of a 1:1 $B_2F_4 \cdot SF_4$ adduct at −80°. The vapor pressure of this adduct increased from approximately 90 mm. at 25° to 101 mm. at 25° after it was stored at room temperature for 1 hr. and 25 min. Analysis of the infrared spectrum of the products volatile at −80° showed the presence of boron trifluoride, diboron tetrafluoride, thionyl fluoride, and sulfur tetrafluoride. The residue was held at room temperature for an additional 64 hr. and then found to be completely volatile at −80°. Based on infrared data, compounds present in this mixture included boron trifluoride, thionyl fluoride, and silicon tetrafluoride. No thionyl fluoride or diboron tetrafluoride was evident in the gaseous products.

CONTRIBUTION NO. 793 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
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Chemistry of Silane. I. Preparation of Silane

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Silane has been synthesized directly in conversions up to 80% from silica and silicates by treatment with superatmospheric pressure hydrogen in the presence of aluminum and aluminum chloride. Evidence is presented for an aluminum chlorohydride intermediate

$$Al + AlCl_3 \overset{H_2}{\rightleftarrows} AlH_xCl_{3-x} \xrightarrow{SiO_2} SiH_4$$

High yield synthesis of pure silane from silicon halides also has been achieved in similar reactions although aluminum chloride is not a critical reactant.

Synthesis from Silicon Oxides.—The low reactivity of silica toward hydrogen, at least below 1000°, is generally recognized since silica is a common catalyst support in hydrogenation of organic compounds. We have found, however, that silica and silicates are readily hydrogenated to silane in the presence of aluminum and aluminum halides. Conversions of 80% are obtained at 175° and 400 atm. pressure, and the purity of the silane is greater than 99%. Thus, this new reaction system constitutes an important new synthesis of silane.

Aluminum and hydrogen alone are not sufficient for the hydrogenation of silica at temperatures below 800°; an aluminum halide must be present for the over-all reaction

$$3SiO_2 + 4Al + 2AlX_3 + 6H_2 \longrightarrow \frac{6}{n}[AlOX]_n + 3SiH_4$$

At atmospheric pressure, reaction rate is insignificant below 800°, and above 800° isolation of silane requires short contact times because of its thermal instability. Superatmospheric hydrogen pressure drastically reduces the temperature requirement. Thus, at 200°, silane conversion goes from 0% at 1 atm. to 10% at 100 atm. to 76% at 900 atm. Since the reaction is primarily heterogeneous, highest conversions are obtained with high-surface-area silicas, *e.g.*, silica gel and diatomaceous earth, and with vigorous agitation of the reaction medium.

The silane produced by this novel method is consistently of very high purity, >99%. Best results were obtained with aluminum chloride in the form of the aluminum chloride–sodium chloride eutectic (m.p. 120°). Mass spectrometric analysis of typical products showed the possible presence of hydrogen chloride and traces of SiH_3Cl (~0.05%) and SiH_2Cl_2 (~0.05%) as principal impurities in the silane. The origin of the chlorosilanes was not established; however, since $SiCl_4$ is not a reaction intermediate, *vide infra*, it is probable that the chlorosilanes were formed by the previously reported aluminum chloride-catalyzed chlorination of silane by hydrogen chloride.[1] At synthesis temperatures above 200°, trace amounts of disilane were detected in the product; the disilane probably was formed by thermal coupling of silane.[2]

Mechanism.—The reaction mechanism for this new silane synthesis has not been definitively characterized. However, the data point very strongly to a volatile aluminum chlorohydride intermediate. The following major points support this thesis:

(1) Silicon tetrachloride is not formed in the reaction of silica with aluminum and aluminum chloride, at, or even significantly above, the temperatures at which high silane conversions are obtained when hydrogen is added to this mixture. Even small equilibrium $SiCl_4$ concentrations are contraindicated since conditions under which the volatile $SiCl_4$ would be removed from the reaction zone did not yield detectable amounts.

(2) Silicon does not appear to be an intermediate since all attempts to hydrogenate silicon under conditions effective for silica were unsuccessful.

(3) A volatile hydride of aluminum is formed in small amounts in the high pressure reaction of Al, AlX_3, and H_2. This species was shown to convert silica to silane and to decompose thermally at 200° in an inert atmosphere to aluminum metal. The final, essentially conclusive proof for the alane intermediate was the formation of silane in a system in which silica was suspended above an aluminum–aluminum chloride–sodium

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[1] A Stock and C. Sonieski, *Ber.*, **52**, 695 (1919).

