68. *Derivatives of Monosilane. Part II. The Iodo-compounds.*

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The compounds *mono-* and *di-iodosilane*, SiH_3I and SiH_2I_2, have been prepared by the reaction between hydrogen iodide and monosilane in the presence of aluminium iodide, which acts as a catalyst. Silicoiodoform and silicon tetraiodide, which have been previously described, are formed simultaneously. The physical properties of the two new substances have been investigated, and a number of their reactions, some of which are of a type not previously found in the chemistry of silicon, are described. Volatile compounds of silicon containing a metal have been prepared with the aid of these iodides, and a reaction with sodium, analogous to the Wurtz reaction in carbon chemistry, has been effected.

A NUMBER of compounds of iodine and silicon were prepared by early workers in the field of silicon chemistry. Friedel and Ladenburg (*Annalen*, 1868, **149**, 96) and Gattermann (*Ber.*, 1889, **22**, 190) prepared tetraiodosilane, Buff and Wöhler having already prepared both this compound and silicoiodoform by the action of hydrogen iodide on heated silicon (*Annalen*, 1857, **104**, 94). Friedel and Ladenburg published further work on these two substances, and also described hexaiododisilane (*Annalen*, 1880, **203**, 244). A lower iodide of empirical formula SiI_2 is also recorded. Mahn (*Jenaische Ztg.*, 1869, **5**, 158) investigated the action of iodine on what was probably a mixture of silanes, and again isolated the tri- and the tetra-iodo-derivative of monosilane. The most recent reference to the iodo-compounds of silicon is that by Ruff (*Ber.*, 1908, **41**, 3738), who describes the preparation of silicoiodoform by the action of dry hydrogen iodide on a suspension of cold silicon imide in cold carbon disulphide.

The work of Besson and Fournier (*Compt. rend.*, 1911, **151**, 1055), later amplified by Stock and his co-workers (*Ber.*, 1919, **52**, 695; 1917, **50**, 1737), resulted in the preparation of the mono- and di-chloro- and -bromo-compounds of monosilane, but although Stock (" Hydrides of Boron and Silicon," p. 27, Cornell University Press, Ithaca, N.Y.) predicted that hydrogen iodide and silane should react under suitable conditions, he records no experiments on this subject.

In the light of Stock's work, and more recently that of Emeléus and Miller (J., 1939, 821) on the reactions of silyl chloride, it seemed that the iodides would possess considerable reactivity, and that their high boiling points would make them useful as intermediates in the preparation of other silicon compounds. A method of preparation on the same lines as that used for the chlorides was therefore attempted, and after certain modifications in experimental technique proved completely successful.

Experimental.

The simultaneous use of reactive iodine compounds and of monosilane immediately introduced difficulties in technique : the use of the usual vacuum apparatus, in which taps are replaced by mercury seals, was precluded, since the iodine compounds rapidly attack mercury. Eventually, monosilane was purified in the apparatus using mercury seals, and transferred for reaction with hydrogen iodide to a similar apparatus with taps instead of mercury seals, and spoon gauges instead of mercury manometers. Even so, the rapid attack of these substances on tap grease made it necessary to keep them at temperatures at which their vapour pressures were not more than a few mm., if storage for any length of time were contemplated.

Frequent lubrication of taps was essential, and for the final determination of physical constants, and in other operations for which a high state of purity was desirable, an all-glass system was used. In this, units were isolated by sealing off fine capillaries which could be opened when required by the use of magnetic breakers.

Reactants.—Monosilane was prepared by the method of Stock and Somieski (*Ber.*, 1916, **49**, 111), modified as described by Emeléus and Reid (J., 1939, 1021); two distillations at — 160° gave a tensimetrically pure sample. Hydrogen iodide was prepared by dropping water on a mixture of red phosphorus and iodine; free iodine was removed by passage through a tube packed with red phosphorus, and the gas dried by calcium chloride and phosphoric oxide. Final purification was by fractional distillation in a vacuum at — 120°, and gave a product identical tensimetrically with that of Steele and Bagster (J., 1910, **97**, 2607). Aluminium iodide was made by the reaction between iodine vapour and heated aluminium filings, the clear, colourless, molten product being filtered through hot aluminium filings and stored in a sealed tube.

