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On the Direct Synthesis of Phenylchlorosilanes With Several Catalysts and Fractional Distillation Analysis

Hajime Kimura

Introduction

On the synthesis of organohalosilanes which are the intermediates of silicone polymer various methods of synthesis have been devised, they may be classified by as either methods, substitution method (i.e. the method of KIPPING-BYGDEN¹⁾, WURTZ-FITTIG²⁾, and GRIGNARD³⁾) or direct method (i.e. the method of E. G. ROCHOW⁴⁾, and TAYLOR, WALDEN⁵⁾). The direct method, however, has suddenly risen in importance in the modern silicon industry, since this method have been adopted by the Dow-Corning Co-operation.

In the direct method, the mixture of crystalline or elementary silicon and suitable catalyst is caused to react directly with a hydro-carbon halide to produce of organosilicon halides. This is a general reaction for both alkyl and aryl hydrocarbon halides in either the liquid or the vapor phase.

However, it is most convenient to use hydrocarbon chlorides as starting material and to carry out the reaction in the gas phase at a temperature of 200–450°C, depending upon the reactivity of the particular chloride.

It is apparent that at the higher temperatures which may be required for reaction of the more inert chlorides the organic compounds may suffer considerable pyrolysis, with consequent deposition of carbon in the reactive zone. Such decomposition can be avoided in large part by the use of a metallic or a metal oxide catalyst which will reduce the temperature required for effective reaction. Powdered copper is one of such catalysts and has been used satisfactorily in a reaction of methylchloride with elementary silicon to prepare methylchlorosilanes. The use of the former copper catalyst enables one to reduce the reaction temperature by about 200–250°C, and to obtain satisfactory conversion of the methyl chloride without large loss by pyrolysis.

1) BYGDEN : Ber. 44, 2640 (1910).

KIPPING & LLOYD : J.C.S. 79, 449 (1901).

2) SCHUMB, ACKERMANN and SAFFER : J.A.C.S. 60, 2486 (1938).

3) SCHUMB and SAFFER : J.A.C.S. 61, 363 (1939).

4) E. G. ROCHOW and GILLIAM : J.A.C.S. 68, 798 (1941).

GILLIAM : J.A.C.S. 63, 1194 (1941).

5) A. G. TAYLOR and WALDEN : J.A.C.S. 66, 842 (1944).

In this case, the yield of methylchlorosilanes was nearly 100 per cent. On the other hand, it is reported that, in the reaction of chlorobenzene with silicon to form phenylchlorosilanes, finely divided silver is more effective than copper as a catalyst, although the reduction temperature is 250°C, and the yield is about 10%.

By the use of reduction with hydrogen gas at 200°C, Dr. T. YAMADA⁶⁾ has recently obtained excellent results to prepare alkylchlorosilanes, showing about 120% yield by weight,

The author carried out a synthetic experiment of phenylchlorosilanes by the reaction of chlorobenzene with metallic silicon in the presence of copper and silver catalysts reduced on YAMADA'S principle.

The author will make a report in this paper with regard to a preparation of catalysts, a fractional distillation analysis of the products, and an influence of the catalysts on the products or yield.

Experimental

a) SYNTHETIC APPARATUS AND GENERAL PROCEDURE

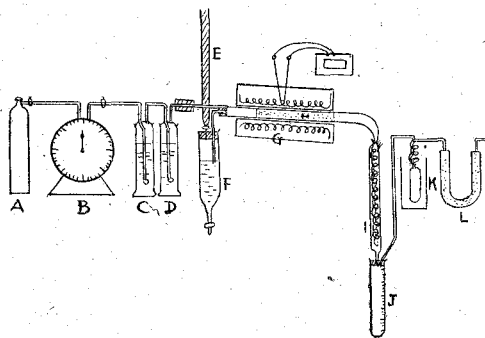


Fig. 1. Apparatus of Synthesis.

The apparatus is shown in Fig. 1.

The reactant consists of metallic silicon powder catalyst, and silica as a carrier in which the latter is 10 per cent of metallic silicon respectively. It packed into a pyrex reaction tube H about 30-40 grams, passing hydrogen gas through the packing at 200°C (in copper catalyst) or 250°C (in silver catalyst), this tube being

heated with electric furnace, then the packing was dried expelling water, and reducing still more, the dehydration was stopped within about 20 hours.

