SILYL COMPOUNDS

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A SILICON HYDRIDE may be defined as a compound which contains at least one Si–H bond. A comparatively large number of substances fall into this category and it is convenient to make sub-divisions into classes according as they contain $\equiv$SiH, $=$$SiH_2$, or —$SiH_3$ groupings. This Review deals specifically with those compounds which contain at least one —SiH_3 or " silyl " group, and they are, therefore, formally inorganic analogues of methyl compounds. There are just over fifty substances of this type known at present.

Until the vacuum-system technique was introduced by Stock during the years 1914—1920, it had not been possible satisfactorily to study volatile compounds which were unstable in air, such as the silicon hydrides. Some silyl compounds had been reported in the latter part of the nineteenth century [1] but the physical and chemical properties given could not be accepted with great confidence since their state of purity was always in doubt. Stock and his co-workers re-investigated these compounds and prepared many new ones between 1916 and 1923. Little further work was carried out in the field until 1938, when Emeléus and his co-workers again began to study silyl compounds in addition to other silicon hydrides. Recently, investigators in the United States [2–4] have begun to take an interest in this class of compound.

The types of compounds involved fall into three main categories: (i) The unsubstituted parent silicon hydrides which may contain one or more silyl groups and possibly —SiH_2— groups as well, *e.g.*, $SiH_3{\cdot}SiH_2{\cdot}SiH_3$. (ii) Partially substituted silicon hydrides which contain one or more unsubstituted silyl groups and in which there is no direct Si–Si linkage, *e.g.*, $SiH_3{\cdot}O{\cdot}SiH_3$. (iii) Partially substituted silicon hydrides which contain one or more unsubstituted silyl groups and at least one Si–Si linkage, *e.g.*, $SiH_3{\cdot}SiH_2Br$. By far the greatest number of compounds known are in the second category.

Preparation, properties, and reactions of silyl compounds

(1) **The Parent Silicon Hydrides.**—A series of silicon hydrides are known corresponding to the simple saturated hydrocarbons of general formula Si_nH_{2n+2}. Those so far isolated are SiH_4, Si_2H_6, Si_3H_8, *n*-Si_4H_{10}, Si_5H_{12},

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[1] (*a*) Wöhler and Buff, *Annalen*, 1857, **103**, 218.

(*b*) Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry ", Longmans, Green and Co., London, 1925, p. 216.

[2] Sujishi and Witz, Report No. 1, Office of Ordnance Research Control DA-11-OLL. Ord. 1264 (March, 1954).

[3] *Idem, J. Amer. Chem. Soc.*, 1954, **76**, 4631.

[4] Burg and Kuljian, *ibid.*, 1950, **72**, 3103.

and Si_6H_{14}. The last two compounds have only been obtained as a mixture of isomers.[5]

Preparation. A mixture of all the known silicon hydrides may be obtained by the action of dilute hydrochloric acid on magnesium silicide,[6, 7] and fairly pure silane, SiH_4, may be prepared in good yields by the reaction of magnesium silicide with ammonium bromide in liquid ammonia. With specially prepared magnesium silicide high yields of disilane, Si_2H_6, are obtained.[8, 9] Pure silane and also disilane are most conveniently prepared by the reduction of the corresponding completely chlorinated compound with lithium aluminium hydride.[10]

Physical properties. All the saturated silicon hydrides are colourless gases or liquids. Their most important physical constants are given in Table 1.[6, 7, 11–13]

TABLE 1

Compound	M.p.	B.p.	*d* (g./ml.)
SiH_4	– 185°	– 111·9°	0·68 (– 185°)
Si_2H_6	– 132·5	– 14·5	0·686 (– 25°)
Si_3H_8	– 117·4	52·9	0·743 (0°)
Si_4H_{10}	– 84·3	107·4	0·825 (0°)
Si_5H_{12}	—	> 100	—
Si_6H_{14}	—	> 100	—

Reactions. The thermal stability of the silicon hydrides is less than that of the analogous carbon compounds and decreases with increasing molecular weight [14] although the stability of the higher hydrides is actually greater than was originally thought.[7] At comparatively low temperatures the higher silicon hydrides decompose to give a mixture of lower, volatile silicon hydrides and solid unsaturated hydrides, all of which decompose completely into silicon and hydrogen at 500°,[14–17] *e.g.*,

$$\begin{aligned} Si_5H_{12} &\longrightarrow Si_2H_6 + SiH_4 + 2(SiH)_x \\ Si_2H_6 &\longrightarrow SiH_4 + (SiH)_x + \tfrac{1}{2}H_2 \\ SiH_4 \text{ also } (SiH)_x &\longrightarrow Si + H_2 \end{aligned}$$

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[5] Stock, " Hydrides of Boron and Silicon ", Cornell Univ. Press, Ithaca, New York, 1933, p. 21.

[6] Stock and Somieski, *Ber.*, 1916, **49,** 111.

[7] Emeléus and Maddock, *J.*, 1946, 1131.

[8] Johnson and Hogness, *J. Amer. Chem. Soc.*, 1934, **56,** 1252.

[9] Johnson and Isenberg, *ibid.*, 1935, **57,** 1349.

[10] Finholt, Bond, Wilzbach, and Schlesinger, *ibid.*, 1947, **69,** 2692.

[11] Wintgen, *Ber.*, 1919, **52,** 724.

[12] Stock, Stiebler, and Zeidler, *Ber.*, 1923, **56,** 1695.

[13] Stock, *op. cit.*, ref. 5, p. 32.

[14] *Idem, ibid.*, pp. 23, 24.

[15] Emeléus and Reid, *J.*, 1939, 1021.

[16] Stockland, *Kgl. Norske Videnskab. Selskabs. Skrifter*, 1950, No. 3, 1–159.

[17] Hogness, Wilson, and Johnson, *J. Amer. Chem. Soc.*, 1936, **58,** 108.

Silane is also decomposed into solid hydrides by an electric discharge or by ultraviolet irradiation.[18, 19]

All the parent silicon hydrides are spontaneously inflammable and explosive in air,[20] with the exception of pure silane which can be mixed with oxygen under certain conditions of temperature, pressure, etc., without inflammation.[21]

None of the silicon hydrides reacts with pure water or with slightly acidified water, but in the presence of even a minute trace of alkali they are rapidly and completely hydrolysed to hydrogen and silicate.[22, 23]

All the silicon hydrides are strong reducing agents. They reduce aqueous solutions of $KMnO_4$ to MnO_2, Hg^{2+} to Hg^+ and Hg, Cu^{2+} to copper hydride, etc. They do not alter solutions of Ni^{2+}, Cr^{3+} or Pb^{2+}.[6, 23]

The free halogens react vigorously with all silicon hydrides—sometimes explosively—one or more of the hydrogen atoms being replaced by halogen.[3, 23] The reaction of hydrogen halides with silane is discussed in the following section,[24] and that with disilane on p. 212. All the silicon hydrides except silane react readily with carbon tetrachloride or chloroform in the presence of aluminium chloride catalyst :[25]

e.g., $$Si_3H_8 + 4CHCl_3 \longrightarrow Si_3H_4Cl_4 + 4CH_2Cl_2$$

(2) **Compounds containing Elements of Group VII or Pseudo-halogens.**—(A) *Compounds containing no* Si–Si *Linkage.—Preparation.* The silyl halides, with the exception of the fluoride which has not been investigated in this type of reaction, may be prepared by the action of the gaseous hydrogen halide on silane at slightly elevated temperatures in the presence of the appropriate aluminium halide catalyst as indicated by the general equation [23, 24, 26]

$$SiH_4 + HX \xrightarrow{Al_2X_6} SiH_3X + H_2$$

Silyl halides may also be prepared by the interaction of a higher silicon halide and silane in the presence of the appropriate aluminium halide catalyst,[23] *e.g.*,

$$SiH_2Cl_2 + SiH_4 \longrightarrow 2SiH_3Cl$$

Silyl chloride is more conveniently prepared by reduction of silicon tetrachloride with formaldehyde on an alumina catalyst at elevated temperatures,[27] while an alternative preparation of the bromide involves the reaction of silane with solid bromine at low temperatures.[3] Silyl fluoride is prepared by the action of silyl chloride on antimony trifluoride.[28]

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[18] Schwarz and Heinrich, *Z. anorg. Chem.*, 1935, **221,** 277.

