

ORGANOSILICON COMPOUNDS. CII.*

DIRECT SYNTHESIS OF METHYLCHLOROSILANES
IN THE PRESENCE OF METHYLDICHLOROSILANE OR TOLUENE

J. JOKLÍK and †V. BAŽANT

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

Received December 7th, 1972

For the purpose of studying the mechanism of the direct synthesis of methylchlorosilanes, the effect of the addition of methyldichlorosilane or toluene was examined. It was found that methyldichlorosilane reacts under these conditions to give dimethyldichlorosilane, methyltrichlorosilane and a small amount of dimethyltetrachlorodisilane. These transformations are not induced by free methyl radicals in gaseous phase, but proceed on the surface of contact mass. Of the products of the direct synthesis in the presence of toluene, a very small amount of ethylbenzene was isolated. No dibenzyl was detected. From the results it was concluded that the direct synthesis of methylchlorosilanes proceeds according to chemisorption mechanism.

In a previous work¹ we studied the reactions of trichlorosilane, methyldichlorosilane, methyltrichlorosilane, and dimethyldichlorosilane with free methyl radicals. We found that the reactivity of the Si—H bond is greatly enhanced over that of the C—H bond. We considered this fact as contradicting the free radical theory of the direct synthesis of methylchlorosilanes^{2,3}. The existence of free methyl radicals in gaseous phase as a main source of reactive intermediates decreases the probability of formation of the compounds containing Si—H bond, due to a high reactivity of this bond towards free methyl radicals. Contrarily, the great amount of ethyldichlorosilane (30%) is formed in the direct synthesis of ethylchlorosilanes⁴.

While in a previous work we studied the action of methyl radicals on chlorosilanes under the conditions differing from the conditions of the direct synthesis (*i.e.* at temperature of 450°C, in the presence of mercury vapours and in the absence of a silicon-copper contact mass) in the present work we considered it useful to investigate the effect of the compounds highly sensitive towards methyl radicals, added to the methyl chloride reacting with silicon in the presence of copper. For this purpose we have chosen methyldichlorosilane and toluene⁵.

EXPERIMENTAL

Substances and procedure. Chloromethane (technical grade purity, supplied by VCHZ Synthesia, Kolín), silicon-copper alloy (composition: 9.8% Cu, 0.52% Fe, 0.24% Al, other admixtures

* Part CI: This Journal 38, 3167 (1973).

not determined; alloy grain size below 0.100 mm), zinc oxide and titanium dioxide (pure, supplied by Lachema). Methylchlorosilane (technical grade purity, supplied by VCHZ Synthesia, Kolin) was chromatographically homogeneous after distillation through a 50 TP column. Toluene (analytical grade purity) was dried over sodium. Reactions were carried out in the apparatus schematically depicted in Fig. 1. Chloromethane from pressure cylinder 1 was introduced via a drying column filled with phosphorus pentoxide 2 and a capillary flow meter 3 into a two-necked evaporator 4 equipped with electric heating. The other neck was connected with inlet of methylchlorosilane or toluene, which were introduced by means of hypodermic syringe 5. The rate of feeding was controlled by a linear feeding device 6. The evaporator was connected via ground fitting with a reactor 7 containing 85 g of silicon-copper alloy activated by 0.5% of zinc oxide and 0.5% of titanium dioxide. The contact mass was mixed with copper spiral stirrer 8 at a rate of 60 r. per min. Reaction products were collected in condensers 9, 10 cooled to -20 and -78°C . The gases, hydrogen and methane, were led to a bottle 11 filled with water. Methylchlorosilanes were analyzed by g.l.c., using fluorinated silicone polymer F 16⁶, dimethyltetrachlorodisilane was first converted by methylmagnesium chloride to hexamethyldisilane; ethylbenzene and dibenzyl were determined with the use of poly(diphenylsiloxane)⁷.

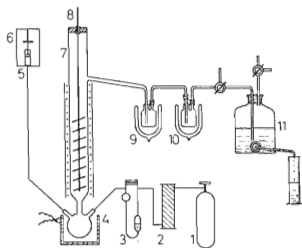


FIG. 1

The Apparatus for Direct Synthesis of Methylchlorosilanes with the Addition of Methylchlorosilane or of Toluene

For description see text.