The higher reduction temperature does not show a good activity for the pyrolysis.

After reduction, stopping the flow of hydrogen, raising the reduction temperature, and dropping mercury from burette E, then the reaction was carried on by forcing chlorobenzene in F to the packing.

Some of this product condensed in the adaptor J through the water-

6) 山田・安永・金指：電氣試験所彙報，13卷，9號，31頁。

cooled condenser I and another the component of low boiling point was exhausted through ice-cooled trap K and phosphor pentaoxyde drying tube L.

The above treatment was done with precautions noticing the bad effect of moisture upon this reaction.

The reaction was continuous but the following velocity was unable to be constant which is in 5–10 g/hr. It required about 24 hours and the product could be distilled.

Furthermore, at the begining of reaction, there was seen a good deal of reddish-violet material which seems the product, and in the end, there was much transparent one which seemed the reactant.

For the inspection of this product, the usual flask was used for the high difference of boiling point of these components, (except for the case of molecular silver catalyst), but it could not be distilled for the scanty of the product, so silicon in each fraction was weighed by the Direct Acid Digestion Method⁷⁾.

For these experiments, commercial benzene was used and metallic silicon (Si 93.6%, Fe 1.82%, Ca 1.41%, Al 2.50%, Mn 0.37%, Mg 0.38%), was from the SHINETSU KAGAKU Co., and powdered to 200 mesh and more.

Direct Acid Digestion Method

High-boiling or resinous samples which will yield 70 to 100 m.g. of silicon dioxide are weighed directly in tarred platinum or Vycor crucibles, or 20 to 30 drops of the high-boiling previously noted are dropped from a weighing pipet into a tarred crucible containing 3 to 4 m.l. of 10% ammonium hydroxide. The water is evaporated, preferably by infrared lamp, and then the digestion is carried out. In either case, 4 or 5 drops of chlorobenzene, which reduces frothing on some samples, are added and the contents are agitated or warmed to the solution of the samples. Two m.l. of 15% fuming sulfuric acid are added to the solution at room temperature. Many samples may be speeded up by addition of 0.5 m.l. of fuming nitric acid immediately following addition of the sulfuric acid. Digestion is accomplished by holding over a low flame or by several hours heating on a micro-Kjeldahl rack. When the mass has solidified and danger of frothing is past, the crucible is heated over a Meker burner to complete expulsion of sulfur trioxide fumes. The residue, usually black, is placed in a muffle for 1 hour at 800°C. Residual silicon dioxide is calculated back to silicon in the original sample.

7) J. A. McHARD, P. C. SERVAIS, CLARK: "Determination of Silicon in Organosilicon Compound".

(b) APPARATUS FOR PRECISE FRACTIONAL DISTILLATION
ANALYSIS AND GENERAL PROCEDURE

The apparatus for precise fractional distillation analysis was the Podbielniak Packed Tower which is a partial condensation type is shown in Fig. 2.

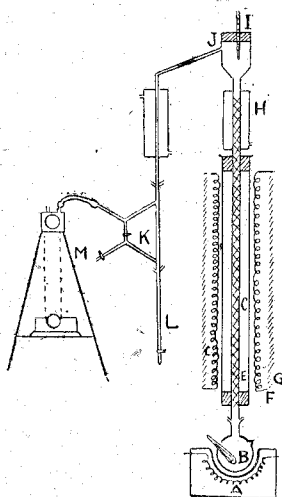


Fig. 2. Apparatus of Fractional Distillation.

A pyrex column C was 4.2 mm (inside diameter) \times 1200 mm (height). On account of perfect and exact control of column thermal conditions and product-withdrawal of this air-jacketed column. It was insulated the heater by asbestos 20 mm in inside diameter. It was surrounded by the nichrom heating wire on the outside of fractionating column.

Many glass cylinders (1.5 mm in diameter, and 3 mm long) were used in packing and their arrangement was at random.

The twice turn wires of nickel were adopted for the higher efficiency.

Then the space ratio was 66%, and reflux ratio was 50 ± 5 .

Ascending vapor was dephlegmated at H and with components of high boiling point were carried out of vacuum distillation. (K; M in this figure is the vacuum adaptor and the vacuum pump respectively).