[19] Emeléus and Stewart, *Trans. Faraday Soc.*, 1936, **32,** 1577.

[20] Stock, *op. cit.*, ref. 5, pp. 20, 22.

[21] Emeléus and Stewart, *J.*, 1935, 1182.

[22] Stock and Somieski, *Ber.*, 1918, **51,** 989.

[23] Stock, *op. cit.*, ref. 5, pp. 25, 26.

[24] Emeléus, Maddock, and Reid, *J.*, 1941, 353.

[25] Stock and Stiebler, *Ber.*, 1923, **56,** 1087.

[26] Stock and Somieski, *Ber.*, 1919, **52,** 695.

[27] Glemser and Lohman, *Z. anorg. Chem.*, 1954, **275,** 260.

[28] Emeléus and Maddock, *J.*, 1944, **293.**

The silyl *iso*-pseudo-halides, $SiH_3{\cdot}NC$, $SiH_3{\cdot}NCS$, may be prepared by the action of silyl iodide vapour on the appropriate silver salt,[29] *e.g.*,

$$SiH_3I + AgNC \longrightarrow SiH_3{\cdot}NC + AgI$$

When this reaction is carried out with silver cyanate the desired silyl derivative is not obtained and only silicon tetra*iso*cyanate is formed.[29]

Physical properties. The silyl halides and silyl *iso*thiocyanate are colourless gases or liquids at room temperatures, but the *iso*cyanide is a solid which readily sublimes to form long colourless crystals. Both silyl fluoride and *iso*thiocyanate are considerably associated in the liquid state.[28, 29] The most important physical constants are given in Table 2.

TABLE 2

Compound	M.p.	B.p.	*d* (liquid)(g./ml.)
SiH_3F[28]	—	− 98·6°	—
SiH_3Cl[26]	− 118·1°	− 30·4	1·145 (− 113°)
SiH_3Br[30]	− 94	1·9	1·533 (0·0°)
SiH_3I[24]	− 57·0	45·4	2·05 (10·1°)
SiH_3NC[29]	32·4	49·6	—
SiH_3NCS[29]	− 51·8	84·0	1·05 (20°)

Reactions. All the silyl halides have a tendency to disproportionate at room temperatures.[24, 28] This is discussed fully later (p. 222). Silyl *iso*cyanide decomposes very slowly at room temperature during 1—2 years with the liberation of silane and hydrogen cyanide, while the *iso*thiocyanate decomposes during 2—3 weeks at room temperature, silane and hydrogen being formed.[29]

Silyl bromide is spontaneously inflammable in air,[30] whereas the chloride,[26] iodide,[24] and *isc*cyanide and *iso*thiocyanate [29] are not, although they will all burn when ignited. All the halides and pseudo-halides (with the exception of the fluoride which has not been tested) are hydrolysed instantaneously by water to disilyl ether (disiloxane) and the hydro-acid, *e.g.*,

$$2SiH_3I + H_2O \longrightarrow (SiH_3)_2O + 2HI$$

They are all completely and rapidly hydrolysed by aqueous alkali with the liberation of hydrogen.[29, 31–33]

All the hydrogen atoms in the silyl halides can be successively replaced by halogen by prolonged treatment with the appropriate hydrogen halide and aluminium halide catalyst.[23, 24]

Silyl chloride does not undergo a true Würtz-type reaction,[34] whereas silyl iodide does react to give large yields of disilane : [24]

$$2SiH_3I + 2Na \longrightarrow SiH_3{\cdot}SiH_3 + 2NaI$$

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[29] MacDiarmid, *J. Inorg. Nuclear Chem.*, 1956, **2,** 88.

[30] Stock and Somieski, *Ber.*, 1917, **50,** 1739.

[31] Maddock, Ph.D. Thesis, London, 1941.

[32] Stock, Somieski, and Wintgen, *Ber.*, 1917, **50,** 1754.

[33] Stock and Somieski, *Ber.*, 1923, **56,** 132.

[34] Stock, *op. cit.*, ref. 5, p. 34.

Other reactions, such as the interaction of silyl halides and pseudo-halides with ammonia, phosphine, amines, non-metals, metals, organometallic compounds, silver salts, etc., are more appropriately discussed in following sections since the halides and more particularly silyl iodide are the chief reagents in the syntheses of silyl compounds.

(B) *Compounds containing* Si–Si *Linkages.*[35]—*Preparation.* Disilanyl chloride, $SiH_3{\cdot}SiH_2Cl$, and disilanyl bromide, which are formally the inorganic analogues of ethyl chloride and bromide, may be prepared by the interaction of disilane with the hydrogen halide in the presence of the appropriate aluminium halide catalyst. More completely substituted compounds such as $Si_2H_4Cl_2$ and $Si_2H_3Cl_3$ are also formed in these reactions but they cannot be separated and are themselves mixtures of isomers.

Compounds such as $Si_3H_4Cl_4$ and $Si_3H_3Cl_5$ are formed in the reaction between chloroform or carbon tetrachloride and trisilane in the presence of aluminium chloride. Because of the formation of isomers it is not possible to separate any pure compounds.[25]

Properties and reactions. The compounds have not been thoroughly investigated. Disilanyl bromide melts at $-100°$ and both this compound and the chloride readily disproportionate. This property is discussed more fully in a later section.[35a] They are completely decomposed by aqueous alkali with the liberation of hydrogen.

(3) **Compounds containing Elements of Group VI.**——(A) *Compounds containing no* Si–Si *Linkage.—Preparation.* Silyl alcohol (silanol), $SiH_3{\cdot}OH$, has never been isolated and appears to have only a transitory existence. It has been detected in the hydrolysis products of silyl chloride and bromide, but it very rapidly condenses to form disilyl ether.[32] Silyl mercaptan (silanethiol), $SiH_3{\cdot}SH$, is formed in an equilibrium reaction between disilyl sulphide and hydrogen sulphide at room temperatures :[36]

$$(SiH_3)_2S + H_2S \rightleftharpoons 2SiH_3{\cdot}SH$$

Disilyl ether (disiloxane), $(SiH_3)_2O$, is formed by hydrolysis of many silyl compounds such as the halides, pseudo-halides,[37] quaternary ammonium salts,[38] disilyl sulphide and selenide.[39] The last two compounds are formed by the interaction of silyl iodide with mercuric sulphide and silver selenide, respectively :[36]

e.g., $$2SiH_3I + HgS \longrightarrow (SiH_3)_2S + HgI_2$$

A mixed alkyl silyl ether, ethyl silyl ether, is reported to be formed by ethyl alcohol with $[SiH_3{\cdot}N(CH_3)_3]Cl$ but it has not been isolated in the pure state.[40]

Properties. The compounds are all colourless gases or liquids. The most important physical constants are given in Table 3.

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[35] Stock and Somieski, *Ber.*, 1920, **53**, 759.

[35a] See p. 223.

[36] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

[37] See p. 212. [38] See p. 215. [39] See p. 213.

[40] (*a*) Emeléus and Miller, *J.*, 1939, 819; (*b*) Miller, Ph.D. Thesis, London, 1939.