The direct synthesis under standard conditions (experiment 1). The reactor was charged with 85 g of the copper-silicon alloy, its temperature was 310°C and the reaction was carried out over a period of 19 h. Chloromethane (177 g) was introduced at the feeding rate of 9.3 g/h. The reaction afforded 179.4 g of the condensate containing 17.8 g of chloromethane, 2.1 g (1.3%) of methylchlorosilane, 1.1 (0.7%) of trimethylchlorosilane 20.2 g (12.4%) methyltrichlorosilane 129 g (80%) of dimethylchlorosilane, and 9.1 g (5.6%) of higher-boiling fractions which contained 1.2 g of dimethyltetrachlorodisilane.

The direct synthesis in the presence of methylchlorosilane (experiment 2). The amount of the contact mass and the reaction temperature were the same as in the previous experiment. The reaction time was 23 h. The feeding rate of chloromethane was 5 g/h, its total amount was 115.7 g. Methylchlorosilane (167 g) was fed in the rate 7.25 g/h. A total of 280 g of the condensate was obtained, which contained 6 g of chloromethane, 3.7 g (1.4%) of trichlorosilane, 96 g (35%) of methylchlorosilane, 0.2 g (0.1%) of trimethylchlorosilane, 50.1 g (18.3%) of methyltrichlorosilane, 116 g (42.3%) of dimethylchlorosilane, and 8 g (2.9%) of a higher boiling fraction, in which 1.9 g of dimethyltetrachlorodisilane was detected by g.l.c. The outlet contained 4.77 l (0.213 mol) of hydrogen and 3.83 l (0.171 mol) of methane. In calculating conversion of methyl-

TABLE I

Calculation of the Amount of Chlorosilanes Formed by Conversion of Methylchlorosilane in Experiment 2

Substance	Recalculated composition ^a	Found g	Difference	
			g	mol
Trichlorosilane	—	3.7	+ 3.7	0.027
Methyldichlorosilane	1.4	96.0	- 72.4	0.630
Trimethylchlorosilane	0.8	0.2	+ 0.6	0.005
Methyltrichlorosilane	13.6	50.1	+ 36.5	0.244
Dimethyldichlorosilane	88.0	116.0	+ 28.0	0.217
Higher-boiling portion	6.1	8	+ 1.9	—
Dimethyltetrachlorodisilane	0.8	1.9	+ 1.1	0.005

^a According to experiment 1 for 110 g of methylchlorosilanes.

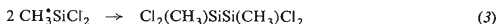
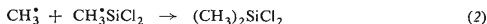
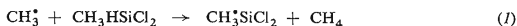
dichlorosilane to individual products we started from the assumption that the reaction of chloromethane with silicon is not influenced by the added methyldichlorosilane and that from the amount of the methyl chloride reacted an equivalent amount of methylchlorosilane is formed of the same percentual composition as in the experiment carried out in the absence of the addend. From the differences of the so calculated values and the values obtained in experiment 2 (in the presence of the addend) we determined weight increase or weight loss of individual methylchlorosilanes. The results are given in Table I.

Decomposition of methyldichlorosilane on contact mass (experiment 3). The alloy (85 g) was pre-reacted with chloromethane at 310°C. After 28.4 g of a mixture of methylchlorosilanes had been collected, the introduction of chloromethane was stopped and the apparatus was purged with nitrogen. Then, methyldichlorosilane (47.2 g) was introduced at a rate of 6.7 g/h. The condensate contained 55.2% of methyldichlorosilane, 21.0% of methyltrichlorosilane, and 23.8% of dimethyldichlorosilane.

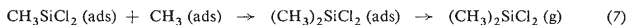
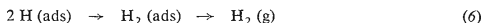
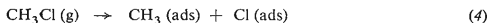
The direct synthesis in the presence of toluene (experiment 4). The amount of the contact mass and the temperature of the reactor was the same as in experiment 1. The reaction time was 22 h, chloromethane (124.3 g) and toluene (174.6 g/h) were introduced at a rate of 5.65 g/h and 7.95 g/h, respectively. The reaction gave 295 g of the condensate, from which we isolated 20.6 g of chloromethane and 101.2 g of methylchlorosilanes of the composition 0.3% of trichlorosilane, 1.2% of methyldichlorosilane, 0.1% of trimethylchlorosilane, 14.9% of methyltrichlorosilane, 75.5% of dimethyldichlorosilane, and 8% of a higher boiling fraction which contained 1.5 g (0.014 mol) of ethylbenzene. Dibenzyl was not detected.

