251. *The Chemistry of the Higher Silanes. Part I. Tetrasilane.*

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Some physical constants of tetrasilane have been redetermined and some new observations made on its chemical properties, especially with respect to its thermal stability and iodination.

In 1902 Moissan and Smiles began the study of the chemistry of the higher silanes with the isolation of a crude specimen of mixed higher hydrides from the product of the action of hydrochloric acid on magnesium silicide. The formula Si_2H_6 was attributed to this material (*Ann. Chim. Phys.*, **27**, 5). Later they prepared a relatively pure specimen of Si_2H_6 from lithium silicide (*Compt. rend.*, 1902, **134**, 1083). In 1909 Lebeau prepared mono- and di-silane and noted the presence of higher hydrides of lower volatility but believed these to be unsaturated compounds (*ibid.*, **148**, 43). The preparation of the silanes from magnesium silicide and acids was investigated in great detail in 1912 by Besson who much improved the yield of previous workers (*ibid.*, **154**, 116, 1603). Stock, in the period 1916—1923, improved but little on the preparative details of

Besson but isolated tri- and tetra-silane from the products. The former he characterised by the determination of a number of its chemical and physical properties. The latter he obtained only in small quantity, all his observations being conducted on 1 c.c. of crude material, but he determined the melting point and a few points on the vapour-pressure curve. The extrapolated boiling point was given approximately. Stock reported both these compounds to be unstable at room temperature. Trisilane was said to show signs of decomposition after 12 months' storage in glass bulbs at room temperature, and tetrasilane was found to have changed its vapour pressure appreciably after 3 months. A yellow polymeric solid silicon hydride was reported to be formed in these reactions. The only other reactions observed with these hydrides were their oxidation by air and oxygen, their complete hydrolysis by alkalis, their reduction by sodium amalgam, and their reaction with chloroform in the presence of anhydrous aluminium chloride. In 1935 Johnson and Isenberg (*J. Amer. Chem. Soc.*, **57**, 1349) prepared silanes by the action of ammonium bromide on magnesium silicide in liquid ammonia, obtaining a 65—80% conversion of silicon into hydrides and thereby much improving on Stock's yield of about 25% conversion. The influence of the mode of preparation of the magnesium silicide on the yield was stressed by these authors.

Experimental.

The yield of silicon converted into hydride by the acid decomposition of magnesium silicide is so dependent on the conditions of the reaction that some details of the preparation are given. The magnesium silicide (Mg_2Si) was prepared by heating crushed silicon of 99·0% purity (sieved 90 mesh) with a 10% excess of magnesium turnings, prepared from a 99·9% magnesium ingot. The mixture, contained in a soft-iron boat, was heated in a stream of pure hydrogen in a steel tube in a furnace. The effects of temperature and duration of heating were investigated. The yield of hydrides increased with up to 24 hours' heating of the magnesium–silicon mixture, but further heating up to 48 hours produced no very pronounced change (these observations were made on silicide prepared at 600° and 700°). The yields of hydrides from preparations carried out at 400° and thence at intervals of 50° up to 800° were determined under the same conditions of decomposition. Each of these preparations was heated for 24 hours at the temperature stated. In the preparations at 400° and 450° the reaction was obviously incomplete and a test-tube experiment showed the yield of hydrides to be very small; these samples were not tested further. Samples of material prepared at the other temperatures were decomposed by acid, as described later, and the percentage of the silicon converted into hydride was determined. The following results were obtained.

Temp. of prepn.	500°	550°	600°	650°	700°	750°	800°
Yield (% of Si converted)	16	22	27	38	30	25	17

The yields in the above table are based on measurements of the quantities of the hydrides isolated by the vacuum-fractionation procedure described below.