The theoretical plate number of this column measured 22.5 plates by means of $C_6H_6-CCl_4$ system and hold up was 24 c.c..

For the research of distillate-temperature relation, the values were read every one minute and the molecular weight of each fraction was measured by the cryoscopic method.

In the rectificational analysis, the following notice must be generally taken, but the author considered only of (b) and (c), and neglected the others for the constant conditions.

- a) Constitution of sample and a specific character for distillation
- b) Total time for distillation
- c) Distillation ratio, reflux ratio, distillatory pressure and all conditions except for (b)
- d) Tenfold for the maximum column volume of over-flow distillate in fractionating section area
- e) Effect of packing
- f) Adiabatic efficiency of column
- g) General design and construction of fractional distillatory apparatus

(c) RESULTS

Owing to the difference of catalyst preparation could be classified as follows:

(1) Reduced Copper catalyst

The preparation of the reactant used in this experiment was as follows, sodium silicate was prepared from the warm solution of silica gel as carrier and sodium hydroxyde diluted in 5% solution, added 5% cuppric chloride solution slowly on heating and stirring. In the end, the blue colloid of cuppric hydroxyde was precipitated. This precipitate was washed by decantation until it showed no-color by phenolphthalein indicator and had very slight reaction of Cl^- in silver nitrate solution. After the powdered elementary silicon was mixed with its precipitate, filtrated in aspirator, dehydrated with pressing, moulded and dried at about 60°C , and formed as tablets.

TABLE 1

Temperature $^\circ\text{C}$	Time hr	Weight of $\text{C}_6\text{H}_5\text{Cl}$ was flowed g	Flowing velocity g/hr	Yield (g)	Yield %	Weight of sample g	Fractional Distillation (%)				Con- version ratio (%)	Reac- tion ratio %
							L.B.	No reac- tion	H.B.	Resi- due		
350	24.5	112.2	4	44	39.2	50	—	39	—	—	—	—
400	21.4	70.4	3	69.2	98.0	50	11.0	50	2.7	30	1.22	1.73
500	27.0	214.5	7.4	185.2	86.5	30	23.0	143	5.7	20	1.24	0.67

(2) Silver chloride catalyst

In the process of this synthesis, silver chloride seemed to form as an intermediate, therefore, the author adopted it.

A colloidal silver silicate solution, which was formed from 5% solution of silver nitrate and sodium silicate, was most difficult to filtrate, therefore, so silver chloride was precipitated completely by the addition of a little hydrochloric acid.

And the subsequent treatment was the same as (1)

TABLE 2

Temp. $^\circ\text{C}$	Time hr	Wei- ght sam- ple g	Weight of $\text{C}_6\text{H}_5\text{Cl}$ g	Flowing velo- city g/hr	s.g.	Yield		Fractional Distillation (%)				Conve- rsion ratio %	Reac- tion ratio %
						g	%	L.B.	No re- action	H.B.	Resi- due		
400	14.4	40	116.9	6.6	1.21	20	102.8	7.0	107.3	1.0	2.0	0.44	0.37
500	21.5	50	216.1	6.6	1.18	218	100.5	33.9	152.7	26.5	2.7	5.83	2.68
500	9	40	179.5	20.4	1.28	193	107.8	8.2	148.2	7.0	—	0.6	0.31
600	18	30	183.7	9.3	1.15	199	108.2	1.5	148.0	7.2	2.0	0.72	0.36

(3) Reduced silver catalyst

By reason of a great effect of the reduction of reactant on the catalytic activities, the reduced copper catalyst was prepared with the same principle of copper catalyst: i.e. dilute sodium hydroxyde solution of silica gel was added to dilute silver nitrate solution on heating, so silver oxide was precipitated, then it was washed until it showed slightly alkaline. The subsequent treatment was the same as (1)

TABLE 3

Temp. °C	Time hr	Weight of C ₆ H ₅ Cl g	Flow- ing velo- city g/hr.	Yield		Fractional Distillation (%)				Conve- rsion ratio %	Reac- tion ratio %	Weight of sample g
				g	%	L.B	No reac- tion	H.B	Resi- due			
400	7.5	86.3	11.6	84.2	98.0	1.0	82.0	—	0.1	—	—	40
450	"	132.3	6.4	128.4	96.4	11.5	111.0	—	2.2	—	—	"
500	"	184.9	7.6	166.0	90.6	26.9	115.0	14.9	1.8	2.74	1.65	"
550	"	255.8	10.9	239.5	93.5	55.0	149.0	29.0	5.5	3.56	1.49	"

(4) Molecular Silver catalyst.