The reaction between monosilane and hydrogen iodide was carried out in a 1·5-l. bulb containing 5 g. of aluminium iodide, and heated to 80° in an air-oven. Equal quantities of the two gaseous reactants at a total initial pressure of about 50 cm. of mercury were used. At room temperature or in the absence of a catalyst, the reaction took place only exceedingly slowly, but under the above conditions the optimum yield of the less highly iodinated compounds was obtained after 24 hours. After reaction, a trap connected between the preparation vessel and the pumps was cooled in liquid nitrogen, and the hydrogen which had been produced in the reaction was pumped away through two further traps similarly cooled. The condensed reaction products in the first trap, consisting of silane and its mono-, di-, and tri-iodo-derivatives, together with unchanged reactants, were then surrounded by an ice-bath, and the volatile matter was pumped off and collected in a trap cooled in liquid nitrogen. Crystals of tetraiodosilane sublimed on the cooler parts of the reaction vessel, and were found to have m. p. 120° and to be optically inactive. Silicoiodoform, which has a vapour pressure of only 14 mm. at 106°, remained in the trap cooled in ice.

Under the conditions of the experiment an equilibrium was set up, only about 75% of the silane being iodinated. Of this about 60% was converted into the mono- and di-iodo-derivatives, the rest being more fully iodinated. After 24 hours, the amount of the higher iodides steadily increased at the expense of the lower ones. The amount of hydrogen formed was variable, but was usually rather more than the amount of silane added. The silyl and silylene iodides, SiH_3I and SiH_2I_2, were separated together from unreacted silane and hydrogen iodide by a fractional condensation at — 100°, the liquid being distilled from a bath at 0°, to remove any further traces of silicoiodoform. Fractional distillation at — 85° next removed final traces of silane and hydrogen iodide from the products, which were then roughly separated by fractional condensation of the silylene iodide at — 45°. The distillation was allowed to proceed for 30 minutes. The *silyl iodide* was then distilled from a bath at — 50°, giving a product as pure as can be obtained in an apparatus employing taps. A very pure sample was obtained by distilling in an all-glass apparatus from a vessel cooled to — 55°, and fractionally condensing the silyl iodide at — 90°. This sample was used for final analysis of the compound, for determination of vapour pressure, and for examination of the absorption spectrum.

Silylene iodide was prepared in a state of purity by repeated fractional condensation at — 40°, and the material was volatilised from a bath at 0°. Again, for a very pure sample, the process was repeated in an all-glass system. Nearly twice as much silyl iodide is formed as silylene iodide.

Analysis.—Use was made of the fact that the compounds are rapidly and completely decomposed by sodium hydroxide, as are all volatile derivatives of silicon. A known quantity of iodide was distilled into a degassed, 30% alkali solution, cooled in liquid air. The mixture was allowed to attain room temperature, and was thoroughly shaken. Hydrogen was evolved according to the equations

$$3NaOH + SiH_3I = Na_2SiO_3 + 3H_2 + NaI$$
$$4NaOH + SiH_2I_2 = Na_2SiO_3 + 2H_2 + 2NaI + H_2O$$

and was pumped off through the Töpler pump and measured. In the preliminary analyses the alkaline solution was diluted somewhat, acidified with dilute sulphuric acid, and the iodine estimated gravimetrically as silver iodide. The results of preliminary analyses are shown below: these gave a rather high value for the iodine content, possibly owing to traces of silicate adsorbed by the silver iodide.

Compound.	Wt. taken, g.	Vol. as gas at N.T.P., c.c.	Vol. of H_2 evolved, c.c.	$\frac{\text{Vol. } H_2}{\text{Vol. subst.}}$	Wt. of AgI.	I, %.	
						Found.	Calc.
SiH_3I	0·2168	30·7	85·6	2·82	0·3241	80·9	80·35
SiH_3I	0·1883	26·06	80·4	3·08	0·2850	81·8	,,
SiH_2I_2	0·3767	29·7	59·1	1·96	0·6260	89·7	89·44
SiH_2I_2	0·3984	31·4	63·0	2·01	0·6629	89·7	,,

Further analyses were therefore made on pure materials contained in thin-walled glass ampoules. These were broken under sodium hydroxide solution (the glass being subsequently weighed), and the iodine determined volumetrically by titration with iodate in presence of concentrated hydrochloric acid. Silicon was determined as silica in the usual manner. The results are shown below.