DISCUSSION

If a free radical mechanism of the direct synthesis of methylchlorosilanes is accepted, the addition of methyldichlorosilane to chloromethane in the synthesis of methylchlorosilanes should be expected to lead to following reactions:



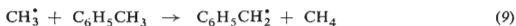
The material balance of experiments 1 and 2 indicates that methylchlorosilane is in a great extent transformed to methyltrichlorosilane and dimethylchlorosilane. The conversion of methylchlorosilane to dimethylchlorosilane might be taken as evidence in favour of the course of reactions (1) and (2), the high content of hydrogen in outlet gases (0.213 mol), which represents 67% of the methylchlorosilane reacted, does not comport, however, with this assumption, but indicates that the hydrogen is cleaved from methylchlorosilane. Processes, which likely proceed on the surface of contact mass, may be depicted by following equations:



The calculated amount of the methylchlorosilane consumed in the conversion to methyltrichlorosilane, dimethylchlorosilane, and dimethyltetrachlorosilane is nearly 75% of all the methylchlorosilane reacted. This portion of methylchlorosilane corresponds to 0.235 mol of hydrogen, which is in satisfactory agreement with the amount determined in outlet gases. The decomposition of methylchlorosilane itself on contact mass has already been observed to take place to a small extent^{8,9}. Other authors¹⁰ presume that this decomposition does not occur in the presence of methyl chloride, due to preferential occupation of the active sites by the latter compound. As the properties of contact masses depend strongly upon both the elements present in silicon as impurities, and the sort and amount of used promoters, we made an experiment aimed at verification of the decomposition of methylchlorosilane in the absence of methyl chloride on the contact mass used in the present work. We have found that under these conditions nearly 50% of methylchlorosilane is converted to methyltrichlorosilane and dimethylchlorosilane. A detailed mechanism of this reaction will be the subject of a subsequent work. The evolution of a great amount of hydrogen upon addition of methylchlorosilane in the course of direct synthesis of methylchlorosilanes and the decomposition of methylchlorosilane on contact mass, according to our opinion, lends support to the assumption that the reaction of methylchlorosilane to give dimethylchlorosilane proceeds on the

surface of contact mass and not in gaseous phase, as supposed by a free radical theory.

As the addition of methylchlorosilane leads to very complicated and as yet not quite clear reactions, we have used toluene as another substance sensitive towards methyl radicals, which, as assumed and tested, does not undergo decomposition under the reaction conditions on contact mass. The reactions of toluene with free methyl radicals may be depicted by the following equations:



In higher boiling fractions we found 1.5 g (0.014 mol) of ethylbenzene and no dibenzyl. Providing that the reaction does proceed according to equations (9) and (10) the above fact would mean that each seventieth methyl group of the transformed chloromethane reacts in this way. It seems however more likely that these reactions do not proceed in the gas phase but occur on the surface of contact mass.

We believe that these results, the results of our previous studies^{1,8} as well as those of other authors⁹⁻¹⁴ lend support to the conclusion that the direct synthesis of methylchlorosilanes proceeds according to chemisorption mechanism.

REFERENCES

- Joklik J., Bažant V.: *This Journal* 37, 3772 (1972).
- Rochow E. G.: *J. Am. Chem. Soc.* 67, 963 (1945).
- Müller R., Gumbel H.: *Z. Anorg. Allgem. Chem.* 327, 302 (1964).
- Andrianov K. A., Golubcov S. A., Petrjakova A. A.: *Chim. Promyšlenost* 1958, 342.
- Szwarc M.: *Chem. Rev.* 47, 75 (1950).
- Avdonin G. V., Alekseeva Z. I., Detrinova V. N.: *Plast. Massy* 3, 56 (1967).
- Čermák J., Franc J.: *This Journal* 30, 3278 (1965).
- Tubjanskaja V. S., Lelčuk S. L., Berliner L. E.: *Plast. Massy* 4, 18 (1958).
- Tubjanskaja V. S., Lelčuk S. L.: *Plast. Massy* 2, 19 (1963).
- Morozova L. P., Andrianov K. A., Morozov N. G., Golubcov S. A.: *Izv. Akad. Nauk SSSR, Chim. Otd.* 1966, 475.
- Joklik J., Kraus M., Bažant V.: *This Journal* 26, 417 (1961).
- Trambouze P.: *Bull. Soc. Chim. France* 1956, 1756.
- Klebanskij A. L., Fichtengol'c V. S.: *Ž. Obšč. Chim.* 26, 2502 (1956).
- Voorhoeve R. J. H., Vlughter J. C.: *J. Catal.* 4, 123, 220 (1965).

Translated by J. Hetflejš.