The preparation of the reactant used in this experiment was as follows.

Silver chloride that was obtained from silver nitrate was washed till the NO₃⁻ was disappeared and then it was reduced with the nascent hydrogen which was produced by the reaction of much dilute sulfuric acid and zinc powder.

Thus, the so-called molecular silver was obtained.

In this operation, to avoid of oxygen, the hydrogen gas was bubbled and washed with hot distilled water till SO₄⁻ was disappeared.

Then this catalyst was mixed with the elementary silicon that was preserved in hydrogen gas, and then dried in vaccum and used for sample in powder about 100 g..

TABLE 4

Temp. °C	Weight of cata- lyst g	Time hr	Weight of C ₆ H ₅ Cl g	Flow- ing velo- city g/hr	Yield		Fractional Distillation (%)							Reac- tion ratio %
					g	%	L.B	No reac- tion	205°C	220°C	305°C	370°C	Resi- due	
350	1	24	30	2.5	18.7	56.7	1.82	36.4	4.26	2.16	0.3	—	2.42	9.0
400	"	"	50	4.1	30.4	55.3	16.3	17.1	2.18	2.18	1.09	—	2.0	9.5
500	"	"	"	"	28.1	51.3	20.0	13.1	5.46	1.09	1.46	—	1.82	17.0
350	10	"	"	"	34.6	62.9	13.4	26.2	8.73	1.46	1.82	—	1.63	19.3
400	"	"	"	"	32.8	59.7	10.4	24.8	6.19	3.64	4.73	—	1.46	20.7
450	"	"	"	"	37.5	68.2	27.3	10.9	3.27	5.1	7.45	0.73	1.09	19.3
500	"	"	"	"	37.0	67.3	21.1	13.8	4.73	5.27	5.83	—	3.1	20.2
600	"	"	"	"	34.4	71.8	21.8	10.2	4.37	10.9	4.73	—	2.73	16.5

(d) DISCUSSION

1) On the kinds of catalyst

In the above four catalysts, the reduced silver (10% by weight) catalyst and molecular silver (10% by weight) catalyst are considered to be favourable, namely differing from other catalysts the reaction is continuous and the product per unit reactant is much, but as a defect it has high carbonization.

Silver chloride catalyst has low carbonization, but cannot react continuously; on the other hand, the product at initial is more than at final. With the molecular silver catalyst it is obtained that the yield depends upon the preparing process (on account of O_2).

2) The most available temperature

The following results are obtained in this experiment.

In the case of silver chloride catalyst, the reaction begins at 400°C and is in the best condition at 500°C.

Reduced silver catalyst has the highest efficiency at 500°C.

Molecular silver catalyst begins at 350°C, but the yield is constant at 500°C. In 600°C the reaction rate becomes to decrease rapidly for the carbonization.

3) On the products

With reduced copper catalyst it is considered that the reaction is the synthesis of phenylchlorosilanes rather than the decomposition of chlorobenzene, because the components of low specific gravity, low boiling point are mainly produced.

But, with silver chloride catalyst, of the first time of reaction there are produced a good deal of such components of high boiling point which have high specific gravity and high silicon content.

On the other hand, at the last time of reaction, there is much diphenyl.

With reduced silver catalyst, it is shown by the above measurement that the resultant is formed on an average.

On the case of molecular silver catalyst which is shown the highest efficiency, it is explained as follows: with 1% of the catalyst, the reaction rate is increased with temperature, because the decomposition and polymerization is accelerated with temperature, then the components of low boiling point and diphenyl is increased.

In this case, the main product R_2SiCl_2 is about constant at higher temperature than 350°C (see Fig. 3).

With 10% of the catalyst, the higher the temperature, the more the components of high boiling point until at 500°C, and at the same time, the less the $RSiCl_3$, the more the diphenyl. In this content the R_2SiCl_2 has the maximum efficiency (8%) at 450°C.

