concentrated sulfuric acid) was admitted into the reaction tube, while the tube temperature was gradually increased using an electric heater. When the temperature reached 150 °C, nitrogen supply was stopped and chlorine with the purity > 99.0% (Takachiho Shozi Co.) was gradually admitted. The chlorine was also dehydrated by passing through concentrated sulfuric acid in advance. When the temperature reached 170 °C, chlorine and ferrosilicon started to react and the temperature increased rapidly due to the heat of reaction. By controlling the electric heater current, the reaction temperature was gradually decreased to the lowest possible temperature for maintenance of a continuous reaction. The reaction proceeded even after the temperature fell to 110 °C. During the reaction, the flow rate of chlorine was maintained at around 1 bubble s^{-1}. Accordingly, as the reaction proceeded, the electric heater was moved so that all of the ferrosilicon packed in the tube could undergo complete reaction. The mixture of silicon chlorides produced was con-

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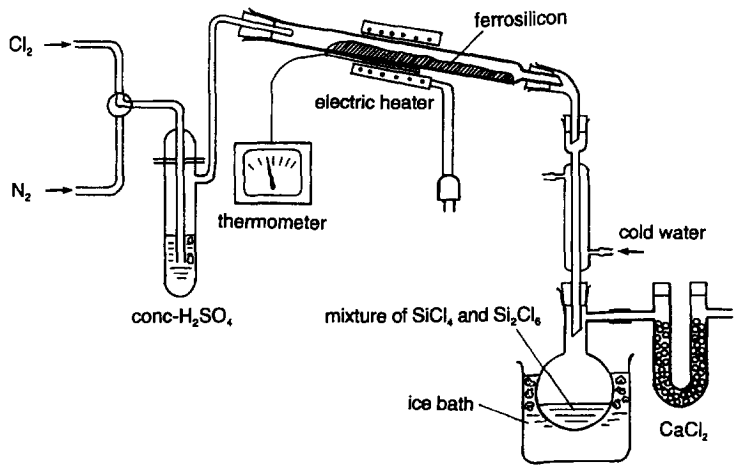

Fig. 1. Apparatus for Si_2Cl_6 synthesis.

densed and collected in a distillation flask cooled in an ice bath.

57 g of a mixture of silicon chlorides was produced from 60 g of ferrosilicon, of which 10 g was Si_2Cl_6 and the rest was $SiCl_4$ with a very small amount of higher polysilicon chlorides. The typical yield of Si_2Cl_6 was 21%, which was markedly affected by the reaction temperature. A yield of less than 10% was obtained from reactions between 180 and 200 °C and a better yield was obtained between 100 and 115 °C, which is the lowest possible temperature for maintenance of a continuous reaction.

The produced gas mixture was condensed with liquid nitrogen in a bulb attached to a vacuum line. Cooled ethanol in a Dewar vessel was prepared at a given temperature (−5 °C in this case or −50 °C in the case of Section 3) by adding liquid nitrogen in advance. The temperature of the bulb was then increased to −5 °C by changing the liquid nitrogen bath to the ethanol bath. More volatile $SiCl_4$, (vapor pressure: 150 Torr at −5 °C) the impurity, was allowed to condense in a second bulb attached to the vacuum line cooled at liquid nitrogen temperature, while less volatile Si_2Cl_6 (vapor pressure < 0.1 Torr) remained condensed in the first bulb. Owing to the large difference in the vapor pressure values, Si_2Cl_6 (b.p. 146 °C, m.p. −1 °C) and $SiCl_4$ (b.p. 58 °C, m.p. −70 °C) can be easily separated by this bulb-to-bulb distillation method.

2.2. *Preparation of Si_2F_6*

Using the Si_2Cl_6 which was produced by the above method, we obtained Si_2F_6 through fluorination of Si_2Cl_6 using SbF_3.

