

A Simplified Method for Preparation of Very Pure Silicochloroform

A NUMBER of methods are available for the preparation of trichlorosilane (SiHCl_3), in the laboratory, for example, by the action of dry hydrochloric acid gas on silicon^{1,2} and by the reaction of hydrochloric acid gas and metallic silicides³⁻⁷, such as magnesium silicide, iron silicide, or 25 per cent copper silicide. Trichlorosilane has also been prepared by passing a mixture of halosilanes and excess of hydrogen or hydrogen-halide over aluminium, zinc, or magnesium⁸, or by halogenation of monosilane (SiH_4), with hydrochloric acid gas in presence of aluminium chloride as a catalyst⁹.

In all these methods the amount of formation of trichlorosilane is low. This is due to the fact that, along with the main reaction, which leads to the formation of trichlorosilane, side reactions also occur. These side reactions give rise to the formation of SiCl_4 , SiH_2Cl_2 , SiH_3Cl , etc. At increasing temperature the reaction leading to the formation of silicon tetrachloride occurs more rapidly⁷. The yield of silicochloroform, calculated from the weight of the reacting silicon, is about 50 per cent⁴. This low yield of silicochloroform is also due to inadequate cooling of the gaseous reaction products. The concentration of silicochloroform in the gaseous reaction products is low, and hence a very good cooling system for condensing trichlorosilane is essential. Unfortunately, liquid air cannot be used for this purpose because unreacted hydrochloric acid gas would also condense along with trichlorosilane. In methods for preparation of trichlorosilane in which silicides of metals such as magnesium, copper, or zinc are used as starting materials, instead of silicon, and hydrochloric acid gas, the process of preparing these metallic silicides is neither simple nor suitable for obtaining pure trichlorosilane. The process of preparing these metallic silicides involves first intimately mixing silicon with at least 10 per cent by weight of one of these foreign metals. After this, the mixture is usually sintered at a high temperature, normally $1,000^\circ\text{C}$., to activate the silicon. Silicon activated in this way is then subjected to the action of hydrochloric acid gas in order to produce silicochloroform. This operation of mixing silicon with another metal and then sintering at a high temperature leads to the contamination of silicon with many impurities. Therefore silicochloroform obtained by this method is not pure. To produce pure trichlorosilane it would be more practical if, instead of activating silicon, which involves contamination of silicon with impurities, the other reagent, hydrochloric acid gas, could be activated by some process.

Considering the drawbacks of these available methods, we have been able to develop an improved simple method, which can be used on a laboratory or production scale for the preparation of pure trichlorosilane. The over-all reaction is:



In this method for the preparation of pure trichlorosilane, instead of activating silicon, which is normally accomplished by mixing it with some other metal such as magnesium, copper, or iron, and sintering the mixture at a high temperature, which results in the contamination of silicon with impurities, hydrochloric acid gas molecules are activated. The activation of hydrochloric acid gas molecules takes place, possibly due to the presence of HCuCl_2 -type com-

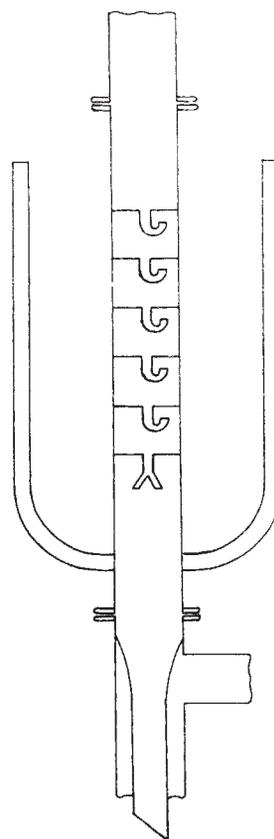


Fig. 1

plexes. These HCuCl_2 -type complexes are formed because of the presence of very small amounts of cuprous chloride, etc., in the reaction tube. The quantity of copper therefore required is very small, being less than 0.1 per cent of the weight of silicon in the reaction tube. These activated hydrochloric acid molecules react with silicon to produce pure trichlorosilane, while the impurities which are present in silicon are left behind. The gaseous reaction products from the reaction tube when condensed in our specially developed condenser, as in Fig. 1, give an average silicochloroform yield of about 90 per cent, calculated from the amount of reacted silicon.

