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## Abstract

## Full Text

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# ON THE MECHANISM OF THE REACTIONS OF FORMATION OF DIALKYLDICHLOROSILANES

We have shown ([1-4]) that the formation of alkyldichlorosilanes in the interaction of silicon-copper contact masses with alkyl chloride is associated with its decomposition on the copper catalyst; the hydrogen chloride liberated during decomposition enters into the reaction of formation of alkyldichlorosilane:

$$CH_3Cl \xrightarrow{Cu} C + H_2 + HCl, \quad HCl + CH_3Cl + Si \xrightarrow{Cu} CH_3SiHCl_2.$$

In studying the interaction of alkyl chlorides with silicon in the presence of copper, it was established that cuprous chloride, formed by the action of methyl chloride on copper, is of great importance in the synthesis of dialkyldichlorosilanes. The concentration of cuprous chloride in the reaction zone largely determines the content of dialkyldichlorosilanes in the reaction products.

The experimental data obtained show that the reaction of formation of dialkyldichlorosilanes proceeds according to the scheme:

$$CH_3Cl + Cu \rightarrow CH_3Cl \cdot Cu, \tag{1}$$

$$2CH_3Cl \cdot Cu \rightarrow 2CuCl + CH_4 + C + H_2, \tag{2}$$

$$Si + 2CuCl \rightarrow SiCl_2 + 2Cu, \tag{3}$$

$$SiCl_2 + CH_3Cl \cdot Cu \rightarrow CH_3SiCl_2 + CuCl, \tag{4}$$

$$CH_3SiCl_2 + CH_3Cl \cdot Cu \rightarrow (CH_3)_2SiCl_2 + CuCl, \tag{5}$$

$$Si + 2CH_3Cl \xrightarrow{Cu} (CH_3)_2SiCl_2. \quad (6)$$

The process consists of the adsorption of alkyl chloride and its interaction with copper with formation of cuprous chloride, the interaction of CuCl with silicon with formation of the intermediate compound $SiCl_2$, and the alkylation of it by alkyl chloride adsorbed on copper. In the alkylation process, cuprous chloride is regenerated, and thus, in the overall scheme for the formation of dialkyldichlorosilane (6), the reaction of decomposition of alkyl chloride (2) does not participate.

The compound $SiCl_2$ is formed at temperatures of 1000–1400° in the interaction of silicon with silicon tetrachloride ([5]). Thermodynamic calculations* showed the possibility of formation of $SiCl_2$ by reaction (3) at the temperatures of direct synthesis of alkylchlorosilanes.

The existence of the intermediate product of partial chlorination of silicon, $SiCl_2$, was confirmed by experiments in which the volatile product of the interaction of silicon and cuprous chloride was carried through a porous ceramic wall; on interaction with methyl chloride and copper it formed methylchlorosilanes.

* Carried out by V. V. Korobov and co-workers.

In other experiments, the interaction of silicon, cuprous chloride, and methyl chloride led to the formation of dimethyldichlorosilane and methyltrichlorosilane, the product ratio (1.33 moles of dimethyldichlorosilane and 0.42 moles of methyltrichlorosilane per 1 mole of cuprous chloride) corresponding to the course of the reactions according to schemes (3, 4, 5, 7):

$$SiCl_2 + CH_3Cl \cdot Cu \rightarrow CH_3SiCl_3 + Cu. \quad (7)$$

The relationship between the selective formation of dialkyldichlorosilane and the concentration of cuprous chloride in the reaction zone is illustrated by an experiment in which cuprous chloride was introduced into the reaction zone of ethyl chloride with a silicon–copper alloy (see Table 1). The introduction of 2% cuprous chloride

**Table 1**

Effect of cuprous chloride introduced into the reaction or of purging the contact mass with hydrogen on the composition of the products of the interaction of ethyl chloride with a silicon–copper alloy*

| Sampling period | CuCl additive, % of alloy weight | Ethyldichlorosilane content in mixture, % | Ethyltrichlorosilane content in mixture, % | Diethyldichlorosilane content in mixture, % |
|---|---|---|---|---|
| a | – | 19 | 37 | 44 |

