

DETERMINATION OF THE Si—Si BOND IN PERPHENYLATED OLIGOSILANES*

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A novel method for determining the Si—Si bond in hexaphenyldisilane is described, which is also suitable for analysis of perphenylated oligosilanes. Decomposition of sample by potassium fluoride in triethylene glycol at 200°C yields the equivalent amount of hydrogen, whose mixture with other gaseous reaction products is analysed by gas chromatography.

Increasing interest¹⁻³ in the chemistry of perphenylated oligosilanes called for appropriate analytical tests among others also for the determination of the content of Si—Si bond. For determining this bond in various substituted silanes, two methods have essentially been used thus far, *i.e.* its cleavage with alkali metal hydroxide⁴ or with moist piperidin at 100°C (ref.⁵) to give hydrogen, the amount of which was then measured. Other reactions which lead to the cleavage of the Si—Si bond, such as the action of cupric chloride, aluminium trichloride, tin tetrachloride, halogens, or alkali metals⁷, have been used to study the structure of alkyl- and arylpolysilanes or for preparative purposes.

Standard procedures for determining the Si—Si bond have failed in our experiments with hexaphenyldisilane, which can be considered the simplest representative of perphenylated oligosilanes. The reason of this failure is obviously steric hinderance due to bulky substituents attached to both silicon atoms⁶. By using hexaphenyldisilane as a model compound, we worked out a novel method for determining the content of Si—Si bonds in perphenylated oligosilanes which is based on decomposition of the sample by potassium fluoride in the medium of triethylene glycol at 200°C and determination of the amount of evolved hydrogen in gaseous reaction products by gas chromatography.

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EXPERIMENTAL

Chemicals. Triethanolamine, triethylene glycol, potassium fluoride, potassium hydroxide, sulphuric acid, and other compounds were analytically or chemically pure preparations. Triethylene glycol contained less than 0.05% water. Pure carbon dioxide, which was used to transfer the hydrogen from decomposition flask to nitrometer, was prepared according to⁸. At a flow rate of approx. 50 ml/min and after absorption in 50% aqueous potassium hydroxide solution in the nitrometer, it showed a blank smaller than 40 μ l/min. Hexaphenyldisilane (prepared and purified in the Department of Organosilicon Compounds of this Institute) was tested by elemental analysis. For $C_{36}H_{50}Si_2$ (518.7) calculated: 83.35% C, 5.83% H, 10.82% Si; found: 83.55% C, 6.04% H, 10.83% Si.

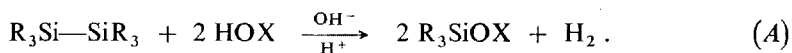
Apparatus. The casklike flask for decomposition of samples of approx. 45 ml volume was equipped with a sealed-in capillary inlet of carbon dioxide which reached to the bottom of the flask, so that the gas stream served also for mixing of the suspension of sample in the reaction mixture. Water reflux condenser (6 mm internal diameter, 12 cm long), set on the ground neck of the decomposition flask, was connected *via* a short capillary tube to the inlet of the nitrometer. The nitrometer of 500 ml total capacity was equipped with a 25 ml microburette, both of which were filled with 50% aqueous potassium hydroxide solution. The flow rate of the carbon dioxide was controlled by a flow-meter placed before the decomposition flask. Gas chromatographic analysis of gaseous reaction products was carried out with a Griffin & George, Model D 6, instrument equipped with gas density balance. The gases were introduced by means of a capillary sampling loop. A stainless steel column (180 \times 0.4 cm) was filled with the molecular sieve Calsit 5 A (Chemické závody J. Dimitrova, Bratislava, 0.16–0.20 mm particle size), which was activated prior to using by heating *in vacuo* at 360°C for 3 h. The carrier gas was argon and its flow rate was 14 ml/min. The column temperature was maintained at 30°C. The hydrogen content was read from the height of the elution peak by means of calibration graph.