20 g of well-ground dried SbF_3 (purity > 99.0%, Kanto Chemicals Co.) was placed in a Pyrex reaction tube (1.5 l) shown in Fig. 2 and 0.8 ml of antimony pentachloride (purity > 95%, Kanto Chemicals Co.) was added to the tube as a catalyst. 5 g of Si_2Cl_6 was placed in the small Pyrex container connected to the tip of the Pyrex reaction tube. While cooling the small container using liquid nitrogen, air in the reaction tube was exhausted using a vacuum pump, and

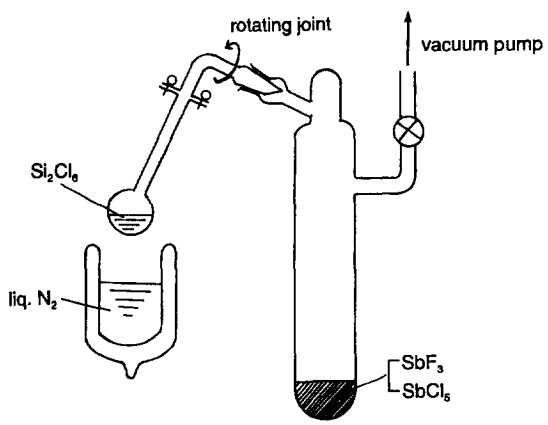

Fig. 2. Preparation of Si_2F_6.

when a sufficient vacuum condition was attained, the vacuum cock was turned off to seal the reaction tube. The tube was then disconnected from the vacuum pump and the small container for Si_2Cl_6 was kept at room temperature to induce liquefaction of Si_2Cl_6. Then the Si_2Cl_6 was slowly poured into the tube for reaction with SbF_3, as the container was rotated around the axis of the joint in Fig. 2. When SbF_3 is used as a fluorinating reagent, the temperature increases due to the heat of reaction but this time the reaction is allowed to proceed at room temperature without application of heat.

The product of the reaction was collected in another container and weighed. The yield of Si_2F_6 was over 90%; however, when the reaction proceeded more rapidly than expected or when SbF_3 was not dried sufficiently, more SiF_4 was formed as a by-product. Therefore, in order to obtain high-purity Si_2F_6, further purification was essential. Using the bulb-to-bulb distillation at a temperature between −50 °C (a cold ethanol bath was used) and liquid nitrogen temperature, Si_2F_6 of 96% purity was obtained.

3. Analysis and purification of Si_2F_6

The Si_2F_6 produced was analyzed by gas chromatography (SHIMADZU GC7A) with a 9 m long stainless steel column

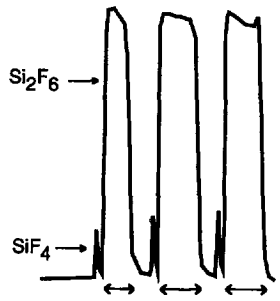

Fig. 3. Chromatogram of Si_2F_6 separated from SiF_4.

with an inner diameter of 3 mm. A powder produced by applying silicone oil over silanized diatomaceous earth was used as the packing material (silicone DC SF 96 20% on Chromosorb W AW-DMCS 60/80, made by SHIMADZU Co.). The column was coiled and incubated at a low temperature of −50 °C using a *m*-xylene slush bath near its melting point. Helium was used as a carrier gas at a flow rate of 30 ml min^{-1}. The retention time of SiF_4 was about 6.5 min and that of the main product, Si_2F_6, was about 8 min. The peaks of these two substances were clearly separated, thereby enabling a quantitative analysis of silicon fluorides. As mentioned previously, Si_2F_6 cannot be purified sufficiently by simple distillation and the impurity, SiF_4, is difficult to remove from the product. In order to obtain high-purity Si_2F_6, we attempted purification by means of fractionation through gas chromatography.

Next, the gas chromatograph used for the analysis was connected to a fractional sample collector and used for the purification. The operation conditions were identical to those described above for the analysis. Fig. 3 shows a gas chromatogram obtained when an aliquot of the product, Si_2F_6 (purity: 95%) is injected into the column through a 6.5 ml sample tube with pressure between 200 and 250 Torr. An intermittent sample injection method is adopted, allowing additional samples to be injected when a SiF_4 peak from the previously injected sample appears. The fractionation operation was repeated over ten times and the collected sample was then analyzed by gas chromatography mentioned before. As a result of this purification step, we obtained Si_2F_6 of 99% purity.

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