The relative proportions of the hydrides present in the crude product also changed with the temperature of the preparation. The product obtained at the higher temperatures was darker and gave a relatively increased yield of the higher silanes. The best over-all yield was obtained from the silicide prepared at 650°. These observations are in accordance with those of Johnson and Isenberg and support the view that the higher silanes result from the decomposition of a magnesium silicide other than Mg_2Si which is stable in the Mg–Si system at temperatures above 600°. Gire's results (*Compt. rend.*, 1933, **196**, 1404) suggest that this silicide may be MgSi. The magnesium silicide prepared in this manner was a purple-blue, crystalline powder. It possessed a musty smell, possibly due to the traces of silicon hydrides formed by atmospheric hydrolysis. When exposed to the atmosphere the silicide deteriorated, and it should therefore be stored in an air-tight container. The yield of hydride from an average specimen fell from 35% to 18% after two months' exposure to a moist atmosphere.

The decomposition of the silicide was carried out in a 3 l. Pyrex flask with walls of double thickness, fitted with inlet and exit tubes and a hopper enabling the silicide to be added in small portions. The inlet tube was connected to supplies of pure hydrogen and nitrogen. The exit tube led through a pair of wash-bottles and a calcium chloride and phosphoric oxide drying train to a pair of condensation traps connected to the vacuum apparatus and a mercury bubbler exit tube. The reaction was carried out in a stream of hydrogen; at the completion of the reaction the hydrogen was replaced by nitrogen to reduce the possibility of explosion on cleaning out the reaction flask. The highest yield was obtained with a 15% hydrochloric acid solution (15% HCl by weight). In each run 2 l. of this acid and 75 g. of silicide were used. Further, the highest yield was obtained when the decomposition was carried out as quickly as possible. It was found inadvisable, however, to allow the temperature of the reaction to rise above 65°, for it then become uncontrollable. Under these conditions a conversion of about 35% of the silicon contained in the silicide into silicon hydrides was consistently obtained.

The fractionation of the crude hydrides was carried out in a Stock-type universal vacuum apparatus. The final purification of materials for determination of physical constants, and a number of the reactions were carried out in all-glass vacuum systems with sealing capillaries, and making use of the magnetic breaker technique. Soda glass (G.E.C. X7) was used entirely in the construction of the apparatus. It was pretreated before use by washing in concentrated nitric acid followed by distilled water. The laboratory in which this research was carried out was illuminated only by diffuse daylight or ordinary electric light.

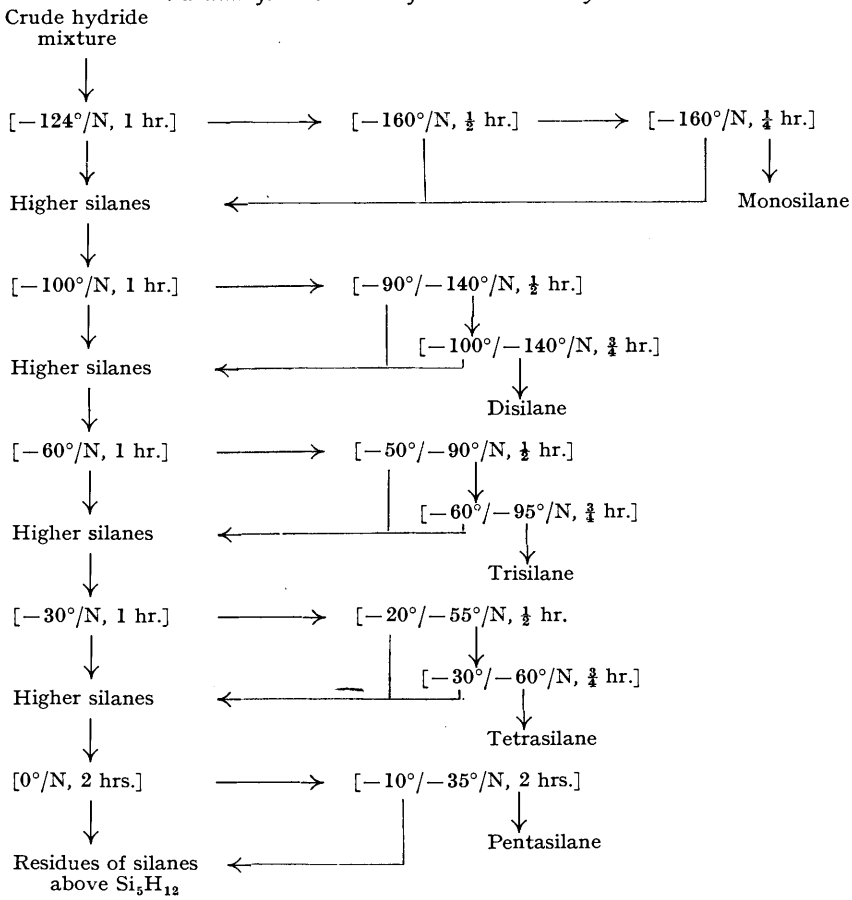
The initial fractionation of the hydrides was performed according to the scheme outlined below.