| Sampling period | CuCl additive, % of alloy weight | Ethyldichlorosilane content in mixture, % | Ethyltrichlorosilane content in mixture, % | Diethyldichlorosilane content in mixture, % |
|---|---|---|---|---|
| b | 1.3 | 15 | 39 | 45 |
| c | – | 17 | 35 | 48 |
| d | – | 11 | 43 | 46 |
| a | – | 14 | 37 | 49 |
| b | 20 | 0 | 37 | 63 |
| c | – | 12 | 36 | 52 |
| d | – | 0 | 52 | 48 |
| a | – | 16 | 33 | 51 |
| b | 10 | 21 | 50 | 29 |
| c | – | 13 | 35 | 52 |
| d | – | 7 | 42 | 51 |
| e | – | 0 | 36 | 64 |
| f | – | traces | 41 | 59 |
| a | – | 23 | 32 | 45 |
| Purging of the mass with hydrogen (0.5 l/min, 1 h) | Purging of the mass with hydrogen (0.5 l/min, 1 h) | Purging of the mass with hydrogen (0.5 l/min, 1 h) | Purging of the mass with hydrogen (0.5 l/min, 1 h) | Purging of the mass with hydrogen (0.5 l/min, 1 h) |
| b | – | 32 | 32 | 36 |
| d | – | 51 | 49 | 0 |
| e | – | 66 | 34 | 0 |

**Note.** a –3 hours after the start of the synthesis; b –0.5 hour after the addition of CuCl (or purging with $H_2$); c –the same after 1 hour; d –the same after 1.5 hours; e –the same after 2 hours; f –the same after 2.5 hours.

* The method for the synthesis of ethylchlorosilanes has been described previously ([8]). The composition of the reaction products was determined by gas-liquid chromatography.

promotes a sharp increase in the content of diethyldichlorosilane, while the introduction of larger quantities of it, in accordance with scheme (7), promotes ethyltrichlorosilane. Removal of cuprous chloride from the reaction zone by hydrogenation with hydrogen leads to cessation of the reaction forming diethyldichlorosilane.

## Experimental Part

**Interaction of silicon, cuprous chloride, and ethyl chloride.** Into the reactor ([6]) were charged 73 g of silicon and 27 g of cuprous chloride, and after

Fig. 1. Reactor for the experiment with transfer of $SiCl_2$ through a porous wall

Figure 1: Fig. 1. Reactor for the experiment with transfer of $SiCl_2$ through a porous wall

drying in a stream of nitrogen at a temperature of 320° methyl chloride was fed in (1 l/min). During 20 min, 11.9 g of a mixture was obtained, containing 10% ethyldichlorosilane, 37% ethyltrichlorosilane, and 46% diethyldichlorosilane; 0.3 l of gas was evolved; over the following 1 h 40 min, 82.4 g of product was obtained (8% ethyldichlorosilane, 21% ethyl-

trichlorosilane, 64% diethyldichlorosilane). The average copper content in the contact mass over the period of the experiment was: during the first 20 min, 3.4%; during the next 40 min, 11.3%; and during the next 60 min, 19.1%. In order to exclude the amount of products that had been obtained through the interaction of ethyl chloride with silicon in the presence of copper liberated in the course of the reaction, blank experiments were carried out with three samples of contact masses having the corresponding copper content, the copper having been reduced from cuprous chloride. In three syntheses of 20, 40, and 60 min duration, respectively, 2.2, 6.7, and 9.6 g of a mixture of ethylchlorosilanes and 0.3, 0.95, and 1.4 l of gases were obtained. The content of ethyldichlorosilane in the mixture was, respectively, 60, 45, and 35%; of ethyltrichlorosilane, 23, 29, and 21%; and of diethyldichlorosilane, 10, 19, and 37%. All gaseous products were formed only as a result of the direct-synthesis reaction.

**Experiment with transfer of the volatile product of partial chlorination of silicon through a porous wall.** Into the reactor shown in Fig. 1 there was charged a mixture of 197 g of silicon powder with a particle size of 100–250 $\mu$ and 70 g of cuprous chloride. In the porous ceramic cup (1) (pore size 20 $\mu$) 70 g of copper powder was placed. The reactor was immersed in a thermostat, and the temperature, measured by a thermocouple in the sleeve (2), was 370–385°. Nitrogen (78 l/hr) was introduced into the reactor through tube (3), and methyl chloride (0.3 l/hr) through tube (4). To prevent diffusion of methyl chloride, the pressure in the inner part of the cup (1) was maintained 30–35 mm Hg lower than in the outer part; when samples were taken from tube (6), methyl chloride and methylchlorosilane were not detected. The reaction products entering through tube (5) were condensed. In 4 hr, 27.9 g of mixture was obtained; after evaporation of methyl chloride, the residue (19.6 g) contained (according to gas–liquid chromatography) 4.9% trichlorosilane, 2.1% dimethyldichlorosilane, 56.7% silicon tetrachloride, 23% methyltrichlorosilane, and 13.3% methyldichlorosilane. The yield of methylchlorosilanes was 23%, based on methyl chloride that had entered into reaction. In a blank experiment (without the use of cuprous chloride, with introduction of silicon tetrachloride into the reactor), methylchlorosilanes were not obtained.

**Fig. 1.** Reactor for the experiment with transfer of $SiCl_2$ through a porous wall

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*Note: Figure translations are in progress. See original paper for figures.*