

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Trichlorosilane¹

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Trichlorosilane was first prepared by Buff and Wöhler^{1a} in 1857 by heating silicon in a current of dry hydrogen chloride. Later workers in the field prepared it by the action of hydrogen chloride on magnesium silicide,² ferrosilicon,³ vanadium silicide⁴ and copper silicide⁵ and other methods. Ruff and Albert⁶ and also Stock and Zeidler⁷ considered the reaction of hydrogen chloride on copper silicide to be the best means for the preparation of trichlorosilane.

Experimental

Copper-silicon alloys of the atomic proportions Cu_2Si , CuSi and CuSi_2 were prepared by pressing the mixture of the powdered metals at 60,000 pounds pressure and sintering the resulting pellets at 900° in a current of hydrogen. The chlorination of these alloys and of the commercial alloy containing 18% silicon by means of anhydrous hydrogen chloride yielded trichlorosilane in good quantity, depending materially, however, on the temperature of the alloy. The yields of trichlorosilane were not any greater than those obtained with silicon, while the bulk and weight of the alloy was much larger per gram of silicon. The alloys, on chlorination, left a residue of metallic copper which often obstructed the reaction tube, whereas silicon left but a skeleton of silica. For these reasons silicon only was used in this work.

Trichlorosilane was prepared by means of the apparatus shown in Fig. 1. While some workers have gone to great lengths to avoid the use of stopcocks in handling trichlorosilane, we found it quite unnecessary provided care was taken to move the gases through the apparatus at a pressure well below the vapor pressure of trichlorosilane at room temperature. Accordingly a continuous suction by a water pump was applied to the system so as to maintain the pressure at 5 to 10 cm. of mercury. It is, however, necessary to dry the apparatus thoroughly and this was best accomplished, as our long experience with fluorine gases has taught, by repeated flushings with dry carbon dioxide-free air.

Hydrogen chloride, generated in flask (A) by dropping concentrated hydrochloric acid into concentrated sulfuric acid, was scrubbed by sulfuric acid in wash bottle (B) and passed through a tube containing approximately a pound of pea-sized pieces of silicon maintained at the opti-

mum temperature of 380° by means of the electric furnace (C). The yield of trichlorosilane was greatly diminished by further increase in temperature, probably due to thermal decomposition of the trichlorosilane to silicon hydride and silicon tetrachloride.

The reaction products passed through a water-cooled condenser, serving as a pre-cooler, and were condensed in the spiral traps (D) and (E) by an acetone-carbon dioxide snow mixture. Small amounts of trichlorosilane and of more volatile silicon compounds, probably dichlorosilane and monochlorosilane, together with excess hydrogen chloride gas were condensed in traps (M) and (G) by liquid air. These latter gases were again passed through the furnace. With a moderately rapid flow of hydrogen chloride, traps (D) and (E) were filled with condensed liquid (approximately 300 cc.) in three to five hours.

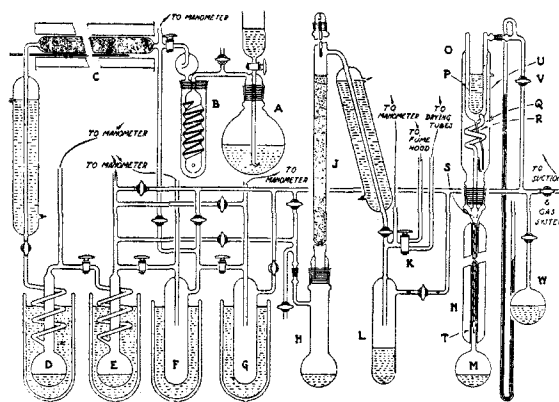


Fig. 1.

The crude trichlorosilane was condensed into the still-pot (H) by liquid air, and then fractionally distilled through the insulated column (J), operated at a high reflux ratio, and the purified trichlorosilane collected in (L).

Final purification of the trichlorosilane was accomplished in the fractionating column shown at the right in Fig. 1. The trichlorosilane in the still-pot M was heated by a micro flame, and passed upward and condensed again to a liquid on contact with the condenser (P) filled with cold water. The liquid then returned to (M) through the tube (N), being forced to take a spiral course in (N) by means of a copper wire wound about a sealed tube, the whole fitting snugly into the passage-way. Holdup of the gas by the liquid was eliminated by the by-passes at (Q) and (R), and (S), and at (T).

To minimize thermal losses the still-head was vacuum jacketed as shown at (U), while the fractionating column was encased in a partly silvered, highly evacuated Pyrex condenser.

After thirty minutes of refluxing, the more volatile impurities (mostly hydrogen chloride) in the trichlorosilane were found to be concentrated in the stillhead, that is, the pressure in the system steadily rose. When these volatile

(1) From a part of a thesis submitted by W. D. Stillwell to the Graduate Faculty of Western Reserve University, 1933, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Original manuscript received July 17, 1933.

(1a) Buff and Wöhler, *Liebigs Ann.*, **104**, 94 (1857).

(2) Gattermann, *Ber.*, **22**, 190 (1898).