Compound.	Wt. used, g.	SiO_2, g.	Si, %. Found.	Si, %. Calc.	I, %. Found.	I, %. Calc.
SiH_3I	0·1365	0·0519	17·70	17·78	80·42	80·35
SiH_2I_2	0·5463	0·1287	10·92	11·05	89·40	89·44

Silyl Iodide.—This is a colourless, refractive liquid, with a pungent, though slightly musty odour. The solid is dimorphous, crystallising as long needles, probably isomorphous with methyl iodide, or in a second, prismatic form.

Physical properties. The vapour-pressure curve was determined in an all-glass system, pressures being recorded by a sensitive " spoon " gauge. This was totally immersed, only the pointer being visible, in a bath fitted with a stirrer, thermoregulator, and standard thermometer. At temperatures close to the b. p. slight decomposition occurred. A sample kept for some time at 40° showed a slight rise in vapour pressure. The results obtained are given in Table I.

TABLE I.

Vapour pressure of silyl iodide.

Temp. ...	−23·5°	−14·0°	−10·0°	0·0°	5·3°	11·2°	16·7°	19·9°	21·0°	22·0°	23·2°
V. p., mm.	34·8	61·5	75·7	123·9	158·7	206·7	259·2	294·2	307·3	320·9	336·9
Temp. ...	25·0°	26·4°	27·4°	28·8°	30·0°	31·5°	34·5°	37·0°	40·0°	41·9°	42·8°
V. p., mm.	360·5	381·3	396·4	417·5	437·3	462·9	516·3	564·6	637·3	669·1	668·6

The vapour density was determined by direct weighing of the quantity of gas which filled, at known temperature and pressure, a calibrated bulb. From the bulb it was transferred to a small weighed tube, provided with a light vacuum tap and ground glass joint. The mean of two results agreeing to 1% gave a molecular weight of 157·6 (Calc. : *M*, 158).

The latent heat of vaporisation, calculated from the vapour-pressure curve, was 7130 cals./g.-mol. between 30° and 40°. The m. p. of silyl iodide was − 57·0°, and its b. p. 45·4°/760 mm.

Density. The liquid density was determined on a specimen of pure iodide between 0·5° and 14·8°. The operation was performed in a calibrated thermometer tube, the results recorded below being obtained. The calculated densities given in the last line were obtained from the formula $d = 2{\cdot}0718\ (1 - 0{\cdot}00204t)$.

Temp.	0·5°	1·5°	5·4°	6·4°	9·9°	10·1°	10·4°	13·8°	14·8°
d, obs.	2·0700	2·0685	2·0595	2·0565	2·0500	2·0490	2·0350	2·0398	2·0350
d, calc.	2·0708	2·0686	2·0593	2·0570	2·0487	2·0483	2·0372	2·0398	2·0372

Surface tension. This was determined by measuring the difference in level of the liquid in two capillary tubes of different diameter, which had been previously calibrated at 15°, pure ethyl alcohol being used as standard liquid. The surface tension so obtained was 30·50 dynes/cm. at 15°, giving a parachor of 182·1, which is rather higher than the calculated value of 170.

Absorption spectrum. The absorption spectrum was examined in a silica absorption cell 5 cm. long, attached to glass apparatus by a silver chloride seal. A hydrogen discharge was used as the source of ultra-violet continuum, and the spectrum was photographed on a Hilger E_2 instrument. Pressures of 0·5 cm. and 2 cm. of silyl iodide were used. In this pressure range there was no evidence of banded absorption. The limit of continuous absorption was in the region 2400—2520 A., and the maximum of absorption was below 2100 A.