Specimens of mono-, di-, and tri-silane were fractionated to constant vapour pressure, and their physical properties found to be in complete agreement with the values given by Stock. Samples of these hydrides stored over mercury showed no signs of decomposition after 2 years' storage (average room temp. = 15°). In no case was an appreciable change in vapour pressure produced.

A sample of 8 c.c. of tetrasilane was isolated from a series of fractionations as described above and further purified by a series of 8 fractional distillations and condensations. The product was tensimetrically homogeneous; 4 c.c. of this material were prepared. The crude tetrasilane decomposed slowly on storage at room temperature. The vapour pressure at 12° of a sample of 2 c.c. of the crude material showed the following change (in mm.):

Initial value	3 months	6 months	9 months
17	22	26	35

Vacuum fractionation of mixed silicon hydrides.



[In the above chart the left-hand temperature of each bracketed group is the temperature at which the material was distilled in vacuum. The other temperatures are those of the baths in which the various fractions were condensed from the vapour stream. N denotes a trap cooled in liquid nitrogen. The times for which the various distillations were run are inserted in each case. All fractions collected at liquid nitrogen temperature (after removal of SiH_4) were united and stored separately. To illustrate the procedure, the separation of monosilane was done by taking that part of the mixture which distilled in a vacuum at −124° but condensed in liquid nitrogen, and redistilling this at −160° for ½ hr. The residue at −160° was added to the material not volatile at −124°. The volatile material was redistilled at −160° for ¼ hr., and the material condensed in the trap at liquid nitrogen temperature was found to be pure monosilane. The residue at −160° was added to the higher silane residue, as shown.]

The purified tetrasilane maintained a vapour pressure of 20·2 mm. at 12° for 12 months. Other observations on samples of intermediate purity support the view that the decomposition is autocatalytic and also strongly catalysed by traces of higher hydrides. The products of this low-temperature catalysed decomposition have not been completely identified. Some hydrogen is produced and traces of liquid silicon hydrides of very low volatility. These must be either much higher members of the silane series or unsaturated silicon hydrides. The latter hypothesis seems unlikely in view of our knowledge of silicon chemistry. At no stage during this research was any compound corresponding to Stock's polymeric yellow hydride obtained. Even in the residues from the decomposition of higher hydrides all the products of decomposition were liquid.

Analysis of the tetrasilane was effected by pyrolysis in a silica tube, giving the silicon content of the compound; and by complete hydrolysis by sodium hydroxide, which determined the number of Si–Si and Si–H bonds (Found: Si, 91·8, 92·0, 91·8. Calc. for Si_4H_{10}: Si, 91·7%). The hydrolysis experiments gave

$$\frac{\text{Vol. of } H_2 \text{ obtained (N.T.P.)}}{\text{Vol. of } Si_4H_{10} \text{ (as gas at N.T.P.)}} = 12{\cdot}98,\ 12{\cdot}97,\ 12{\cdot}98 \text{ (Calc. for } Si_4H_{10}\text{: } 13{\cdot}0).$$

The m. p. was determined with a carbon dioxide vapour-pressure thermometer. Two samples were examined, and each had a sharp m. p.: − 84·5°, − 84·2°, − 84·3°, − 84·2° (mean − 84·3°).