[2] K. Stokland, *Kgl. Norske Videnskab. Selskab. Skrifter*, **3**, 1 (1948).

TABLE I
PREPARATION OF SILANE

Silicon source	g.	% Si	Al (g.)	Reaction medium	H_2 pressure (atm.)	Temp. (°C.)	Time (hr.)	Conv. to SiH_4 (%)
Silica gel	20	43.9	20	$AlCl_3$ 113 g. NaCl 30 g.	400	200	8	62
Silica gel	20	43.9	20	$AlCl_3$ 113 g. NaCl 30 g.	800	200	16	76
Silica gel	20	43.9	20	$AlCl_3$ 113 g.	750	175	16	60
Silica gel	20	43.9	20	$AlBr_3$ 100 g.	750	200	15	57
Diatomaceous earth	20	45.0	20	$AlCl_3$ 113 g. NaCl 30 g.	800	200	15	66
Clay (bentonite)	35	26.3	30	$AlCl_3$ 113 g. NaCl 30 g.	800	250	8	17
Sand (Ottawa)	20	46.7	30	$AlCl_3$ 113 g. NaCl 30 g.	900	250	16.2	1.0
Ignited fine silica	20	44.7	30	$AlCl_3$ 113 g. NaCl 30 g.	850	250	6	20
Sodium silicate	30	34.9	30	$AlCl_3$ 113 g. NaCl 30 g.	900	250	8	16
$Si(OC_2H_5)_4$	62.5	13.4	20	$AlCl_3$ 113 g. NaCl 30 g.	750	200	7	12[a]
$Si(SC_2H_5)_4$	27.3	10.3	20	$AlCl_3$ 113 g. NaCl 30 g.	800	200	12	35[b]
$Si(C_2H_5)_4$	14.4	19.5	3	$AlCl_3$ 2 g.	2500	300	14	53[c]

[a] Considerable ethane was formed along with the silane. [b] Mass spectrographic analysis also indicated $C_2H_5SiH_3$, ethane, and ethylene in the product. [c] Other products were $C_2H_5SiH_3$ (7%), $(C_2H_5)_2SiH_2$ (1%), and ethane.

chloride slurry at 750 atm. pressure of hydrogen. Since alanes are not particularly stable thermally, a labile equilibrium of the type

$$AlCl_nH_{3-n} \rightleftarrows \frac{2n}{3}Al + \frac{n}{3}AlCl_3 + \frac{3-n}{2}H_2$$

is reasonable and also is fully consistent with the pressure dependence of our silane synthesis.

The data do not permit selection of a specific alane; however, the non-volatile nature and the very low thermal stability of $(AlH_3)_x$ would seem to preclude this alane as an intermediate. The chloroalanes reportedly are volatile and appear more stable than $(AlH_3)_x$ and, accordingly, are the more probable intermediates.

Scope of Reaction.—Preparation of silane by hydrogenation in the presence of aluminum and an aluminum halide appears generally applicable to silicon–oxygen compounds, as shown in Table I. Thiosilicates also are operable; tetraethyl thiosilicate gave silane in 35% conversion along with some ethylsilane, ethylene, and ethane. Interestingly, hydrogenolysis of SiC bonds occurs in this system to yield silane and alkanes. Thus, tetraethylsilane gave 53% silane with ethane, ethylsilane, and diethylsilane being the other products of this reaction.

Synthesis from Silicon Tetrachloride.—Several syntheses of silane by direct hydrogenation of silicon halides have been reported,[3] but these methods require temperatures of 300 to 2000° and give low yields of silane mixed with various halosilanes. We have now found that silane can be prepared by treatment of silicon tetrachloride with hydrogen, a molar excess of aluminum, and a catalytic quantity of lithium aluminum hydride. The synthesis proceeds according to the equation

$$3SiCl_4 + 4Al + 6H_2 \longrightarrow 3SiH_4 + 4AlCl_3$$

At 175° and a hydrogen pressure of 900 atm., conversions range from 70 to 100% and silane purity is greater than 99%. No chlorosilanes are produced.

Silane forms in only trace amounts in the hydrogenation of silicon tetrachloride unless the aluminum is "activated." This activation may simply involve removal of an oxide coating from the aluminum surface. Ionic hydrides are excellent activators, being operable at a level of less than 3% of the weight of aluminum. Specific hydrides which effect this activation are noted in Table II.