TABLE 3

Compound	M.p.	B.p.	d (g./ml.)
$SiH_3 \cdot SH$[36]	~ − 134°	14·2°	—
$(SiH_3)_2O$[32]	− 144	− 15·2	0·881 (− 80°)
$(SiH_3)_2S$[36]	− 70·0	58·8	0·9294 (10·0°)
$(SiH_3)_2Se$[36]	− 68·0	85·2	1·36 (20°)

Reactions. Silanethiol has not been examined in detail. It begins to decompose slowly even at − 78° to produce disilyl sulphide and hydrogen sulphide.[36]

Disilyl ether is not spontaneously inflammable in air although it will burn when ignited.[32, 33] The sulphide is spontaneously inflammable in moist, but not in dry, air.[36] Disilyl ether is very stable thermally and may be heated to 300—400° without much decomposition,[33] while the sulphide suffers only slight thermal decomposition when held at 100—125° for several hours.[36] The selenide is stable at room temperatures but decomposes slightly when held near its boiling point for 2—3 hours.[36]

Both disilyl sulphide and selenide are instantaneously hydrolysed by water to disilyl ether, *e.g.*,

$$(SiH_3)_2S + H_2O \longrightarrow (SiH_3)_2O + H_2S$$

and all the compounds are decomposed by aqueous alkali with liberation of hydrogen.[36]

Disilyl ether, sulphide, and selenide all react with halogens. The ether reacts explosively with chlorine even at low temperatures to give a mixture of silicon tetrachloride and $(SiCl_3)_2O$.[32] With solid iodine at room temperatures, the following reaction occurs (M = O, S, or Se) : [36]

$$(SiH_3)_2M + I_2 \longrightarrow 2SiH_3I + M_2$$

The sulphide and selenide both react with hydrogen iodide to give silyl iodide,[36] *e.g.*,

$$(SiH_3)_2Se + 2HI \longrightarrow 2SiH_3I + H_2Se$$

Methyl iodide reacts neither with the sulphide nor with the selenide to form " onium " type compounds and no sulphonium compound is formed by disilyl sulphide and silyl iodide.[36] The sulphide does not form an addition compound with either mercuric chloride or iodide. With the former, the reaction proceeds quantitatively : [36]

$$(SiH_3)_2S + HgCl_2 \longrightarrow 2SiH_3Cl + HgS$$

Complex reactions occur between disilyl sulphide and ammonia or trimethylamine to yield silane and unidentified solids.[36]

(B) *Compound containing* Si–Si *Linkages.*—Only one compound in this category is known, *viz.*, $(SiH_3 \cdot SiH_2)_2O$,[35] and even this has not been completely characterised. It is formed by the hydrolysis of disilanyl chloride or bromide, *e.g.*,

$$2SiH_3 \cdot SiH_2Br + H_2O \longrightarrow (SiH_3 \cdot SiH_2)_2O + 2HBr$$

It is a colourless liquid which can be volatilised without decomposition. When dissolved in benzene it instantaneously reduces silver nitrate.

(4) **Compounds containing Elements of Group** V.—(A) *Nitrogen Compounds.—Preparation.* The mono- and di-silylamines, $SiH_3{\cdot}NH_2$ and $(SiH_3)_2NH$, are formed in the reaction between silyl chloride and excess of ammonia but they have not been obtained in the pure state since they are comparatively unstable.[41] Trisilylamine, $(SiH_3)_3N$, may be prepared by the action of excess of silyl chloride on ammonia : [41]

$$3SiH_3Cl + NH_3 \longrightarrow (SiH_3)_3N + 3HCl$$

The alkyl-substituted amines such as $(SiH_3)_2NMe$, $(SiH_3)_2NEt$, $SiH_3{\cdot}NMe_2$ are formed readily in the reaction between silyl chloride or bromide and the appropriate amine at room temperature,[3, 40] *e.g.*,

$$SiH_3Br + NHMe_2 \longrightarrow SiH_3{\cdot}NMe_2 + HBr$$

Quaternary ammonium type compounds such as $[(SiH_3)_2NMe_2]Cl$, $(SiH_3{\cdot}NMe_3)Cl$, $(SiH_3{\cdot}NMe_3)I$, and $(SiH_3{\cdot}NEt_3)I$ are formed in instantaneous reactions at room or reduced temperatures between the appropriate silyl halide and amine,[40, 42] *e.g.*,

$$SiH_3I + NMe_3 \longrightarrow (SiH_3{\cdot}NMe_3)I$$

An addition compound with a formula approximating to $SiH_3I,(NMe_3)_2$ can be prepared by the action of silyl iodide on excess of trimethylamine.[42]

Properties. The simple amines and alkyl-substituted amines are all colourless gases or liquids, and the quaternary and addition compounds are colourless solids. Physical constants, where available, are given in Table 4.

TABLE 4

Compound	M.p.	B.p.	*d* (g./ml.)
$(SiH_3)_3N$[41]	− 105·6°	52°	0·895 (− 106°)
$(SiH_3)_2NMe$[40]	—	32·3	—
SiH_3NMe_2[3, 40]	3·4	—	—
$(SiH_3)_2NEt$[40]	− 127	65·9	—

Reactions. The compounds $SiH_3{\cdot}NH_2$ and $(SiH_3)_2NH$ rapidly condense in the gaseous state to form $(SiH_3)_3N$ and ammonia. The disilylamine also decomposes to some extent as shown below :

$$(SiH_3)_2NH \longrightarrow SiH_4 + ({\cdot}SiH_2{\cdot}NH{\cdot})_x$$

Trisilylamine is spontaneously inflammable in air and is vigorously decomposed by water to give silica, ammonia, and hydrogen.[41]

The alkyl-substituted amines are comparatively stable although $SiH_3{\cdot}NMe_2$ decomposes at a measurable rate at its melting point.[3] Hydrogen chloride reacts with $(SiH_3)_2NMe$, $(SiH_3)_2NEt$, and also $(SiH_3)_3N$ to form silyl chloride,[40, 41] *e.g.*,

$$(SiH_3)_2N{\cdot}CH_3 + 3HCl \longrightarrow 2SiH_3Cl + CH_3{\cdot}NH_2,HCl$$

No alkylsilylamine hydrochloride is formed in this type of reaction.

The amines form addition compounds of varying degrees of stability

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[41] Stock and Somieski, *Ber.*, 1921, **54,** 740.

[42] Aylett, Emeléus, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1,** 187.

with boron hydrides and their derivatives such as $(SiH_3)_2N{\cdot}B_2H_5$, $(SiH_3)MeN{\cdot}B_2H_5$, $SiH_3{\cdot}NMe_2,BMe_3$, and $(SiH_3)_3N,BCl_3$ which subsequently decomposes to give $(SiH_3)_2NBCl_2$:

$$(SiH_3)_3N + BCl_3 \longrightarrow (SiH_3)_2NBCl_2 + SiH_3Cl$$

These compounds have, in general, been completely characterised.[3, 4]

The quaternary ammonium type compounds containing only one silyl group are stable and decompose only slowly in air, while dimethyldisilyl ammonium chloride is unstable and decomposes readily.[40, 42]

A solution of $(SiH_3{\cdot}NMe_3)Cl$ in acetone conducts electricity,[40] as does also a solution of $(SiH_3{\cdot}NMe_3)I$ in acetonitrile. However, the addition compound $SiH_3I,(NMe_3)_2$ does not conduct an electric current in this solvent.[42]

In contrast to the action of hydrogen chloride on the alkylsilylamines, hydrogen iodide does not react with $(SiH_3{\cdot}NMe_3)I$ or even with $SiH_3I,(NMe_3)_2$.[43]

The compound $(SiH_3{\cdot}NMe_3)Cl$ is an excellent " silylating " agent and can be used to introduce silyl groups into such substances as ethyl alcohol, water, etc.[40]

(B) *Phosphorus Compounds.*—*Preparation.* Monosilylphosphine, $SiH_3{\cdot}PH_2$ can be prepared by heating a mixture of silane and phosphine,[44] while trisilylphosphine, $(SiH_3)_3P$, iododisilylphosphine, $(SiH_3)_2PI$, di-iodosilylphosphine, $SiH_3{\cdot}PI_2$, and tetrasilylphosphonium iodide, $[(SiH_3)_4P]I$, are found amongst the products of the reaction between silyl iodide and white phosphorus.[42] Trisilylphosphine and iododisilylphosphine have not yet been isolated in the pure state.

No simple alkylsilylphosphines have been reported but there are several alkylsilylphosphonium compounds known, such as $[SiH_3{\cdot}PMe_3]I$, $[SiH_3{\cdot}PEt_3]I$, $[SiH_3{\cdot}PHMe_2]Br$, $[SiH_3{\cdot}PHMe_2]I$, and $[SiH_3{\cdot}PH_2Me]Br$. These are all formed by direct reaction between the appropriate silyl halide and alkylphosphine at or below room temperatures.[2, 42]

Properties and reactions. Very little is known about silylphosphorus compounds and only $SiH_3{\cdot}PI_2$ has been characterised to any extent. This substance boils at 190° but decomposes at measurable rate at room temperatures.[42]

The compound $SiH_3{\cdot}PH_2$ reacts with ammonium hydroxide to produce silane, phosphine, and hydrogen,[44] and $(SiH_3)_3P$ yields phosphine on hydrolysis.[42]

The phosphonium compounds are all white solids some of which, *e.g.*, $(SiH_3{\cdot}PHMe_2)Br$ and $(SiH_3{\cdot}PH_2Me_2)Br$, are largely dissociated even at low temperatures.[2]

Silyltriethylphosphonium iodide, $(SiH_3{\cdot}PEt_3)I$, is a very stable solid at room temperatures and its solution in acetonitrile conducts an electric current.[42]

(C) *Arsenic Compounds.*[42]—*Preparation.* Monosilylarsine, $SiH_3{\cdot}AsH_2$, iododisilylarsine, $(SiH_3)_2AsI$, and di-iodosilylarsine, $SiH_3{\cdot}AsI_2$, have been

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[43] Aylett, Ph.D. Thesis, Cambridge, 1954.

