Preparation of Hexafluorodisilane and Reactions of Hexafluorodisilane and Hexachlorodisilane with Sulfur Trioxide

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Synopsis. Hexafluorodisilane has been prepared by the fluorination of hexachlorodisilane or hexabromodisilane by potassium fluoride in boiling acetonitrile, in yields approximating 45 and 60% respectively. Hexafluorodisilane has been characterised by infrared spectral data, vapour density measurements and analytical data. Both hexafluorodisilane and hexachlorodisilane are found to react with sulfur trioxide when heated to 400 °C for 12 h. The products of reaction are silicon tetrafluoride, silica and sulfur dioxide with hexafluorodisilane while hexachlorodisilane in addition gives rise to hexachlorodisiloxane.

The chemistry of hexahalodisilanes is interesting because of the presence of Si–Si bond and Si–X (halogen) bond which can undergo oxidation and cleavage. The bond energy of Si–Si bond is relatively weak when compared to C–C bond and therefore it undergoes homolytic cleavage on application of thermal energy. However, the Si–Si bond is thermodynamically favoured to undergo oxidation and this happens in reactions involving phosphine and phosphetane oxides[1,2] as well as phosphine sulfides.[3] In these cases, the hexachlorodisilane gets oxidised to hexachlorodisiloxane in the case of the oxides and to hexachlorodisilathiane with the sulfides. Therefore, it was of interest to see the action of sulfur trioxide on hexafluorodisilane and hexachlorodisilane.

In the reported methods for the preparation of Si_2F_6[4,5] disproportionation occurs and the product is contaminated with mixed halide fluorides. In the present modified procedure, based on the synthetic procedures evolved in this laboratory,[6,7] wherein the hexachlorodisilane or hexabromodisilane is treated with potassium fluoride in boiling acetonitrile, considerable improvement in the yields and purity are noted. Hexachlorodisilane and hexabromodisilane are prepared by standard methods.[8,9] The procedural details of preparation of Si_2F_6 and the reaction of sulphur trioxide on these hexahalodisilanes are given below.

Experimental

A Preparation of Hexafluorodisilane (Si_2F_6). Hexachlorodisilane (≈12.0 g) or hexabromodisilane (≈24 g), prepared and purified by standard methods,[8,9] is dissolved in 1,2-dichloroethane (20 ml) and added dropwise to a suspension of potassium fluoride (finely ground and dried at 110 °C in vacuum for 20 h) in boiling acetonitrile held in a three necked flask provided with a dropper, reflux condenser (with an outlet for the evolved gas) and a nitrogen inlet. The exit of the condenser is connected to two traps T_1 and T_2 maintained at −40 °C and liquid nitrogen temperature respectively. The addition is done slowly (about 2 h) and then the contents of the flask are allowed to reflux for a further period of 30 min in a slow stream of nitrogen. At the end of this period, heating and nitrogen flow are stopped, trap T_2 containing the solidified product gas is disconnected from the assembly. The uncondensable gases are removed at the pump and the solid is then allowed to sublime into a previously evacuated dry glass globe.

The infrared spectrum of the gaseous sample was recorded and the impurities SiF_4 and HCl were removed by low temperature fractional distillation (sublimation point of SiF_4=−95.7 °C, boiling point of HCl=−85 °C and of Si_2F_6=−18.4 °C). The infrared spectrum of the purified sample exhibits all the reported bands[10] of Si_2F_6 along with an absorption band at 1030 cm^{-1} characteristic of SiF_4, is as following, Observed: 420 (s), 440 (m), 520 (w), 740 (w), 840 (s), 850 (vs), 860 (s), 875 (m), 910 (w), 975—1010 (vvs, br) 1030 (SiF_4), 1060 (w), 1180 (m). (The intensities of the absorption bands are given in parentheses; vvs=very very strong, vs=very strong, s=strong, m=medium, w=weak and br=broad). The sample is found to contain more than 90% of Si_2F_6, remaining being SiF_4 as impurity as seen from the gas density measurements and chemical analysis. The compound; preparation mode (a) Si_2Cl_6 (b) Si_2Br_6; vapour density (reported, found); chemical analysis (Si(%): calcd, found, F(%): calcd, found); purity and yields are given below. a) Si_2F_6; Si_2Cl_6 and KF; (7.74,[4] 7.30); (33.01, 32.41; 66.99, 67.59),>90%; ≈45%. b) Si_2F_6; Si_2Br_6 and KF; (7.75,[4] 7.39); (33.01, 32.59, 66.99, 67.40); >93%; ≈60%. The yield of hexafluorodisilane is found to be approximately 45% with hexachlorodisilane and 60% with hexabromodisilane. This increase in yield can be attributed to the decreased bond energy of Si–Br bond compared to Si–Cl bond.