Silicon tetrachloride also is hydrogenated to silane in the system employed for conversion of silicon oxides to silane. Highest conversions are obtained by use of the $NaCl-AlCl_3$ eutectic melt as the reaction medium. Hexachlorodisilane and dimethyldichlorosilane are converted to disilane and dimethylsilane, respectively, under these conditions. Conversions are low, however, because competing reactions involving hydrogenolysis of silicon–silicon and carbon–silicon bonds predominate.

Synthesis from Fluorosilicates.—Sodium and potassium fluorosilicates are hydrogenated cleanly to silane in high conversions in the presence of activated aluminum. Thus, treatment of potassium fluorosilicate with hydrogen at 800 atm. and 200° in the presence of a mixture of aluminum, aluminum chloride, and sodium chloride gave a 92% conversion to silane having a purity of at least 99.9%. Under these synthesis conditions, barium and zinc fluorosilicate also gave silane, but in lower conversions.

The reaction variables of the silane synthesis from fluorosilicates have not been thoroughly investigated,

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(3) D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1545 (1945); D. B. Hatcher, U. S. Patent 2,458,703 (1949); C. H. Wagner and C. E. Erickson, U. S. Patent 2,595,620 (1952); N. C. Cook, J. D. Cobine, and J. D. Wolfe, U. S. Patent 2,768,061 (1956).

TABLE II

SYNTHESIS OF SILANE FROM SILICON TETRACHLORIDE

Reactants (30 g. $SiCl_4$–20 g. Al)			Reaction conditions		
Activator	Wt., g.	H_2 pressure, atm.	Temp., °C.	Time, hr.	SiH_4 conversion, %
$LiAlH_4$	0.5	950	175	6	100
$LiAlH_4$	.5	950	150	6	95
LiH	.5	850	175	4	37
NaH	.5	800	175	4	64
BaH_2	.5	820	175	4	75
SrH_2	.5	850	175	4	64
$(i\text{-}C_4H_9)_2AlH$	.7	800	175	4	75
$(i\text{-}C_4H_9)_3Al$	.4	990	150	4	9
C_2H_5I	1.5	800	150	5	10
I_2	0.4				
$AlCl_3$	.4				
$AlCl_3$	113	800	170	9.5	27
$AlCl_3$	113	750	170	4	84
NaCl	30				

but the process appears quite similar to the hydrogenation of silicon tetrachloride and of silicon oxides. Unlike the synthesis from silicon oxides, however, it is believed that the silane synthesis from fluorosilicates does proceed through silicon tetrachloride as an intermediate. On heating a mixture of sodium fluorosilicate, aluminum chloride, sodium chloride, and aluminum in the absence of hydrogen, silicon tetrachloride is formed

$$3Na_2SiF_6 + 4AlCl_3 \longrightarrow 6NaF + 4AlF_3 + 3SiCl_4$$

and the presence of aluminum fluoride in the reaction residue has been confirmed by X-ray analysis.

Experimental

Starting Materials.—The silica gel used was a commercial product of 28–200 mesh having a silicon content of 43.9%. Other silicon oxides were commercially available materials which were used as dry powders. A commercial grade of granular aluminum (20–80 mesh) was employed in most of the experiments. This commercial aluminum was as effective as spectroscopically pure aluminum. The hydrogen had a purity of at least 99.8%. Sodium chloride, anhydrous aluminum chloride, and silicon tetrachloride were reagent grade.

High Pressure Hydrogenation of Silica.—A stainless steel-lined pressure vessel (shaker tube) of 400 ml. capacity was purged with dry nitrogen. A mixture of 20 g. (0.314 mole available Si) of silica gel, 20 g. (0.742 mole) of granular aluminum, 113 g. (0.847 mole) of anhydrous aluminum chloride, and 30 g. (0.514 mole) of sodium chloride was charged under an atmosphere of dry nitrogen. To aid in mixing the contents during the reaction, thirty $^3/_8$ in. diameter stainless steel balls were added to the vessel. The vessel was evacuated, pressurized with hydrogen to 175 atm., and then heated with shaking to 200°. Hydrogen pressure then was increased to 400 atm. and maintained at 400–475 atm. for 8 hr. at 200° with shaking.