[44] Fritz, *Z. Naturforsch.*, 1953, **8***b*, 776.

reported amongst the products of the reaction between silyl iodide and arsenic. Disilylarsine, $(SiH_3)_2AsH$,[43] and trisilylarsine, $(SiH_3)_3As$, are formed by the reaction of silyl iodide with K_3As, but they have not been obtained in the pure state.

No alkylsilylarsines are known, but the quaternary arsonium compound $(SiH_3{\cdot}AsMe_3)I$ is formed by direct reaction between silyl iodide and trimethylarsine. Tetrasilylarsonium iodide, $[(SiH_3)_4As]I$, is formed by the action of silyl iodide on mercuric arsenide.

Properties and reactions. Di-iodosilylarsine, $SiH_3{\cdot}AsI_2$, is the only silyl–arsenic compound which has been characterised to any extent. It melts at 4° and boils at 201°; it begins to decompose rapidly at about 80°.

Trisilylarsine boils at 97—98° and arsine is formed when it is hydrolysed with aqueous alkali. Little is known of the other substances apart from $(SiH_3{\cdot}AsMe_3)I$ which melts at 8·1—9·6° and has a high dissociation pressure at low temperatures.

(5) **Compounds containing Elements of Group** IV.—*Preparation.* Several compounds have been reported in which an alkyl or a phenyl group is attached to a silyl group. In general they can be synthesised by reaction of silyl chloride with an organo-metallic compound [26] or by reducing a trichloride, in which all the chlorine atoms are attached to the silicon, with $LiAlH_4$.[10] The latter method is the one most commonly used, *e.g.*,

$$2SiH_3Cl + ZnMe_2 \longrightarrow 2SiH_3Me + ZnCl_2$$

$$SiCl_3Me \xrightarrow{LiAlH_4} SiH_3Me$$

Properties. All the compounds are colourless liquids or gases. Their chief physical constants are given in Table 5.

TABLE 5

Compound	M.p.	B.p.	*d* (g./ml.)
$SiH_3{\cdot}CH_3$[26]	− 157°	− 57°	0·62 (− 57°)
$SiH_3{\cdot}CH_2{\cdot}CH_3$[10] . . .	—	− 14	—
$SiH_3{\cdot}[CH_2]_2{\cdot}CH_3$[10] . . .	—	23°	0·6434 (20°)
$SiH_3{\cdot}[CH_2]_3{\cdot}CH_3$[10] . . .	—	55	0·6764 (20°)
$SiH_3{\cdot}C_6H_5$[10]	—	120	0·8681 (20°)

Reactions. All these compounds are very stable. They are not spontaneously inflammable in air, and they react very slowly with water but somewhat more rapidly with aqueous alkali. No measurable decomposition occurs on prolonged storage in a sealed container at room temperatures.[10, 26]

With silylmethane, and presumably with the other alkyl derivatives, a hydrogen atom may be replaced by a chlorine or iodine atom when the compound is heated with the appropriate hydrogen halide and aluminium halide catalyst,[26, 45] *e.g.*,

$$CH_3{\cdot}SiH_3 + HCl \xrightarrow{Al_2Cl_6} CH_3{\cdot}SiH_2Cl + H_2$$

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[45] Emeléus and Onyszchuk, private communication, December, 1954.

(6) **The Free Silyl Radical.**—There is no definite evidence for the existence of the free silyl radical. The fact that SiH_3I undergoes a Würtz type of reaction with sodium to give high yields of disilane [24] might be due to the existence of short-lived silyl radicals ; *e.g.*,

$$\begin{array}{llrcl} & \text{(i)} & SiH_3I + Na & \longrightarrow & SiH_3 + NaI \\ & \text{(iia)} & 2SiH_3 & \longrightarrow & Si_2H_6 \\ \text{or} & \text{(iib)} & SiH_3 + Na & \longrightarrow & NaSiH_3 \\ \text{followed by} & & NaSiH_3 + SiH_3I & \longrightarrow & Si_2H_6 + NaI \end{array}$$

However, this reaction could probably proceed without the formation of free radicals, merely by the combination of two adjacent SiH_3I molecules as they react on the surface of the sodium.

Recent experiments on the pyrolysis of silane and disilane with the subsequent passage of the hot gases over films of metals and non-metals gave no indication of the existence of free silyl radicals.[46]

(7) **Silyl Metallic Compounds.**—There is some very slight evidence that silyl iodide may combine with metals to form analogues of the methyl organo-metallic compounds. This was indicated in the preceding section when it was suggested that silyl iodide may react with sodium to form disilane through the intermediate formation of $NaSiH_3$.

It has been observed that silyl iodide reacts with metallic zinc to give a solid product—possibly $SiH_3{\cdot}ZnI$.[24] However, the reaction has recently been re-examined and no trace of this compound was obtained.[43] A solid substance, possibly $SiH_3{\cdot}HgI$,[24] has been reported as being formed in the reaction between silyl iodide and mercury but no details of its properties have been given. It has also been reported that magnesium dissolves in a solution of silyl iodide in di*iso*pentyl ether.[24] It appears likely that an unstable Grignard-type compound may be formed in this reaction, although no Grignard compound could be isolated from the reaction of silyl bromide with magnesium.[46a]

Theoretical aspects of silyl chemistry

(1) *Melting Point.*—There are fourteen pairs of analogous silyl and methyl compounds whose melting points are known. In six cases the silyl compound melts at a lower temperature than the methyl compound, and in eight cases at a higher temperature. If the melting points of the silicon compounds are plotted against those of their respective carbon analogues, there is a very general linear trend, but the points do not fall on, or near, any sort of line or curve. Consequently, there is no simple relationship between the melting points of these substances.

Nevertheless, several interesting comparisons may be made between the silyl and methyl compounds. For instance, in the XH_4 compounds the replacement of a hydrogen by a halogen atom has a smaller effect on the melting point of the silicon than on that of the carbon compound if the

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[46] Emeléus, Kuchen, and Maddock, private communication, December, 1954.
[46a] Von Artsdalen and Gavis, *J. Amer. Chem. Soc.*, 1952, **74**, 3196.

halogen is chlorine; if it is bromine the effects are approximately equal; and if it is iodine the effect is greater in the silicon derivative. Another noticeable trend is that the melting points of silyl chloride, bromide, and iodide increase regularly with increasing molecular weight. This effect is not observable in the methyl compounds.

The insertion of an oxygen or sulphur atom between silicon atoms in Si_2H_6 raises the melting point much less than their insertion between carbon atoms in C_2H_6. For instance, the difference in melting points of C_2H_6 and $(CH_3)_2O$ is 45·2°, while the difference for Si_2H_6 and $(SiH_3)_2O$ is only 11·5°. Also, the difference in melting points of C_2H_6 and $(CH_3)_2S$ is 100·5°, while that between Si_2H_6 and $(SiH_3)_2S$ is only 62°.

It is not surprising that no simple relationship exists between the melting points of corresponding silyl and methyl compounds, since this property depends largely on the crystal structure which could vary greatly between analogous compounds because of the larger size of the silicon atom and the different molecular structure of some silyl derivatives.

(2) *Boiling Point.*—There are twenty-one pairs of analogous silyl and methyl compounds whose boiling points are known. If the boiling points of the silicon derivatives are plotted against those of their respective carbon analogues there is a general linear trend over the group as a whole, and a very close linearity within each sub-group of compounds (see Fig. 1). In all three sub-groups where there are three or more members of similar formula type, a very close linear relationship is observed. From this it follows automatically that the molar heats of vaporisation must also bear a linear relationship to each other since the Trouton constants for silyl and methyl compounds are generally similar.