Silylene Di-iodide.—This compound is only just sufficiently volatile for ready manipulation in the vacuum apparatus at room temperature. Vapour pressures were determined in the same manner as for the more volatile silyl iodide, except that the whole was immersed in an oil-bath fitted with a stirrer and variable thermostat, so that the temperature could be taken up to about 140°. Results are recorded in Table II.

At the higher temperatures, considerable decomposition occurred, and the liquid became coloured by iodine. On cooling, a residual pressure of 0·6 cm. was exerted down to − 100°, and it is therefore probable that the vapour pressure values given for the higher temperatures are a little high, and the b. p. correspondingly low. From the vapour-pressure curve, the b. p. at 760 mm. was found to be 149·5°. The m. p. of the solid was − 1°.

TABLE II.

Vapour pressure of silylene di-iodide.

Temp.	0·1°	5·3°	10·0°	15·1°	21·7°	25·12°	30·0°	36·42°	40·9°	45·7°	51·4°
V. p., mm.	4·2	6·4	8·4	10·7	13·4	14·9	17·9	22·4	26·8	31·5	39·2
Temp.	56·1°	63·1°	66·4°	70·5°	74·8°	75·9°	83·4°	93·4°	98·6°	104·9°	
V. p., mm.	45·8	58·0	64·4	75·2	86·8	88·5	114·5	155·7	182·0	220·9	
Temp.	112·2°	116·2°	121·5°	123·7°	127·1°	131·8°	135·0°	136·3°	138·0°	140·2°	
V. p., mm.	274·7	308·7	356·8	385·2	422·0	481·7	532·4	542·8	567·5	600·8	

The vapour density was not determined, owing to the low volatility at room temperature and the difficulty of working at high temperatures in the vacuum apparatus. It is very unlikely, however, that the vapour is other than monomeric.

The latent heat, as calculated from the vapour-pressure curve, is 8050 cals./g.-mol. between 83·4° and 93·4°. This temperature was chosen, although well below the b. p., as being below the temperature at which appreciable decomposition sets in.

The density was determined in the same way as for silyl iodide, with the following results. The calculated values were obtained from the formula $d = 2·7943\ (1 - 0·00320t)$. The surface tension was determined at 15° by the same method as was used for silyl iodide. The result, 44·1 dynes/cm., gave a parachor of 267, again rather higher than that calculated (250).

Temp.	5·1°	7·0°	10·8°	10·8°	15·1°	15·5°	20·0°	20·5°
d, obs.	2·777	2·772	2·761	2·760	2·746	2·745	2·730	2·729
d, calc.	2·778	2·772	2·760	2·760	2·746	2·745	2·730	2·729

The absorption spectrum was examined as for silyl iodide, on a Hilger E_2 spectrograph, the cell being filled with the vapour of silylene di-iodide at a pressure of 2 cm. There was no indication of a banded spectrum, and the continuum commenced in the range 3530—2730 A.

The Action of Light on the Iodides.—Silylene di-iodide. During the ultra-violet exposure necessary for the examination of the absorption spectrum a fairly rapid liberation of iodine was found, and further preliminary experiments were therefore carried out. At 20° it appeared that a stationary concentration of iodine was set up after a few minutes' exposure. This was not perceptibly increased in 12 hrs., and rapidly disappeared on placing the cell in the dark for a few minutes. Exposure at 50° for an hour, however, caused a further reaction to occur, with the removal of the iodine, and the deposition of a white crystalline solid. In a quantitative experiment at this temperature, 0·75 g. of di-iodide yielded 11 c.c. of hydrogen after 2 hrs.' exposure. No silanes were found, but there were 0·015 g. of silyl iodide and 0·0739 g. of unchanged silylene iodide. The residue consisted of a difficultly volatile liquid of m. p. 8°, assumed to be silicoiodoform, and two crystalline solids, both optically inactive, the less volatile of which melted at 120°, and was probably tetraiodide. The more volatile solid condensed out as a liquid which supercooled strongly but eventually crystallised. An attempt at its analysis was forestalled by its rapid decomposition in air, with the deposition of iodine. However, from the deficit of iodine, silicon, and hydrogen in the gaseous products, and on the assumption that no free silicon was formed, the compound was probably an iodo-di- or -tri-silane. The following series of reactions is suggested:

$$(a)\ SiH_2I_2 = SiH_2I^- + I$$

$$(b)\ 2SiH_2I^- = SiH_2I{\cdot}SiH_2I$$

Further iodination, by iodine or hydrogen iodide, may then take place, with the formation of silicon tetraiodide.