The reaction vessel and its contents were cooled to room temperature. In order to prevent plugging of the inlet during the reaction, care was taken throughout the experiment to keep a higher pressure in the hydrogen line than in the reaction vessel. While the mixture was being cooled, hydrogen was injected at 150, 130, and 110° to clear the inlet of any solid material. After cooling, volatile reaction products were carefully vented through a series of two traps cooled with liquid nitrogen. The condensate (6.2 g.) was transferred under high vacuum to a stainless steel cylinder and was essentially pure silane (>99.5%) as determined by mass spectroscopic analysis. Conversion was 62% based on the silicon content of the charged silica gel.

By conducting the synthesis at a hydrogen pressure of 800 atm. for 15 hr., the conversion was increased to 76%. Substitution of nitrogen for hydrogen in the reaction system gave neither silicon tetrachloride (a possible intermediate) nor any other volatile silicon compounds.

To provide a liquid reaction medium, the aluminum chloride usually was employed in the form of a molten salt eutectic (m.p. 120°) composed of 63 mole % aluminum chloride and 37 mole % sodium chloride. The presence of a molten salt reaction medium is not necessary, however, for the formation of silane from silica gel, since high conversions also are obtained from hydrogen, aluminum, and silica gel in anhydrous aluminum chloride alone at a temperature of 175°, which is well below the melting point (190°) of aluminum chloride. The synthesis proceeded equally well when aluminum bromide was substituted for aluminum chloride.

Surface areas of the solid reactants are important in obtaining high conversions of silica to silane. Highest conversions (50–80%) were obtained from such finely divided silicon oxide sources as silica gel or diatomaceous earth, while Ottawa sand, which is of relatively low surface area, gave conversions of the order of 1–5%. Coarse aluminum turnings gave poorer results in the synthesis than did either aluminum dust or 20–80 mesh granular aluminum.

High-Pressure Hydrogenation of Other Silicon Oxides.—Silicon oxides other than silica gel were converted to silane by hydrogenation in the presence of aluminum and aluminum chloride according to the above procedure. Experimental data on these syntheses are summarized in Table I.

Hydrogenation of Silica at Atmospheric Pressure.—Hydrogen was passed at a rate of 1.74 l./min. over a mixture of 4.3 g. (0.159 mole) of aluminum powder (80–100 mesh) and 6.4 g. (0.100 mole available Si) silica gel (28–200 mesh) contained in an alumina boat supported in a horizontal quartz tube heated to 1000–1200°. The product gas stream was rapidly quenched by a trap cooled with solid carbon dioxide and a second trap cooled with liquid nitrogen connected in series directly to the outlet of the quartz tube. After a 2-hr. reaction period, 0.5 g. of condensate had formed which was shown by mass spectrographic analysis to contain 2.5% silane with the remainder being principally carbon dioxide. The same result was obtained upon substitution of 20–80 mesh magnesium powder for aluminum in this experiment. No silane was formed under similar experimental conditions at temperatures below 800°.

Preparation of Silane from Silicon Tetrachloride, Hydrogen, and Aluminum Activated with a Metal Hydride.—A stainless steel-lined 400 ml. pressure vessel (shaker tube) which had been purged with nitrogen was charged with 20 g. (0.176 mole) of silicon tetrachloride, 20 g. (0.74 mole) of aluminum powder, 0.5 g. (0.013 mole) of lithium aluminum hydride, and thirty $^3/_8$ in. diameter stainless steel balls. The steel balls were added to the vessel to facilitate the mixing of the contents. The pressure vessel was cooled to −78°, evacuated, pressured with hydrogen to 400 atm. at room temperature, and then heated with shaking to 175°. Hydrogen pressure was increased to 950 atm. and maintained at this pressure for 6 hr. at 175° with continuous shaking. The contents of the pressure vessel were allowed to cool to 80°, and volatile materials were released slowly through a series of two traps cooled with liquid nitrogen. Condensate was transferred to a vacuum system and allowed to distil through a trap at −85° into a trap cooled with liquid nitrogen. Product which condensed in the liquid-nitrogen-cooled trap was shown by mass spectrographic analysis to be 99.0–99.5% silane. This product weighed 5.8 g. and represents a 100% conversion based on the available silicon in the silicon tetrachloride. The residue in the pressure vessel was a mixture of aluminum chloride and unchanged aluminum metal.

As shown in Table II, hydrides other than lithium aluminum hydride which are activators for aluminum include lithium hydride, sodium hydride, barium hydride, strontium hydride, and di-(isobutyl)-aluminum hydride. Less effective but still showing some activation of aluminum are tri-(isobutyl)-aluminum and a mixture of an alkyl iodide and iodine with or without aluminum chloride. Sodium borohydride, lithium borohydride, and a mercury–mercury(II) chloride mixture proved ineffective as activators.