The apparatus used in its simplest form consists of a horizontal 'Pyrex' tube. A weighed quantity of small crystals of silicon, 1-5 mm. in size, is placed in a quartz boat. This boat containing silicon is introduced into the reaction tube, which is 500 mm. long and has an inner diameter of 25 mm. The inner wall of the middle part of the reaction tube, where the boat containing the silicon lies, is fitted with a copper spiral. This copper spiral weighs approximately 0.1 per cent of the weight of silicon in the boat. The copper spiral is so arranged that it cannot possibly come in contact with the silicon and lies quite apart from it. A chromium-nickel resistance wire is wound around the middle portion of the reaction tube to heat it to the required reaction temperature in conjunction with an ordinary 10-amp. and 0-250 V. 'Variac'. At one end of the reaction tube is an inlet for the incoming gases while its other end is joined to a specially developed condenser (Fig. 1) for condensing silicochloroform vapours. This condenser in turn is connected to a col-

lecting flask, for collecting trichlorosilane, which has an outlet allowing the uncondensed gases to escape into the atmosphere. A thermo-couple, nickel/nickel-chromium, is placed in such a way that it lies just on the surface of the silicon for measuring the reaction temperature. After arranging the apparatus, a current of hydrogen is passed through it to drive out all the air. The reaction tube is next heated to the reaction temperature of 400° C. by passing a current through the resistance wound around it. At the same time, the condenser is cooled by means of alcohol and dry ice (-78° C.). Next hydrochloric acid gas is led into the reaction tube at the rate of 105 litres per hour, while the flow of hydrogen is stopped. The reaction starts, the pure silicochloroform forming in the condenser and collecting in the storing flask. The relationship between the rate of overall reaction, $\text{Si} + 3\text{HCl} \longrightarrow \text{SiHCl}_3 + \text{H}_2$, and the reaction temperature and the rate of flow of hydrochloric acid gas was investigated. The results obtained from these investigations are given in Tables 1 and 2.

Table 1. RELATIONSHIP BETWEEN THE RATE OF REACTION AND THE REACTION TEMPERATURE

Reaction temperature (° C.)	Hydrogen chloride rate of flow (l./hr.)	Weight of silicon reacting (gm./hr.) In absence of copper spiral	Weight of silicon reacting (gm./hr.) In presence of copper spiral
300	105	0.80	2.1
350	105	2.3	5.1
400	105	3.1	8.0

Table 2. RELATIONSHIP BETWEEN THE RATE OF REACTION AND THE RATE OF FLOW OF THE HYDROCHLORIC ACID GAS

(The investigation was carried out only in presence of a copper spiral)

Hydrochloric acid gas rate of flow (l./hr.)	Reaction temperature (° C.)	Weight of silicon reacting (gm./hr.)
43	400	5.9
72	400	8.0
105	400	8.0

From trichlorosilane, obtained by this method, silicon was produced. The results of the spectroscopic analysis of this silicon and that used as the starting material for the preparation of trichlorosilane are given in Table 3.

Table 3. COMPARISON OF THE SPECTROSCOPIC ANALYSIS OF RAW AND PURE SILICON

Elements present as impurities	Raw silicon concentration (per cent)	Pure silicon concentration (per cent)
B	0.002	—
Fe	0.0005	—
Mg	0.0002	—
Al	0.002	—
Cu	0.0002	—
Ti	0.0005	—
Ni	0.0005	—
Mn	0.001	—
Ca	0.002	0.002

—, Not detectable by spectroscopic analysis.

We thank Mr. Biert and Miss Reindle for carrying out the various spectroscopic analyses.

P. G. DUDANI
H. G. PLUST

Brown, Boveri and Co., Ltd.,
Baden,
Switzerland.