Silyl iodide. When this iodide was irradiated at 50° for 2 hours it decomposed with the formation of a yellow solid deposit on the walls of the cell, together with a non-volatile oil. The solid did not contain iodine, was soluble in benzene, and is believed to be a polymeric silicon hydride. The liquid may be a heavily iodinated higher silane. Further work is proceeding on these reactions.

Photodecomposition of both iodides appears to be accelerated by the presence of oxygen, and it is thought that this fact may on fuller investigation prove to be parallel to the accelerated decomposition of methyl iodide in presence of oxygen (Spence and Bates, *J. Amer. Chem. Soc.*, 1931, **53**, 1689).

Chemical Properties and Reactions of the Iodides.—Neither of the two iodides is spontaneously inflammable in dry air or oxygen, but the vapour of either will burn with a reddish flame if ignited in air. Iodine vapour and a cloud of silica are among the products. In moist air, rapid hydrolysis, accompanied by simultaneous oxidation, takes place.

With mercury, the vapour of silyl iodide reacts in sunlight to give a small quantity of hydrogen, together with mono- and di-silane and mercurous iodide. In the liquid phase, in absence of sunlight, however, a white, volatile, crystalline solid is formed as a rather labile intermediate which decomposes into mercurous iodide and silane. The compound has not yet been isolated in a state of purity, but it may be $HgI{\cdot}SiH_3$, the analogue of methylmercury iodide.

A slow reaction occurs between silyl iodide and zinc. A tube containing the two substances was sealed up, and opened after a year. It was found that 1 mol. of silyl iodide had given 0·56 mol. of hydrogen, 0·28 mol. of monosilane, 0·07 mol. of unchanged iodide, and about 0·25 c.c. of a liquid containing silicon, hydrogen, and iodine, which was slightly volatile at 0°. There remained a liquid which could only be distilled with great difficulty by heating to about 300°. This liquid evolved hydrogen with aqueous sodium hydroxide, giving a solution containing silicate, iodide, and zinc, and is probably silylzinc iodide, $ZnI{\cdot}SiH_3$.

With magnesium, under the conditions of the Grignard reaction in di*iso*amyl ether, which was used in preference to a lower-boiling liquid so that fractionation of the products would be less difficult, a dark solid is deposited, and the metal is dissolved. 1 Mol. of silyl iodide gave 0·33 mol. of monosilane and 0·37 mol. of hydrogen after reaction for 3 hours. There were no other volatile substances, and no unchanged iodide. Addition of water led to the formation of a further 0·116 mol. of monosilane, and 0·082 mol. of hydrogen. These results may be interpreted as due to the formation of an unstable " Grignard compound ", $MgI{\cdot}SiH_3$, readily splitting off silyl radicals, which react thus : $2SiH_3 = SiH_4 + H_2 + Si$. This would account for 90% of the silicon in the above reaction, but it might be expected that some disilane would be formed. Although carefully sought, however, this gas could not be detected.

With silver cyanide, silyl iodide reacts explosively in the liquid phase, a red flame running through the reaction vessel, and a mixture of silver iodide with a brown polymeric solid is formed, together with much hydrogen. By passing the vapour of silyl iodide at about 25 cm. pressure and at room temperature over silver cyanide, a volatile white solid is formed. The solid has been obtained in the pure state, and has m. p. 34°. On distillation into aqueous sodium hydroxide, the hydrogen evolved, and the cyanide in solution (estimated by Liebig's method), indicate that it is silyl cyanide, $SiH_3{\cdot}CN$; 0·44 g. of material gave 53·3 c.c. of hydrogen (at N.T.P.) and 0·20 g. of cyanide.