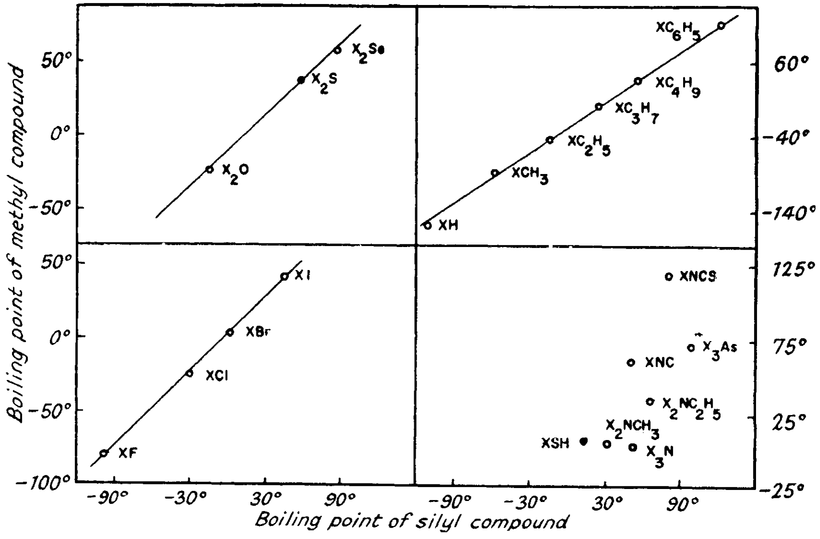

FIG. 1

Boiling points of silyl ($X = SiH_3$) *and methyl* ($X = CH_3$) *compounds.*

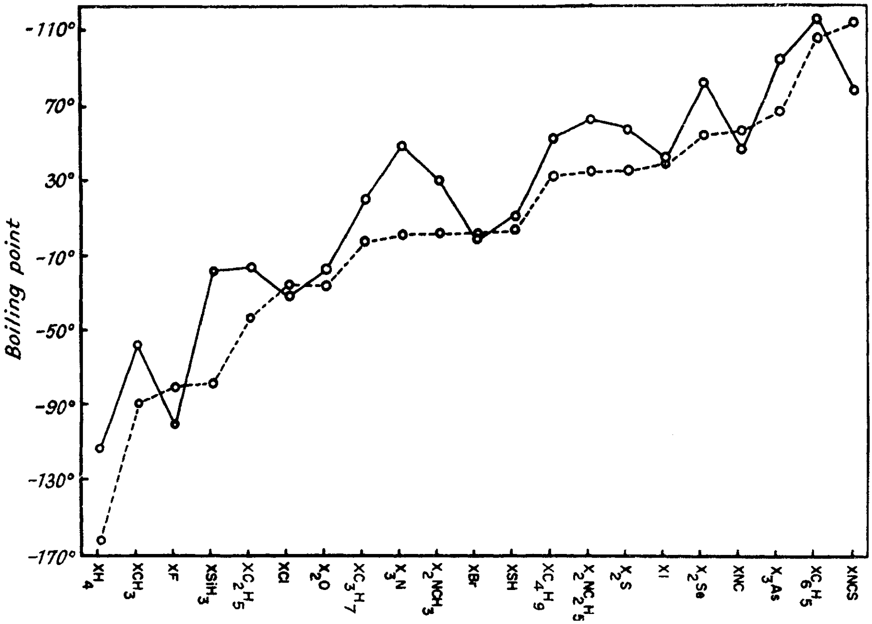

FIG. 2

Boiling points of silyl (——) and methyl (- - - -) compounds.

In Fig. 2 the boiling points of the carbon compounds are plotted in order of increasing value and those of the silicon derivatives are then added in the same order. It can be seen that all silyl compounds boil at a higher temperature than their methyl analogues except the halogen and pseudo-halogen compounds (except that silyl iodide boils 2·9° above methyl iodide). The (algebraic) difference between the boiling points of the silyl and methyl halides becomes less with increasing atomic weight of the halogen.

From Table 6 it can be seen that replacement of a hydrogen in SiH_4 or CH_4 by a halogen raises the boiling point much less in the silicon compound than in the carbon analogue. This effect becomes *less* noticeable as the atomic weight of the halogen increases. Also, from Table 7, it is apparent that the replacement of a hydrogen in SiH_4 or CH_4 by an aliphatic or aromatic group raises the boiling point much less in the silicon than in the carbon compound. This effect becomes *more* noticeable as the molecular

TABLE 6

Y	B.p. (SiH_3Y) − B.p. (SiH_4)	B.p. (CH_3Y) − B.p. (CH_4)	Δ
F	13·3°	82·7°	69·4°
Cl	81·5°	137·2°	55·7°
Br	113·8°	165·8°	52·0°
I	157·3°	203·8°	46·5°

weight of the substituted group increases, *i.e.*, the reverse of the trend noted with the halogens.

TABLE 7

Y	B.p. (SiH_3Y) − B.p. (SiH_4)	B.p. (CH_3Y) − B.p. (CH_4)	Δ
CH_3	54·9°	72·6°	17·7°
C_2H_5	97·9°	119·1°	21·2°
C_3H_7	134·9°	160·4°	25·5°
C_4H_9	166·9°	197·5°	30·6°
C_6H_5	231·9°	271·9°	40·0°

From Table 8 it can be seen that the insertion of an oxygen, sulphur, or selenium atom between the silicon atoms in Si_2H_6 raises the boiling point far less than when they are inserted between the carbon atoms in C_2H_6. The effect becomes *less* noticeable as the atomic weight of the substituted atom increases.

TABLE 8

Y	B.p. (S_2H_6Y) − B.p. (Si_2H_6)	B.p. (C_2H_6Y) − B.p. (C_2H_6)	Δ
O	— 0·7°	65·0°	65·7°
S	73·5°	126·2°	52·7°
Se	99·7°	146·9°	47·2°

The boiling point of a substance depends on the magnitude of the intermolecular attractive forces acting between its molecules. These forces depend on a number of factors such as the molecular weight of the species, molecular structure, dipole moment, degree of hydrogen bonding, etc. Their effects may reinforce or oppose one another, and it is therefore difficult to predict what the net effect on the intermolecular attractive forces, and hence on the boiling point, will be when one atom in a compound is replaced by a different atom or group. Consequently, it is not surprising to find that silyl fluoride, chloride, bromide, *iso*cyanide, and *iso*thiocyanate boil at lower temperatures than their methyl analogues even though their molecular weights are greater. This may well be related to the fact that the dipole moments of simple halogenated silanes are generally smaller than those of the corresponding carbon compounds,[47] and hence the intermolecular attractive forces might also be less.

(3) *Methods of Preparation of Silyl Compounds.*—There are two general methods of preparation which appear to have great potential value.

(A) "*Conversion series.*" The vapour of a simple silyl compound is allowed to react with a silver salt and double decomposition ensues. This type of reaction (carried out under different experimental conditions) has already been used for the preparation of several organo-silicon deriva-

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[47] (*a*) Brockway and Coop, *Trans. Faraday Soc.*, 1938, **34,** 1429 ; (*b*) Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61,** 3036 ; (*c*) Spauschus, Mills, Scott, and MacKenzie, *ibid.*, 1950, **72,** 1377.

tives.[48, 49] The modified " conversion series " proposed for silyl compounds is given below. It is postulated that treatment of a compound with the appropriate silver salt will bring about a conversion into any compound later in the series but into none earlier therein.

$$(SiH_3)_2Te \rightarrow SiH_3I \rightarrow (SiH_3)_2Se \rightarrow (SiH_3)_2S \rightarrow SiH_3Br \rightarrow SiH_3Cl \rightarrow SiH_3{\cdot}NC \rightarrow SiH_3{\cdot}NCS \rightarrow SiH_3{\cdot}NCO \rightarrow (SiH_3)_2O \rightarrow SiH_3F$$

This postulate has so far been tested successfully in six reactions,[29, 36] *viz.*, the conversion of silyl iodide into the selenide, *iso*cyanide, *iso*thiocyanate, and *iso*cyanate, that of the *iso*thiocyanate into the *iso*cyanate, and the non-conversion of the *iso*cyanide into the chloride. No silyl *iso*cyanate has yet been isolated from the above reactions since it is apparently very unstable and decomposes rapidly to the tetra*iso*cyanate, $Si(NCO)_4$. Thermodynamic calculations [50] using Si—M (M being the attached element) bond energies where available,[51, 52a] and the free energies of formation of the silver salts [52b] substantiate the order of compounds in the series. These calculations are not exact in that it is necessary to assume that the entropy change between the silyl reactant and product is zero, but they are completely general, and in contrast to those of some investigators,[48] they apply regardless of the mechanism of the reactions.