¹ Buff, H., and Wöhler, F., *Ann. Chem.*, **104**, 94 (1857).

² Friedel, C., and Ladenburg, A., *Ann. Chem.*, **143**, 118 (1867).

³ Gattermann, L., *Ber.*, **22**, 190 (1889).

⁴ Brauer, G., *Handbuch der präparativen anorg. Chemie* (F. Enke, Verlag, Stuttgart, 1954).

⁵ Warren, F., *Ber.*, **22**, 657 (1889).

⁶ Taylor, A. G., and Walden, G., *J. Amer. Chem. Soc.*, **66**, 842 (1944).

⁷ Ruff, O., and Albert, K., *Ber.*, **38**, 2222 (1905).

⁸ Hurd, R., *J. Amer. Chem. Soc.*, **67**, 1545 (1945). U.S. Patent 2,406,605.

⁹ Stock, D., *Hydrides of Boron and Silicon* (Cornell Univ. Press, Ithaca, New York).

BIOCHEMISTRY

Calculated Composition of a 'Messenger' Ribonucleic Acid

A SPECIAL type of ribonucleic acid, the 'messenger' RNA, has been postulated recently, which is assumed to specify the sequence of the amino-acid constituents of a given protein¹. This RNA is said to be made under the control of deoxyribonucleic acid and to mirror the composition and the regularities (base-pairing, etc.)² of the latter, with uracil substituting for thymine³⁻⁶. The existence, in DNA, of a non-overlapping, 'degenerate' code, composed of nucleotide triplets that are 'read' from a fixed starting point, has also been put forward⁷. These advances have been paralleled by the equally recent elaboration of what would seem to be the complete amino-acid code in the form of a series of nucleotide triplets⁸⁻¹¹.

If all this be accepted, a way towards the indirect establishment of the nucleotide sequence of 'messenger' RNA would seem to be open. The composition of many proteins is known precisely, and in several instances also the specific sequence of the amino-acids. The determination of the nucleotide arrangement in RNA, on the other hand, is beset with great difficulties.

I have attempted to reconstruct the composition of the supposititious 'messenger' RNA that would code for bovine pancreatic ribonuclease, in order to see whether a plausible structure would emerge. The results are peculiar. The computation is based on the well-established composition of this protein¹² and on the triplet 'letters' proposed in recent papers. Thirteen of the required nineteen coding units were taken from Speyer *et al.*¹⁰; those for glutamic acid and alanine came from Martin *et al.*¹¹; with regard to four components, aspartic acid (UAG), methionine (UAG), asparagine (UAA) and glutamine (UCG), only information published in the daily Press was available¹³.

The following approximate composition of the 'coding' RNA results: $\text{A}_{6.3} \text{G}_{5.9} \text{C}_{7.7} \text{U}_{17.3}$; or, as mole per cent, A, 16.9; G, 15.9; C, 20.7; U, 46.5. (A, G, C, U, stand, respectively, for adenylic, guanylic, cytidylic and uridylic acids.)

A ribonucleic acid of this composition must create some surprise. If it exists, it has not been seen. The strikingly high content in uridylic acid, nearly a half of the hypothetical molecule, is in contrast to almost all available information¹⁴. Also other features of the constructed molecule are most unusual: the ratio of A to U is 0.36; the purines account for only one-third of the nucleotides; the ratio of 6-amino to 6-keto nucleotides¹⁵ is 0.60. Moreover, the inspection of the proposed code, with its baffling richness in uridylic acid, makes it unlikely that many proteins would be found to demand less implausible 'messengers'. If the assignment of coding units really proved to be correct, auxiliary hypotheses would be required, in order to explain the discrepancy between the composition of the 'coding' RNA under discussion and that of 'messenger' RNA exhibiting the regularities of DNA. The most obvious, but still unwarranted, assumption may summarize the production of the 'messenger' in the form of two polynucleotides, complementary with respect to base-pairing, of which only one determines the protein; a postulate that leaves the function and the fate of the other half very much in doubt. Here,