Preparation of Silane from a Fluorosilicate, Hydrogen, Aluminum, and Aluminum Chloride.—The aluminum chloride–sodium chloride eutectic melt also was effective as an activating medium for the hydrogenation of salts of fluorosilicic acid to silane. Treatment of a mixture of 33 g. (0.149 mole) of potassium fluorosilicate, 30 g. (1.11 moles) of powdered aluminum, 113 g. (0.847 mole) of anhydrous aluminum chloride, and 30 g. (0.514 mole) of sodium chloride with hydrogen at 750–830 atm. pressure at 200° for 11.5 hr. gave a 92% conversion to silane. Mass spectrographic analysis showed the silane to have a purity 99.9%.

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Mass Spectra of Volatile Hydrides. I.
The Monoelemental Hydrides of the Group IVB and VB Elements[1]

BY FRED E. SAALFELD AND HARRY J. SVEC

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The mass spectra of SiH_4, GeH_4, SnH_4, PbH_4, PH_3, AsH_3, SbH_3, and BiH_3 have been obtained. Fragment ions, after careful test, have been found to have negligible excess kinetic energy. The average M–H bond energies and the ΔH_f^0 obtained from appearance potential data agree well with other values when they exist.

Introduction

The mass spectra of silane, germane, stannane, phosphine, and arsine have been reported by various workers.[2-5] These reports include fragmentation patterns for the compounds but appearance potential (a.p.) data are cited only for the positive fragment ions from germane,[3] stannane,[5] and phosphine.[3a] While there is generally good agreement among the fragmentation patterns, where more than one study is reported, there is not good agreement among the a.p. data. In some cases authors have not attempted to identify particular processes with their data and in two instances[3a,3c] misinterpretation of the data is evident in the published accounts. In none of the studies have attempts been made to determine whether or not the a.p. data contain excess kinetic energy. This paper reports an extension of the scope of mass spectrometric studies of the volatile hydrides as well as careful determinations of whether or not the fragment ions have excess kinetic energy.

Experimental

Silane was prepared in an all-glass vacuum apparatus by the reduction of silicon tetrachloride with lithium aluminum hydride according to the method of Finholt, *et al.*[6] Purification of the product was achieved by distilling through a trap at −117° (m.p. of absolute ethanol), condensing at the temperature of boiling liquid nitrogen, evacuating, and repeating the procedure three times. No higher homologs were observed in the mass spectrum.

Germane was prepared from $^{74}GeO_2$ according to the method of Jolly and Drake.[7] Purification of the product was as described above for silane except that a trap cooled to −111.6° (m.p. of carbon disulfide) instead of −117° was used.

Stannane was prepared from ^{120}Sn according to the procedure outlined by Saalfeld and Svec.[5]

Plumbane was prepared by the reaction of 50 ml. of 0.8 *N* HCl with 117 g. of a metallic mixture corresponding to the composition Mg_2Pb. The acid was added dropwise to the metal mixture under vacuum. Products were swept directly into a paraffin-lined trap cooled with boiling liquid nitrogen. When the reaction was complete, this trap was isolated from the reaction vessel, allowed to warm to −111.6°, and then thoroughly evacuated. The trap again was isolated and slowly warmed to −22.9° (m.p. of carbon tetrachloride). It was opened to a Toepler pump and the gases quickly were transferred to a specially designed sample bulb which was cooled to −111.6°. The plumbane was isolated in the bulb and quickly transferred to the mass spectrometer. After the bulb had been attached to the evacuated inlet system of this instrument it was warmed slowly to −22.9° and the plumbane allowed to distil into the ion source of the mass spectrometer. In spite of these precautions, the yields were low and rapid decomposition took place. Each preparation allowed only 10 to 15 min. of observation time in the instrument and thus several preparations were needed to complete the mass spectrometric studies.

Phosphine was prepared by the procedure of Gunn and Green.[8] Purification of the product was as described above for silane except that the trap was cooled to −63.5° (m.p. of chloroform) instead of −117°.

Arsine was prepared by the reduction of an acidic solution of

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[1] This report is based in part on a Ph.D. dissertation by F. E. Saalfeld and submitted to Iowa State University, Ames, Iowa. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1124.

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