Another conversion series using mercuric salts may well exist and four reactions have already been studied.[36] Thermodynamic calculations give results similar to those of the silver salts.[50] Somewhat similar reactions occur with some alkyl iodides and salts of the heavy metals.[53]

(B) " *Acid replacement series.*" The silyl compound in the form of liquid or vapour is allowed to react with the appropriate hydro-acid. The " acid replacement series " proposed for silyl compounds is given below. It is postulated that treatment of any substance in the series with the appropriate hydro-acid will bring about a conversion into any compound later in the series but into none earlier therein.

$$SiH_3H \rightarrow (SiH_3)_2Se \rightarrow (SiH_3)_2S \rightarrow SiH_3I \rightarrow SiH_3Br \rightarrow SiH_3Cl \rightarrow SiH_3F \rightarrow (SiH_3)_2O$$

This postulate has so far been tested successfully in twelve reactions, *viz.*, the conversion of silane into silyl halides, that of silyl halides and pseudohalides into disilyl ether, that of disilyl sulphide and selenide into disilyl ether and that of disilyl sulphide and selenide into silyl iodide. Thermodynamic calculations again substantiate the order of the compounds given in the series.[50]

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[48] Eaborn, *J.*, 1950, 3077.

[49] (*a*) Anderson and Fischer, *J. Org. Chem.*, 1954, **19**, 1296 ; (*b*) Anderson and Vasta, *ibid.*, p. 1300.

[50] MacDiarmid, unpublished work.

[51] Gilman and Dunn, *Chem. Rev.*, 1953, **52**, 77.

[52] (*a*) Sidgwick, " The Chemical Elements and Their Compounds ", Oxford Univ. Press, 1950, p. xxxi ; (*b*) Latimer, " Oxidation Potentials ", 2nd edn., Prentice-Hall Inc., 1952, p. 190.

[53] Karrer, " Organic Chemistry ", Elsevier Press, New York, 1938, pp. 66, 168.

(4) *The Electron-attracting Character of the Silyl Group.*—From theoretical considerations supported by physical and chemical observations, it may be shown that the silyl group, when joined to many atoms or groups, may act as a powerful electron acceptor. At first sight it would appear that the silyl radical should act as a less powerful electron acceptor than the methyl group since the electronegativity of silicon (1·8) is less than that of carbon (2·5). However, it has recently been shown that π bonds may play a considerable part in the bonding of atoms with one or more lone pairs of electrons to atoms with vacant *d*-orbitals. This often occurs in bonds between silicon and elements of Groups V, VI, and VII where there is an overlap between a vacant silicon d_π orbital and a p_π orbital on an atom to which the silicon is already bound by a σ bond.[42, 54, 55] The π bond is usually stronger the *more electronegative* the donor atom. Consequently, the silicon actually attracts electrons more strongly than would be expected from simple electronegativity data. This effect cannot take place with carbon since it has no 3*d* orbitals. The shortening [56–58] of silicon–halogen and silicon–oxygen bond lengths is consistent with this concept, although other causes have been suggested.[59] The small dipole moments of simple halogenated silanes also support this viewpoint.[47]

The infrared absorption spectrum of $(SiH_3)_3N$ indicates that this molecule is planar, in contrast to that of $(CH_3)_3N$ which is pyrimidal. This could be explained if there were some resonating bonding structures present such as $H_3Si\underline{\leftarrow}N(SiH_3)_2$.[60] Further evidence for this type of bonding is given by the infrared spectrum of $SiH_3{\cdot}NCS$ which indicates a linear molecule whereas $CH_3{\cdot}NCS$ is non-linear.[61] This is consistent with a structure such as $H_3Si\underline{\leftarrow}N{=}C{=}S$.

Chemical support for the π-bonding concept is given by the unexpected properties of many organo-silicon compounds,[51, 55, 61a] and also by the unsubstituted silyl derivatives which will be discussed in the following sections.

(5) *Silyl Halides.*—All the silyl halides tend to disproportionate as shown : [24, 28]

$$2SiH_3X \longrightarrow SiH_2X_2 + SiH_4$$

The effect is greatest in the fluoride and becomes progressively less on passing to the chloride, then to the bromide and finally to the iodide, in which it is negligible.

[54] Craig, Maccoll, Nyholm, Orgel, and Sutton. *J.*, 1954, 344.

[55] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112.

[56] (*a*) Pauling, " The Nature of the Chemical Bond ", 2nd edn., Cornell Univ. Press, Ithaca, New York, 1948, p. 164 ; (*b*) Dailey, Mays, and Townes, *Phys. Rev.*, 1949, **76**, 136 ; (*c*) Mays and Dailey, *J. Chem. Phys.*, 1952, **26**, 1695 ; (*d*) Sheridan and Gordy, *ibid.*, 1951, **19**, 965.

[57] Huggins, *J. Amer. Chem. Soc.*, 1953, **75**, 4126.

[58] Schomaker and Stevenson, *ibid.*, 1941, **63**, 37.

[59] (*a*) Pitzer, *ibid.*, 1948, **70**, 2140 ; (*b*) Mulliken, *ibid.*, 1950, **72**, 4493.

[60] Hedberg and Stosick, Abstracts of the XII International Congress of Pure and Applied Chemistry, New York, September 10–13, 1951, p. 543.

[61] MacDiarmid and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 411.

[61a] Lord, Robinson, and Schumb (*J. Amer. Chem. Soc.*, 1956, **78**, 1327) report that $(SiH_3)_2O$ is a linear molecule ; this is further evidence of π bonding in silyl compounds.

The two known disilanyl halides disproportionate as shown : [35]

$$2SiH_3{\cdot}SiH_2X \longrightarrow Si_2H_4X_2 + Si_2H_6$$

where X is either chlorine or bromine. The effect is most noticeable in the chloride and the rates of disproportionation are greater than in the simple silyl compounds.

Thermodynamically, the reactions may proceed, at least to a measurable extent, because of the entropy changes involved in the redistribution of the hydrogen and halogen atoms, although this will be modified by the variation of Si–X bond lengths in the products and reactants.[57, 62]

The rate of disproportionation will be decided by the mechanism of the reaction and the magnitude of the activation energy involved. Three possible mechanisms are given below in which SiH_3F is used as an example. A similar argument would apply to the other silyl halides.

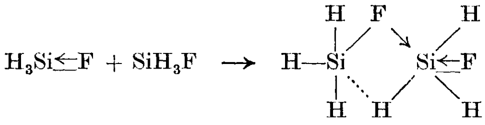
$$\begin{array}{lllll}
(1) & SiH_3F \longrightarrow & SiH_3 + F & & \\
 & & F + SiH_3F & \longrightarrow & SiH_2F_2 + H \\
 & & H + SiH_3 & \longrightarrow & SiH_4
\end{array}$$

$$\begin{array}{lllll}
(2) & SiH_3F \longrightarrow & SiH_3^+ + F^- & & \\
 & & F^- + SiH_3F & \longrightarrow & SiH_2F_2 + H^- \\
 & & H^- + SiH_3^+ & \longrightarrow & SiH_4
\end{array}$$

$$(3)\quad 2SiH_3F \longrightarrow (SiH_3F \rightarrow SiH_3F)^* \longrightarrow SiH_2F_2 + SiH_4$$

Mechanisms (1) and (2) are unsuitable because they suggest that the rate of disproportionation should be greater the smaller the silicon–halogen covalent bond energy (mechanism 1), or the smaller the ionic bond energy (mechanism 2). It would appear that the activation energy needed for homolytic or heterolytic fission of the silyl halide would be the rate-controlling factor in these mechanisms. If this were the case, the rate would increase from the fluoride to the iodide since this is the direction of decreasing covalent [51] and ionic [48] bond strengths. Experimental data show that the disproportionation rate is the reverse of that given by this treatment. In addition, no hydrogen fluoride is found amongst the products of the disproportionation, as might be expected if free hydrogen or fluorine atoms or ions were involved. This fact would also tend to discourage any other mechanism involving free hydrogen or fluorine atoms.