With sodium, silyl iodide reacts at room temperature with the evolution of gas from the surface of the metal. The main product of this reaction is disilane. After a few minutes, the sodium becomes coated with a tenacious skin, and the reaction ceases, in spite of the fact that considerable unchanged silyl iodide remains. In a quantitative experiment, 0·9725 g. of silyl iodide and 0·16 g. of freshly distilled sodium gave as products : H_2, 2·0 c.c.; SiH_4, 3·1 c.c.; Si_2H_6, 22·5 c.c., and 0·5987 g. of unchanged silyl iodide were recovered, so that 0·3738 g. were used. From these results, it may be calculated that 2 mols. of the iodide decompose to give 0·85 mol. of disilane. It is clear, therefore, that the main reaction may be represented as $2SiH_3I + 2Na = Si_2H_6 + 2NaI$. The small quantity of hydrogen may have been produced by the reduction of some of the disilane by the sodium. The reaction of silyl chloride with sodium is different and yields chiefly monosilane (Stock and Somieski, *Ber.*, 1921, **54**, 524). In a precisely analogous manner methyl chloride, when treated with sodium, yields methane, whereas methyl iodide yields chiefly ethane. Both silicon iodides may be rapidly fluorinated by silver or mercurous fluoride. Details of these reactions will be described in a later paper.

The investigation of the reactions of silyl iodide already shows that its behaviour often contrasts with that of silyl chloride under similar conditions. This is, no doubt, due to the great difference in bond energies of the Si–Cl and Si–I linkages. These values are not accurately known, but approximate figures have been calculated from the thermal data given by Bischowsky and Rossini (" Thermo-Chemistry of Chemical Substances," Reinhold Pub. Corpn., New York). The calculation involves a knowledge of the heat of atomisation of silicon, or of its heat of sublimation, if the vapour is assumed to be monatomic. The value of 103 kg.-cals. has been chosen as the most likely figure on the basis of the somewhat unsatisfactory vapour-pressure data for elementary silicon (Ruff, *Trans. Electrochem. Soc.*, 1935, Reprint **68**, 32; von Wartenberg, *Z. anorg. Chem.*, 1912, **79**, 71; Ruff and Konschak, *Z. Elektrochem.*, 1926, **32**, 515; Bauer and Brunner, *Helv. Chim. Acta*, 1934, **17**, 958). This value differs from that given by Pauling (" Nature of the Chemical Bond," p. 53). Ogier measured the heat of formation of monosilane by oxidising it to silica. The value obtained (13·7 kg.-cals.) is close to the value of 8·7 kg.-cals. obtained by von Wartenberg in a study of the kinetics of the formation of monosilane. Using Ogier's value, and taking the heat of atomisation of hydrogen as 51·3 kg.-cals., we obtain for the Si–H bond the value 80·5 kg.-cals.

The energy of the Si–Si bond is probably given approximately by the heat of activation of the disilane molecule, which from experiments on the pyrolysis of this substance is 51·3 kg.-cals. (Emeléus and Reid, J., 1939, 1021). This agrees with a value of half the heat of sublimation of silicon (51·5 kg.-cals.) deduced from the crystal structure of the element. For the Si–Cl link, Troost and Hautefeuille's figure for the heat of formation of tetrachlorosilane (150·1 kg.-cals.) has been used. Taking into account the heat of atomisation of chlorine (28·5 kg.-cals.), the value obtained for the strength of the Si–Cl link is 90·8 kg.-cals. For the Si–I link, the heat of formation of tetraiodosilane, which is given by Berthelot as 29·8 kg.-cals., may be similarly employed, if a value is assumed for the heat of sublimation of silicon tetraiodide. A value of 12 kg.-cals. was used from a consideration of values for similar compounds. If the heat of atomisation of iodine be taken as 18·1 kg.-cals., the value of 48·4 kg.-cals. is obtained for the Si–I bond. The fact that this is lower than the strength of the Si–Si bond may explain the formation in the irradiation experiments of relatively non-volatile liquids, which are believed to be iodinated higher silanes. The large difference in strength between the two halogen bonds is responsible for the marked difference between the chlorides and iodides of the silyl and silylene radicals in many of their reactions.

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