A Novel Synthetic Procedure for the Preparation of Silicon Sesquioxide at Room Temperature

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Hexabromodisilane reacts with sulphur trioxide at room temperature to give pure silicon sesquioxide in almost quantitative yield, together with bromine and sulphur dioxide as the only by-products.

During the course of our investigations with hexahalogenodisilanes we observed that hexabromodisilane reacted with sulphur trioxide at room temperature to give a white amorphous solid containing intact Si–Si bonds. The solid was found to be silicon sesquioxide, Si_2O_3 (m.p. 1 635 °C, surface area 50—60 $m^2\ g^{-1}$, apparent density 0.16—0.22 $g\ cm^{-3}$), previously prepared [1] by a high-temperature method which involved heating silicon oxyhydride ($Si_2H_2O_3$) in an inert atmosphere at 900 °C. The present method is much simpler, occurs at room temperature, and the reaction goes to completion.

Experimental

Hexabromodisilane was prepared by bromination of calcium silicide.[2] It is a pure white crystalline solid melting at 90.8 °C. Sulphur trioxide was prepared by a standard method,[3] and stored in a clean, dry, evacuated glass bulb fitted with vacuum stopcocks.

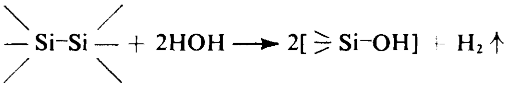
Procedure.—The reaction vessel consisted of a 1-l round-bottomed flask fitted with ground-glass joints and vacuum stopcocks containing a magnetic stirrer pellet. Prior to the reaction, the vessel was dried by evacuation with simultaneous flaming for about 3 h and filled with nitrogen on cooling. A known amount of well powdered hexabromodisilane was introduced into the reaction vessel, cooled in liquid nitrogen, and the uncondensed gases pumped out. The vessel was then brought to room temperature and an excess (*ca.* five-fold) of sulphur trioxide was introduced. Immediate evolution of bromine from the solid was observed, increasing rapidly with time. The solid was stirred by means of a magnetic pellet. The contents were left overnight at room temperature by which time reaction was complete.

An i.r. spectrum of the gaseous mixture showed only sulphur dioxide. The bromine liberated was condensed out and estimated. The compound left in the reaction vessel was a white solid. This was freed from adhering sulphur trioxide by prolonged pumping (6 h). The reaction vessel was then filled with dry nitrogen and the solid washed several (about six) times with dry diethyl ether to remove any adhering sulphur trioxide and dried under vacuum. The weight of the solid was determined. In a typical experiment Si_2Br_6 (6.630 g, 12.38 mmol) and SO_3 (*ca.* 5.0 g, 60.0 mmol) gave Br_2 (found, 5.860 g; calc., 5.936 g) and Si_2O_3 (found, 1.28 g; calc., 1.2870 g).

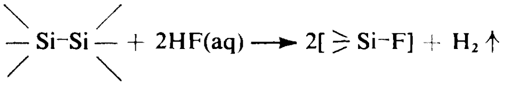
Properties of the Solid.—The reaction product is a white, non-sticky, powdery solid which is odourless and does not fume in moist air. It is insoluble in solvents such as water, benzene, and diethyl ether, but dissolves rapidly in concentrated aqueous sodium hydroxide and aqueous hydrofluoric acid solutions with liberation of hydrogen, identified by mass spectrometry. The hydrolysed solution does not give a positive test for bromide, indicating the absence of the latter in the solid. The i.r. spectrum of the solid recorded in a KBr pellet shows broad absorptions; of interest is the intense broad band centred around 1 050 cm^{-1} due to Si–O stretching vibrations. The solid is amorphous to *X*-rays and does not show any lines due to silica or silicon.

Results and Discussion

The results indicate that hexabromodisilane undergoes a complete reaction with sulphur trioxide at room temperature to give bromine, sulphur dioxide, and silicon sesquioxide (Si_2O_3). The quantitative liberation of bromine shows that all the Si–Br bonds are being cleaved and replaced by Si–O bonds. This is supported by the absence of any bromide in the solid obtained after the reaction. The formation of sulphur dioxide indicates that an oxygen atom from each molecule of sulphur trioxide is transferred to hexabromodisilane. The intense broad band at 1 050 cm^{-1} in the i.r. spectrum of the compound can be assigned to ν(Si–O) stretching vibrations by comparison with ν(Si–O) of silica (1 100 cm^{-1}) and of $(H_2Si_2O_4)_x$, a similar compound having Si–Si bonds attached to oxygen (prepared by careful hydrolysis of Si_2Cl_6 or Si_2Br_6 in a neutral or acidic medium) (1 050 cm^{-1}). The observation that the solid product gives hydrogen with strong sodium hydroxide solution and aqueous hydrofluoric acid indicates the presence of Si–Si bonds in the solid. The compound $(H_2Si_2O_4)_x$ exhibits similar behaviour.[4,5] The reactions involved in these tests can be represented by equations (1) and (2).[5,6]



(1)



(2)

The retention of the Si–Si bond present in hexabromodisilane in the present reaction is not surprising because sulphur trioxide is not able to oxidize the Si–Si bond at room temperature, as is evident from the reactions of hexafluoro- and hexachloro-disilanes [7] which occur only above 400 °C to give silica as one of the products.

The overall reaction may be represented by equation (3).

$$Si_2Br_6 + 3SO_3 \xrightarrow{25\,^{\circ}C} Si_2O_3 + 3SO_2 + 3Br_2 \qquad (3)$$

It is of interest that one of the applications of silicon sesquioxide is in vacuum plating of mirrors.[1]

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