Mechanism (3) satisfies the experimental data if it is assumed that the silicon–halogen π bond could also act in an *inter*molecular fashion,[3] and so cause the formation of the activated complex shown below. This could readily break down to give SiH_4 and SiH_2F_2 :



Since the strength of the π bond decreases with decreasing electronegativity

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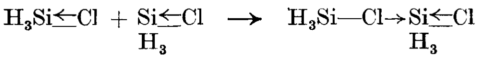
[62] Sharbaugh, Heath, Thomas, and Sheridan, *Nature*, 1953, **171**, 87.

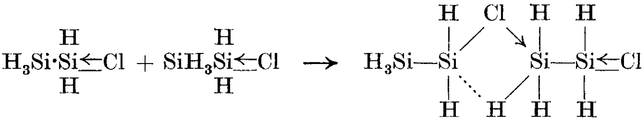
of the halogen, the ease of formation of the activated complex would decrease on going from the fluoride to iodide, with a consequence decrease in the rate of disproportionation.

The fact that disilanyl halides disproportionate at a greater rate than the simple silyl halides could also be explained by this treatment. With silyl chloride, for example, there will always be a tendency for the intramolecular π bonding to reduce any intermolecular π bonding by increasing the negative charge on the silicon atom, *e.g.*,



$$H_3Si\underline{\leftarrow}Cl + \underset{H_3}{Si}\underline{\leftarrow}Cl \longrightarrow H_3Si—Cl\rightarrow\underset{H_3}{Si}\underline{\leftarrow}Cl$$

However, in $SiH_3{\cdot}SiH_2Cl$, the silyl group is not attached directly to the halogen atom and hence it is not affected by the increase of negative charge caused by the intramolecular π bond. Therefore, the silyl group can accept an intermolecular π bond much more easily than in the case of silyl chloride, and consequently the disproportionation proceeds much more rapidly, *e.g.*,



The activated complex could then readily break down to give $SiH_3{\cdot}SiH_3$ and $SiH_2Cl{\cdot}SiH_2Cl$. It would appear that the disproportionation product should be the 1 : 2-dichlorodisilane and not 1 : 1-dichlorodisilane.

Although the fluoride and iodide have not yet been prepared, it would seem safe to predict from the discussion above that the former would disproportionate very rapidly and the latter very slowly.

On developing the argument further it becomes apparent that the halides of the next higher homologues, *e.g.*, $SiH_3{\cdot}SiH_2{\cdot}SiH_2Cl$, might be expected to disproportionate at an even greater rate. In this case, the number of silicon atoms per molecule to which the intermolecular π bond may be attached is greater.

(6) *Silyl Derivatives of the Pseudo-halogen Acids.*—There is at present very little evidence to indicate whether the compounds $SiH_3{\cdot}NC$ and $SiH_3{\cdot}NCS$ are the normal or *iso*-derivatives. Until there is evidence to the contrary it seems reasonable to assume that they are *iso*-compounds, by comparison with their methyl analogues, since the reaction of methyl iodide with silver cyanide produces the *iso*-derivative.[63]

Hydrolysis cannot be used to distinguish the isomers as with the carbon compounds since the cyanide group is removed instantaneously from the silyl group by treatment with water. It is not slowly hydrolysed while still attached to the group to give substances similar to $CH_3{\cdot}CO_2NH_4$ or $CH_3{\cdot}NH_2$.[29]

The infrared spectra of $SiH_3{\cdot}NC$ and $SiH_3{\cdot}NCS$ cannot be used directly to determine whether the compounds are the normal or *iso*-derivatives.

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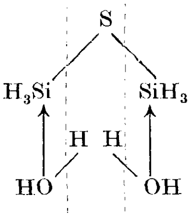
[63] Gauthier, *Ann. Chim. Phys.*, 1869, **17**, 203.

However, infrared data indicate that the thiocyanate is a (linear) symmetrical-top molecule, which is more consistent with its being the *iso*- rather than the normal derivative.

The fact that silyl *iso*thiocyanate is associated in the liquid state may be due to the presence of *inter*molecular π bonding [29] as suggested for the vapour association of $SiH_3{\cdot}NMe_2$.[3]

(7) *Silyl Derivatives containing Group* VI *Elements.*—The reactions of $(SiH_3)_2O$, $(SiH_3)_2S$, and $(SiH_3)_2Se$ are not at all like those of their methyl analogues, presumably because the π bonding (back-co-ordination) to the silicon is so strong that the central atom has lost most, if not all, of its powers of co-ordination. Structures such as $H_3Si\overset{\leftarrow}{=}M{-}SiH_3$ are probably involved.[61a] The compounds no longer show any tendency to form oxonium, sulphonium, or selenonium compounds of the type $[(SiH_3)_2RS]I$, where R is an alkyl or silyl group. Even compounds containing only one silyl group such as $[SiH_3{\cdot}SMe_2]I$ are not formed.[31] Substances which might form these compounds or other addition compounds [64] either do not react at all, *e.g.*, SiH_3I and $(SiH_3)_2S$, or if they do react, they do not give the product expected by analogy with carbon chemistry, *e.g.*, I_2 or HI, and $(SiH_3)_2S$ or $(SiH_3)_2Se$ give only SiH_3I. Addition compounds of $(SiH_3)_2S$ with $HgCl_2$ or HgI_2, which are known with the methyl analogue,[65] are not formed with the silyl derivatives.

The hydrolysis of disilyl sulphide and selenide to form the ether is characteristic of silyl compounds but it is interesting to note that a gelatinous intermediate compound is first formed which then rapidly decomposes to give the hydrolysis products.[36] The intermediate probably has one or more water molecules co-ordinated to the silicon, *e.g.*,



Hydrogen sulphide could then split off with the formation of $SiH_3{\cdot}OH$, which could then condense to give the ether.

The experimental parachor value of disilyl sulphide indicates that the Si–S bond probably possesses a considerable amount of π-bonding character. The parachor of silyl compounds might serve as an empirical physical method for determining the presence of back-co-ordination in these substances.[66]

(8) *Condensation Reactions.*—Compounds which have at least one silyl

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[64] (*a*) Steinkopf and Müller, *Ber.*, 1923, **56**, 1928; (*b*) Sidgwick, *op. cit.*, ref. 52*a*, pp 955, 958.

[65] (*a*) Smiles, *Proc.*, 1899, **15**, 240; (*b*) Phillips, *J.*, 1901, **79**, 250.

[66] MacDiarmid, *J. Inorg. Nuclear Chem.*, in the press.

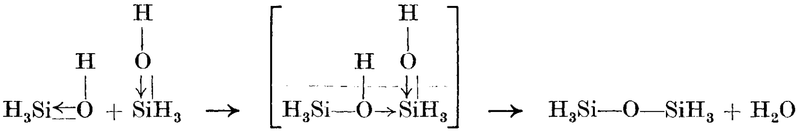
group and one hydrogen atom attached to a central atom frequently undergo spontaneous condensation, *e.g.*

$$\begin{array}{rcll} 2SiH_3{\cdot}OH & \longrightarrow & (SiH_3)_2O + H_2O & \text{Rapid} \\ 2SiH_3{\cdot}SH & \longrightarrow & (SiH_3)_2S + H_2S & \text{Slow} \\ \\ 2(SiH_3)_2NH & \longrightarrow & 2(SiH_3)_3N + NH_3 & \text{Rapid} \\ 3SiH_3{\cdot}NH_2 & \longrightarrow & (SiH_3)_3N + 2NH_3 & \text{Rapid} \\ 2SiH_3{\cdot}PH_2 & \longrightarrow & (SiH_3)_3P + 2PH_3 & \text{Slow} \\ 3SiH_3{\cdot}AsH_2 & \longrightarrow & (SiH_3)_3As + 2AsH_3 & \text{Slow} \end{array}$$

In many systems spontaneous condensation is thermodynamically possible but it takes place infinitesimally slowly, *e.g.*, the free-energy change for the reaction below, under standard conditions, is $-$ 19·6 kcal.