Procedure. The weighed amount of finely powdered sample (50–300 mg, depending upon expected content of Si—Si bonds) was mixed in the decomposition flask with a small amount of the decomposition reagent (2% solution of potassium fluoride in triethylene glycol) and then the flask was filled nearly up to the neck by this reagent. After connecting the inlet of the pure carbon dioxide (the flow rate approximately 50 ml/min), the air in the flask was expelled by a 15 min bubbling. The nitrometer was then filled with 50% potassium hydroxide solution and sealed with a capillary three-way valve placed on the top of the gas burette. The decomposition flask was placed in a 200°C liquid bath. After 60–80 min, approximately 15 ml of gaseous reaction products were collected in the nitrometer and their volume was read to ± 0.02 ml. They were then transferred to a gas sampling flask of a capacity approx. 30 ml, containing water as sealing liquid. This portion of gaseous reaction products contained most of the total amount of hydrogen, usually 97–99%. After another 60 min, additional 10 ml of the gaseous mixture were collected in the flask. Samples of both portions were introduced by means of the capillary sampling loop to the gas chromatograph. The content of Si—Si bonds was calculated from the total hydrogen volume, as evaluated from the chromatographic peak heights after correcting for normal conditions (pressure, temperature, water vapour tension), assuming that one hydrogen molecule corresponds to one Si—Si bond.

RESULTS AND DISCUSSION

None of the methods for determining the Si—Si bond reported thus far is reliable for analysis of perphenylated oligosilanes which, in dependence on the method

of their synthesis, may contain the arrangement $R(C_6H_5)_2Si-Si(C_6H_5)_2R$ (where R stands for alkyl, alkylene, aryl, arylene, and alkyl- or aryl-substituted silyl or siloxy group). In experiments with hexaphenyldisilane, the simplest model compound of this series, we have found that even on using a suitable solvent, *e.g.* piperidine or triethanolamine, decomposition of the substance does not occur at temperatures from 100 to 200°C. After cooling these solutions, a crystalline precipitate appeared whose melting point was identical with that of the starting compound (340°C). Hexaphenyldisilane is only little soluble even in hot sulphuric acid, whereby no observable evolution of hydrogen occurs. Bulky phenyl or phenylene groups attached to both silicon atoms hinder the Si—Si bond to such an extent that the following reaction (X is H^+ or alkali metal cation) cannot take place:



The method for determining Si—Si bonds described in this work makes use of triethylene glycol as a solvent. The cleavage of the Si—Si bond to form stoichiometric amount of hydrogen is effected by potassium fluoride at 200°C. Under similar conditions the action of alkali metal hydroxides, antimony trifluoride, or water on hexaphenyldisilane does not lead to formation of detectable amounts of hydrogen. The cleavage of the Si—Si bond then does not proceed strictly *via* a mechanism similar to reaction (A). It seems more likely that some of the substituents of the arrangement $R(C_6H_5)_2Si-Si(C_6H_5)_2R$ is first split off, which leads to a decrease of steric hindrance. This assumption is in good agreement with the fact that a mixture of gaseous products from decomposition of hexaphenyldisilane contained also a great amount of benzene, and from decomposition of methyl- or ethyl-substituted perphenylated oligosilanes great amounts of methane or ethane. With hexaphenyldisilane as an

TABLE I

Determination of the Content of the Si—Si Bond (as mmol H_2/g) in Hexaphenyldisilane(I)
Calculated 1.927 mmol H_2/g

I, mg	Found	Deviation, % rel.
40.32	1.874	-0.053
50.41	1.967	+0.040
89.27	1.892	-0.035
100.95	1.938	+0.011
107.14	1.899	-0.028
200.17	1.963	+0.036
201.93	1.930	+0.003

example it was proved that the decomposition described above proceeds quantitatively, since the cleavage of one mole of Si—Si bond results in formation of one mol of hydrogen (Table I). Under the conditions described in the Experimental part, 96–99% of the total amount of hydrogen is transferred to the gas burette approximately in 60–80 min, and in another 60 min the evolution of the gas is essentially complete. With tetraphenyldihydrodisiloxane it was proved that C—Si and Si—O—Si bonds are not cleaved under formation of hydrogen. The analysis of a mixture of gaseous reaction products by gas chromatography is necessary. Hydrogen content in these mixture amounts to max. 30% v. The residue contains inert gases present in the carbon dioxide, the hydrocarbons formed by destructive cleavage of analysed compounds, and several unidentified substances which are formed in the course of the analysis, likely by decomposition of triethylene glycol.

The method is suitable for substances which are not appreciably volatile at temperatures to 200°C and which do not undergo decomposition by the reagent at ambient temperature. The accuracy of the method is characterised by the standard deviation $s = \pm 0.040$ mmol/g.

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