The vapour-pressure curve was determined on a pure sample of tetrasilane sealed in a glass spoon-gauge tensimeter. The tensimeter gave a deflection of about 3 mm./mm. Hg pressure difference, and hence by reading with a magnifying glass the pressure could easily be measured, correct to 0·1 mm. Hg. A calibrated thermometer graduated in 0·2° and read to a tenth of a degree was used. The tensimeter was immersed in a thermostatically controlled oil-bath. The mercury column used to record the pressure was at 20° during the experiment. The following values were obtained:

Temp.	0·0°	5·2°	11·0°	15·3°	19·2°	21·8°	24·8°	32·5°	36·2°	42·1°	47·2°	53·9°
Press. (mm. Hg at 20°)	9·1	11·8	16·1	20·6	24·7	28·7	33·2	48·5	56·9	75·1	94·1	123·4
Temp.	56·0°	61·0°	64·3°	69·2°	73·1°	77·8°	81·7°	84·9°	88·7°	91·1°	94·3°	96·2°
Press. (mm. Hg at 20°)	133·9	161·9	182·5	221·2	254·1	297·2	339·2	377·0	426·4	458·9	504·8	535·4

Extrapolation gave the b. p. of Si_4H_{10} as 107·4°. The latent heat at the b. p. was 8500 cals./mol. and Trouton's constant was 22·2. The determination of the vapour-pressure curve occupied 7 hours, for 3 hours of which the tetrasilane was at above 70°. At the end of the experiment the vapour pressure of the specimen at 22° had increased by 1 mm. The liquid was still crystal clear, and the material could still be condensed completely by liquid nitrogen, showing that no hydrogen had been formed. In view of the unexpected thermal stability of the tetrasilane further investigation was deemed desirable.

A second sample of pure tetrasilane was sealed in a glass tensimeter. The quantity was arranged to be such that at about 300 mm. Hg pressure the compound had all volatilised. The system was then steadily heated in an oil-bath, and readings of the pressure, temperature, and time from the commencement of heating noted. The state of the tetrasilane vapour could also be visually examined. 0·03 G. of tetrasilane was taken and rapidly heated to 107°; subsequently the temperature was raised gradually to 284°, a series of measurements of the temperature and pressure being made. From the observed values of the quotient P/T it was found that decomposition of the vapour of tetrasilane commenced at 220—230°. The reaction products were not examined, but they probably consist of simpler and of more complex saturated hydrides. At considerably higher temperatures it is known that decomposition into silicon and hydrogen is complete.

A few experiments were made on the reactions of tetrasilane, but the products are of such low volatility and complexity that they were not fully characterised. Tetrasilane did not react with pure chloroform or bromoform even on prolonged storage at room temperature or on heating to 50° for 1 hour in a sealed tube with an excess of either reagent. However, in the presence of 1 or 2% of anhydrous aluminium chloride considerable halogenation of the tetrasilane took place in a few hours. The products were all of low volatility and the mixture produced was believed to be very complex. So far it has proved possible to isolate only methylene chloride and bromide as two of the most volatile products of the two reactions.

With iodoform, however, tetrasilane reacts in the absence of a catalyst. A small quantity of tetrasilane (0·6 g.) was sealed up with some iodoform (0·8 g.). At room temperature some of the iodoform dissolved to give a yellow solution. Heating to 60° for 10 minutes only dissolved more iodoform, which recrystallised on cooling. No reaction was apparent on a further 15 mins.' heating to 65°. After ten days at room temperature all the iodoform had reacted, and a small amount of silicon tetraiodide had been formed and was identified by crystal form and m. p. The other products were liquid, colourless, and of low volatility; they were spontaneously inflammable, burning with a flame evolving clouds of iodine vapour. Tetrasilane was also shown to react slowly with phosphorus tri-iodide. A sample of tetrasilane, sealed up with some of the tri-iodide and heated to 100° for 15 minutes, produced hydrogen and, in addition to some unchanged tetrasilane, a less volatile fraction consisting of a spontaneously inflammable, colourless liquid which evolved clouds of iodine vapour on combustion. These last two reactions obviously produce iodotetrasilanes whose characterisation must await more refined technique.

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[*Received, March 20th,* 1946.]