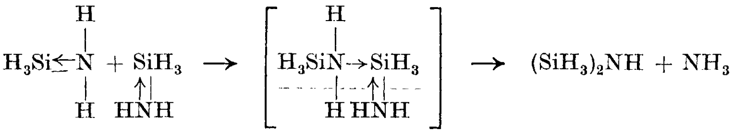
$$2CH_3{\cdot}OH \longrightarrow (CH_3)_2O + H_2O$$

The problem is essentially kinetic and not thermodynamic in character once it has been established, either theoretically or experimentally, that the changes are thermodynamically possible. It seems probable that the Group V or VI atom could form an *inter*molecular π bond to the silicon of an adjacent molecule and so produce very easily activated complexes in which the silicon atoms of two molecules are already joined to the same oxygen, sulphur, nitrogen, phosphorus, or arsenic atom. The ease with which this could occur would decrease on descending Group V or Group VI since the π-bonds would become progressively weaker. With carbon the effect would be non-existent. This is illustrated below for $(SiH_3)_2O$.



The water could be split out from the activated complex as indicated by the broken line.

For a Group V element the condensation could proceed in two stages, *e.g.*,



Ammonia could split off at the broken line as shown and the $(SiH_3)_2NH$ could then combine with another $SiH_3{\cdot}NH_2$ molecule in a similar manners

(9) *Silyl Compounds containing Group* V *Elements.*—Silyl compounds containing elements of Group V may be divided into two groups—the simple amine type and those which can be formulated as quaternary ammonium salts. The most outstanding property common to both groups is the inertness—either partial or complete—of the lone pair of electrons on the nitrogen phosphorus, or arsenic atoms.

Physical properties of the amines, such as the planarity of $(SiH_3)_3N$, the association of the vapour of $SiH_3{\cdot}NMe_2$, and the non-association of the vapour of $(SiH_3)_2NMe$ have been explained by using the π-bonding concept.[3]

The chemistry of $(SiH_3)_3N$ is readily understood if it is assumed that the lone pair of electrons on the nitrogen can no longer be donated to other atoms. This explains why it will not combine with the hydrogen halides or silyl chloride to form quaternary ammonium type salts although atomic models [66a] of the $(SiH_3)_4N$ grouping indicate that sterically it is capable of existence. It also shows why the basic properties of the following series of compounds towards $B(CH_3)_3$ increase as shown :

$$(SiH_3)_3N < (SiH_3)_2NMe_3 < SiH_3{\cdot}NMe_2 < NMe_3$$

Addition compounds are formed with the last two but not with the first two.[3] BF_3 and BCl_3 form only very weak addition compounds with $(SiH_3)_3N$ and strong ones with $(CH_3)_3N$.[4] The fewer the number of silyl groups present in the molecule, the fewer will be the possible resonance structures involving the π-bond, and the greater will be the donor properties of the lone-pair electrons on the nitrogen.

Compounds formed by a 1 : 1 combination of silyl halide and tertiary amines have been formulated in this Review as quaternary ammonium salts, since there is no evidence to the contrary, but rather some good evidence for this type of structure, *e.g.*, the good electrical conductance of solutions of $(SiH_3{\cdot}NMe_3)Cl$ and $(SiH_3{\cdot}NMe_3)I$ in organic solvents.

However, trimethylamine adducts with di-, tri-, and tetra-chlorosilane are known,[67] and the possibility that the compounds formed with monochlorosilane, etc., are also simple co-ordination compounds involving a five-co-ordinated silicon atom, cannot be dismissed lightly. Consider the two alternative structures below for this type of compound :

$$\underset{(a)}{(SiH_yCl_{4-y}),NMe_3} \qquad \underset{(b)}{(SiH_yCl_{3-y},NMe_3)^+Cl^-}$$

Structure (*b*) will be most favoured when there are no chlorine atoms inside the cation, since the presence of chlorine atoms attached to the silicon would increase the electron-attracting powers of the cation as a whole, and consequently reduce the chance of ionisation. Structure (*b*) will therefore be most favoured with SiH_3Cl (or any silyl halide), and consequently silyl halide adducts with tertiary amines are the most likely to have the quaternary ammonium type structure A similar type of argument should apply to phosphonium and arsonium compounds, although the results of some investigators have led them to formulate phosphorus compounds containing hydrogen, *e.g.*, $(SiH_3{\cdot}PH_2Me)Br$, as addition compounds.[2]

No stable ammonium type compound has yet been obtained in which there is more than one silyl group. As with the simple amines, more than one silyl group would probably decrease the lability of electrons on the nitrogen atom to a point where transfer to the halogen atom could take place only with difficulty. The compounds $(SiH_3{\cdot}NMe_3)Cl$ and $(SiH_3{\cdot}NMe_3)I$

[66a] Courtauld Atomic Models, Griffin and Tatlock and Co., London.

[67] Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674.

follow the same trend in stability as their methyl analogues, *i.e.*, the iodides are more stable than the chlorides.[43]

Whereas the tetramethylammonium compounds become less stable as nitrogen is replaced successively by phosphorus and arsenic, the tetrasilyl compounds appear to become more stable (the tetrasilyl phosphorus and arsenic compounds can be prepared, but not the nitrogen analogue). Again, this could be related to the decrease in π bonding as the electronegativity of the Group V element decreases, with a consequent increase in the lability of their lone-pair electrons. In the mixed salts such as $[SiH_3{\cdot}M(CH_3)_3]I$ the former trend overcomes the latter and the compounds become less stable as M is replaced by nitrogen, phosphorus, and arsenic.

(10) *The Silicon–Hydrogen Bond.*—The Si–H bond in unsubstituted silyl compounds reacts in many circumstances where the C–H bond will not, *e.g.*, it is readily hydrolysed and reacts with halogen acids. Other reactions, which have so far been investigated only for completely substituted silyl compounds, are also known,[51] *e.g.*, the interaction of acyl halides in the absence of catalyst with trisubstituted silanes :

$$R_3SiH + R^1{\cdot}COCl \longrightarrow R_3SiCl + R^1{\cdot}CHO$$

The Si–H bond is thermodynamically able to undergo many reactions, partly because it is weaker than the C–H bond (79·9 as compared to 98·1 kcal./mole),[51] and partly because the bonds which silicon forms with other elements are all stronger than those formed by carbon with the exception of the Si—S bond.[51, 52a]

The rapidity with which an Si–H bond reacts as compared to a C–H bond depends primarily on the following factors, all of which greatly affect the ease of formation of the activated complex.[51] (i) The silicon atom can increase its co-ordination number from four to either five or six, and consequently can allow the relatively easy formation of the intermediate complex. (ii) The silicon atom is sterically more vulnerable to attack—more so than the carbon atom in the methyl group since the silicon is almost half as large again as the carbon atom. (iii) The polarity of the Si–H bond is relatively large, and is in the reverse direction from that of the C–H bond, and is actually more similar to the C–Br link. It is, therefore, reactive to nucleophilic polar reagents, and from (i) and (ii) above, it would be expected to react more rapidly than the C–Br bond, *e.g.*,

	$\overset{\delta+}{\mathrm{Si}}$ –	$\overset{\delta-}{\mathrm{H}}$	$\overset{\delta-}{\mathrm{C}}$ –	$\overset{\delta+}{\mathrm{H}}$	$\overset{\delta+}{\mathrm{C}}$ –	$\overset{\delta-}{\mathrm{Br}}$
Electronegativity .	1·8	2·1	2·5	2·1	2·5	2·8
Δ	+ 0·3		− 0·4		+ 0·3	

(11) *The Silyl Group.*—Compounds containing the silyl group are generally much more reactive than their methyl analogues in reactions in which the group itself preserves its identity and suffers no attack on its hydrogen atoms. This is very noticeable in the instantaneous hydrolysis of most silyl compounds to give disilyl ether, and in their rapid reaction with silver salts. In addition, silyl halides react rapidly with amines even at low temperatures, whereas their carbon analogues generally need heating.

The rapidity of the reactions is dependent primarily on three factors which greatly affect the ease of formation of the activated complex.[51] The first two are identical with (i) and (ii) in the preceding section, and the third is dependent on the fact that the bonds formed by silicon with other elements are usually highly polar in character—at least much more so than in the case of carbon. Since most of the reactions involve polar reagents the intermediate complex can be formed much more easily.

(12) *Conclusion.*—In general, silyl compounds are of similar formula type to their methyl analogues, but they do not necessarily have similar molecular structures. They are usually more reactive than the corresponding methyl compounds, not because of an inherent thermodynamic instability but because of the smaller electronegativity and greater co-ordination number of silicon which effect greater rates of reaction.