(3) Warren, *Chem. News.*, **60**, 158 (1889).

(4) Moissan and Holt, *Compt. rend.*, **135**, 78 (1902).

(5) Combes, *ibid.*, **122**, 531 (1896).

(6) Ruff and Albert, *Ber.*, **38**, 53, 2222 (1905).

(7) Stock and Zeidler, *ibid.*, **56B**, 986 (1923).

fractions were drawn off and discarded, the pressure dropped sharply and condensation became more rapid. This signaled the removal of the more volatile impurities.

With constant heat input at (M) and constant still-head temperature at (P) the vapor pressure of the system remained constant as long as trichlorosilane continued to boil off. The distillate was condensed in bulbs such as (W) where it was stored until required. When the vapor pressure again dropped, distillation was stopped, and the tailings were discarded. Trichlorosilane obtained by this method of purification was used in the preparation of fluorine derivatives.⁸

Analysis and Determination of Physical Properties.—Trichlorosilane, a colorless, mobile liquid which freezes to a white solid, hydrolyzes readily in moist air to yield hydrochloric acid, and silico formic acid or its decomposition products, hydrogen and hydrated silica.

Since the boiling points and melting points of trichlorosilane as given in the literature vary from 30 to 42° and -126 to -134°, respectively, it was thought advisable to purify a sample of trichlorosilane thoroughly and measure these physical constants.

A sample of trichlorosilane, prepared and purified as described above, was further purified by repeated fractional distillations in the fractionating column, only the middle third of the distillate being retained each time. As fractionation proceeded, the slight variation in vapor pressure indicated that even the original sample was quite pure.

A weighed sample of this pure trichlorosilane was absorbed in sodium hydroxide solution and the chlorine was found by the Volhard method to be 78.4%; calcd. for trichlorosilane, 78.5%.

Vapor pressures (Table I) were measured upon an apparatus, combining the isotenoscope of Smith and Menzies⁹ and the barometer of Germann,¹⁰ devised by P. E. Burchfield of this Laboratory for volatile liquids (to be reported later). A Physikalisches-Technisches Reichsanstalt thermometer was used to measure the temperature.

TABLE I
VAPOR PRESSURE OF SiHCl_3

Temp., °C.	0.00	5.60	9.51	14.58	19.36
Press., mm.	224.2	282.5	332.8	406.6	489.1
Temp., °C.		24.68	29.48	34.42	38.99
Press., mm.		595.2	704.0	838.4	971.0

These values agree very well with those obtained by Stock and Zeidler⁷ who measured the vapor pressure over a much greater range. By interpolation of the vapor pressure data, at 760 mm., the boiling point of trichlorosilane was found to be $31.5 \pm 0.1^\circ$.

(8) Booth and Stillwell, *THIS JOURNAL*, **56**, 1531 (1934).

(9) Smith and Menzies, *ibid.*, **32**, 1412 (1910).

(10) A. F. O. Germann, *ibid.*, **36**, 2456 (1914).

The melting point of trichlorosilane under its own vapor pressure was determined from cooling curves using accurately calibrated multiple thermocouples in conjunction with a special high speed Leeds & Northrup recording potentiometer to be $-128.2 \pm 0.1^\circ$. The liquid sample was well stirred electromagnetically during the cooling process.

In the table below, the boiling point and melting point of trichlorosilane as found in this investigation are given for comparison with the values found by Stock and Zeidler,⁷ and by Ruff and Albert⁶ whose values seem to be generally accepted.

TABLE II

	Ruff and Albert	Stock and Zeidler	This investigation
M. p., °C.	-134	-126.5	-128.2 ± 0.1
B. p., °C.	35-34	31.8	31.5 ± 0.1

Some volatile gases were produced along with the trichlorosilane. At one time in the course of this work eight liquid layers were visible in trap (F) when the solidified gases were carefully liquefied. Hydrolysis products formed in the water pump were also an indication of volatile gases.

Heavy liquid residues were produced, of which silicon tetrachloride was the chief product; Si_2Cl_6 was identified by its boiling point.

The possible products of this reaction, with their boiling points and estimated amount obtained are tabulated.

Compound	B. p., °C.	Approx. % of total liquid products	Identified by
Si_3Cl_8	+216	1	{ High boiling Liquid residues
Si_2Cl_6	147		
SiCl_4	56.8	20-25	Boiling point
SiHCl_3	31.5	80-75	Boiling point; analysis
SiH_2Cl_2	12	...	{ Hydrolyzable Gaseous products
SiH_3Cl	-10	...	
SiH_4	-112	...	

Schumb and Young¹¹ have studied carefully the very similar reaction of gaseous hydrogen bromide on silicon, reporting optimum conditions and results entirely analogous to those reported here.

Summary

The best yields of trichlorosilane were obtained by the action of hydrogen chloride gas on silicon at a furnace temperature of 380° . The melting point and boiling point of the highly purified trichlorosilane were found to be respectively, $-128.2 \pm 0.1^\circ$ and $31.5 \pm 0.1^\circ$.

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(11) Schumb and Young, *ibid.*, **52**, 1464 (1930).