B. Reaction of Hexafluorodisilane with Sulfur Trioxide. Hexafluorodisilane (≈0.200 g, ≈1.1 m moles) containing some silicon tetrafluoride (≈10%) is condensed in a reaction vessel cooled by liquid nitrogen. Sulfur trioxide (≈0.240 g, 3.0 m moles) is condensed on to this and the reactant gases allowed to attain room temperature by withdrawing the coolant. At room temperature for 12 h no reaction occurred. Even at 300 °C the infrared spectrum shows only the reactants. The contents of the reaction vessel are then heated to 400 °C for 12 h. A white solid deposit is observed at the bottom and sides of the reaction vessel. The gas-phase infrared spectrum shows complete absence of the absorption bands of hexafluorodisilane and presence of enhanced absorption bands of SO_2,[11] 520 (s), 1150 (s), 1360 (vs), and SiF_4,[12] 1030 (s). The spectrum also shows the absence of any other compound such as hexafluorodisiloxane and sulfuryl fluoride.

The white solid in the reaction vessel is found to be silica by infrared spectroscopy. This is further confirmed by chemical tests. The solid dissolves rapidly in aqueous hydrofluoric acid to give fluorosilicic acid. The latter is identified by the formation of a white precipitate (K_2SiF_6) when potassium chloride solution is added.

C. Reaction of Hexachlorodisilane with Sulfur Trioxide. Sulfur trioxide (≈0.240 g; ≈3.0 m mole) is taken in an evacuated reaction vessel. Into this hexachlorodisilane (≈0.538 g, ≈2.0 m moles) is condensed and then the reactants are brought to room temperature. As the condensed hexachlorodisilane melts it dissolves in sulfur trioxide to form a clear colourless liquid. This is kept for 12 h at room temperature and the gas phase infrared spectrum is taken

which shows unreacted hexachlorodisilane. This is the case up to 300 °C. The reactants are then heated at 400 °C for 12 h. The infrared spectrum of the gaseous products now show the presence of hexachlorodisiloxane, sulfur dioxide and silicon tetrachloride. Sulfur dioxide and silicon tetrachloride are removed from the reaction mixture by low temperature fractional distillation. The gas phase infrared spectrum of the remaining products in the reaction vessel show the presence of only hexachlorodisiloxane,[13] 480 (s), 640 (vs), 1130 (vs), and complete absence of hexachlorodisilane.[14] The volatile hexachlorodisiloxane is removed from the reaction vessel by slow pumping till the gas phase does not show any absorption bands. It is observed that no other nonvolatile higher polychlorosiloxanes are present in the reaction vessel, except a white solid deposit at the bottom of the reaction vessel. The solid is found to be silica.

It is important to mention that these compounds are moisture sensitive and strictly anhydrous conditions have to be maintained.

The experimental results indicate that Si_2F_6 has been prepared in improved yields and greater purity. Mixed halides of silicon are not produced.

Both hexafluoro- and hexachloro-disilane have been found to undergo complete reaction with sulfur trioxide at 400 °C in 12 h. The products of reaction with Si_2F_6 are silicon tetrafluoride, sulfur dioxide and silica while hexachlorodisilane in addition gives rise to hexachlorosiloxane. With hexachlorodisilane some oxidation of the Si–Si bond occurs to form siloxane (Si–O–Si) linkage. However, with hexafluorodisilane no such oxidation is observed possibly because the nucleophilic attack on silicon by oxygen through a barrier of highly electronegative fluorine atoms occurs less predominantly at 400 °C and cleavage takes an upper hand. It has also been shown in the present investigation that higher molecular weight polysiloxanes, whose formation requires radical type cleavage and recombination, are not formed. This observation suggests the formation of the products *via* cleavage and disproportionation in both the cases.

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