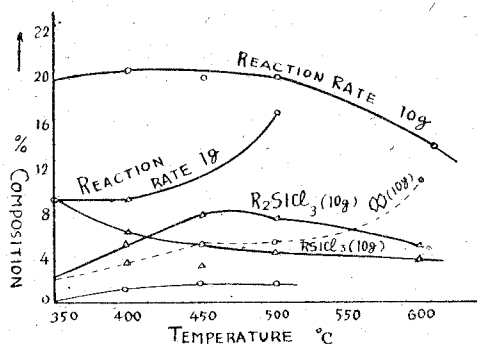


Fig. 3. The change of composition with the reaction temperature

In the end, this molecular silver is one of the best catalysts for the preparation of phenylchlorosilanes, because of the total efficiency being reached to 20%. (see Fig. 3)

4) On the flowing velocity.

The greater the velocity, the less the reaction rate and the more the carbonization may be carried out. The satisfactory value seemed to be 5–12 g/hr.

5) On the rectifying distillation.

Using the above mentioned apparatus by which temperature-control is very difficult, and that with such a reflux ratio, the good plate curve is scarcely obtainable in normal distillation, but it is made in the careful vacuum distillation which is shown in Fig. 4, Fig. 5, Fig. 6, and Fig. 7.

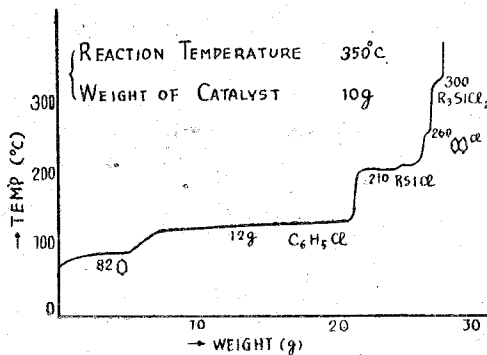


Fig. 4.

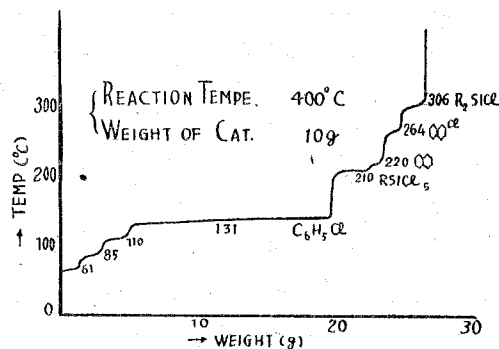


Fig. 5.

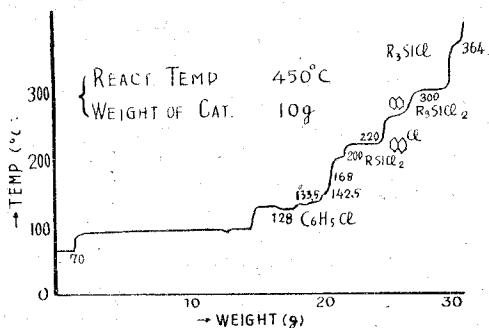


Fig. 6.

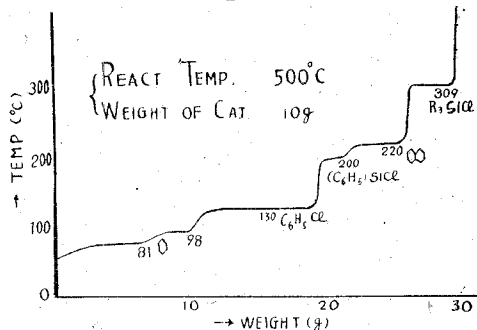


Fig. 7.

However, the column with higher efficiency is necessary for the components of low boiling point.

Summary

The author carried out the synthetic experiments for direct synthesis of phenylchlorosilanes, and concluded the most available conditions in these reactions (such as kinds of catalyst, reaction temperature, and etc.) by using reduced copper, silver chloride, reduced silver, and molecular silver catalyst.

These experiments lead to the conclusion that the yield of direct synthesis is worse than the substitution method (such as GRIGNARD-method) for phenylchlorosilanes. And yet, by applying rectificational analysis, the author obtained successful results.

The author wishes to express his hearty thanks to Dr. T. YAMADA, E. YASUNAGA and his co-workers (Electrotechnical Laboratory) for their kind guidance and aid in this work and to Professor M. SHINDO for his kind advice in this report.

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