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Abstract

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INTERACTION OF DICHLOROSILANE WITH ORGANOCHLORIDES AT HIGH TEMPERATURES

The condensation of silicon hydrides with organochlorides at high temperatures is attracting the attention of many investigators, since it makes it possible, under relatively simple conditions, to synthesize various valuable organosilicon monomers.

However, in the reaction of high-temperature condensation, mainly silicon hydrides containing one Si—H bond have been studied. The behavior of silicon hydrides containing two Si—H bonds in this reaction has received little attention ([1,2]), although the latter reaction opened a new convenient route for the synthesis of organosilicon monomers of the type $RSiHCl_2$, R_2SiCl_2, etc. In addition, the literature contained no information on the influence of the structure of the organochloride on the composition and yield of the products of high-temperature condensation with silicon hydrides containing two Si—H bonds. It was therefore of interest to investigate the influence of the structure of the organochloride on the composition and yield of the products of condensation with dichlorosilane at high temperatures.

Under conditions of high-temperature condensation, dichlorosilane, depending on the structure of the organochloride, in contrast to silicon hydrides containing one Si—H bond, can form not two but five principal reaction products according to the scheme:

$$H_2SiCl_2 \quad RCl \begin{cases} \xrightarrow{1} & RSiHCl_2 \\ \xrightarrow{2} & R_2SiCl_2 \\ \xrightarrow{3} & RSiCl_3 \\ \xrightarrow{4} & HSiCl_3 \\ \xrightarrow{5} & SiCl_4 \end{cases}$$

where $R = C_6H_5, CH_3C_6H_4, C_{10}H_7, CH_2{=}CH$, etc.

As our investigations show (see the experimental part), the predominant direction of the reaction along 1-3 or 4-5 depends mainly on the structure of the organochloride, while the overall yield of condensation products depends on the temperature, the ratio of the initial reagents, and the contact time.

Of the five organochlorides subjected to the reaction of high-temperature condensation with dichlorosilane (chlorobenzene, *p*-chlorotoluene, α-chloronaphthalene, allyl chloride, and benzyl chloride), only chlorobenzene, *p*-chlorotoluene, and α-chloronaphthalene formed condensation products. The greatest yield of condensation products was obtained in the case of α-chloronaphthalene (52%) (see Table 1).

Condensation of dichlorosilane with organochlorides with formation of adduct 2 proceeds in two stages. First, one Si—H bond reacts with the organochloride, and then the second:

$$H_2SiCl_2 + RCl \rightarrow RSiHCl_2 + HCl, \tag{I}$$

$$RSiHCl_2 + RCl \rightarrow R_2SiCl_2 + HCl. \tag{II}$$

In this case the relative rate of condensation at the first Si—H bond, as was also noted earlier (1), is approximately 2-3 times higher than at the second Si—H bond; therefore, the principal product of the condensation of dichlorosilane with organochlorides is a compound of the type $RSiHCl_2$. The composition of the condensation products is strongly influenced by the reaction temperature. For example, dichlorosilane with *p*-chlorotoluene at 600° formed only one adduct—

Table 1

High-temperature condensation of dichlorosilane with organochlorides

No.	Starting substances	Amount, g (mol.)	Temp., °C	Main reaction products	Yield, g	Yield, % of theory
1	H_2SiCl_2 C_6H_5Cl	18.0 (0.18) 40.5 (0.36)	650	$C_6H_5SiHCl_2$ $(C_6H_5)_2SiCl_2$ $C_6H_5SiCl_3$	5.04.14.0	15.59.010.5
2	H_2SiCl_2 *n*-$CH_3C_6H_4Cl$	18.0 (0.18) 46.0 (0.36)	600	*n*-$CH_3C_6H_4SiHCl_2$	6.5	19.0
3	H_2SiCl_2 *n*-$CH_3C_6H_4Cl$	19.0 (0.19) 48.0 (0.38)	650	*n*-$CH_3C_6H_4SiHCl_2$ (*n*-$CH_3C_6H_4)_2SiCl_2$ *n*-$CH_3C_6H_4SiCl_3$	12.33.71.8	34.07.04.0

No.	Starting substances	Amount, g (mol.)	Temp., °C	Main reaction products	Yield, g	Yield, % of theory
4	H_2SiCl_2 α-$ClC_{10}H_7$	22.1 (0.22) 71.6 (0.44)	650	$C_{10}H_7SiHCl_2$ $(C_{10}H_7)_2SiCl_2$	14.4 17.8	29.1 023.0

tolyldichlorosilane (n-$CH_3C_6H_4SiHCl_2$), whereas at 650°, first, the yield of tolyldichlorosilane increased almost twofold, and second, ditolyldichlorosilane [(n-$CH_3C_6H_4)_2SiCl_2$] and tolyltrichlorosilane (n-$CH_3C_6H_4SiCl_3$) were formed in appreciable amounts (see Table 1). Adduct 3 is formed mainly through a side reduction reaction:

$$RSiHCl_2 + RCl \rightarrow RSiCl_3 + RH,$$

although a small amount of it may also be formed as a result of the following reactions:

$$H_2SiCl_2 + RCl \rightarrow HSiCl_3 + RH, \tag{a}$$

$$HSiCl_3 + RCl \rightarrow RSiCl_3 + HCl. \tag{b}$$

Raising the reaction temperature above 650° leads to noticeable pyrolysis of both the starting materials and the reaction products. Silicon and carbon are deposited on the walls of the quartz tube. The yields of condensation products decrease.

Chlorobenzene, p-chlorotoluene, and α-chloronaphthalene, in terms of their relative activity in high-temperature reactions with dichlorosilane ($t = 650°$, contact time ~25 sec), are arranged in the following order:

$$\alpha\text{-}C_{10}H_7Cl > n\text{-}CH_3C_6H_4Cl > C_6H_5Cl.$$

This series of relative activity fully corresponds to the series obtained by Petrov and Chernyshev (3) in the condensation of these organochlorides with silicon hydrides containing one Si—H bond.

Allyl chloride with dichlorosilane at high temperatures (600–650°) forms a fairly complex mixture of reaction products, from which it was not possible to isolate individual condensation substances. From the literature data (3, 4) it is known that allyl chloride with trichlorosilane and methyldichlorosilane forms allyltrichlorosilane and allylmethyldichlorosilane, respectively, in yields of up to 40%.

Benzyl chloride does not enter into a condensation reaction with dichlorosilane either at 600° or at 650°, but forms, in high yield, only the reduction product—toluene.

Experimental Part

1. Interaction of dichlorosilane with *p*-chlorotoluene at 600°. Through an empty quartz tube with an internal diameter of 19 mm and a reaction-zone length of 400 mm, heated to 600°, there was passed* a mixture of 18.0 g (0.18 mole) of dichlorosilane and 46.5 g (0.36 mole) of *p*-chlorotoluene at such a rate that the substances remained in the reaction zone for ~25 sec.

The reaction products were condensed first in a receiver placed in an ice bath, and then in a trap cooled with a mixture of acetone and dry ice. The uncondensed gaseous reaction products were passed through a bottle containing a titrated KOH solution to trap HCl.**

From the condensate obtained (60 g), distillation gave 6.5 g (19.0%) of tolyldichlorosilane—b.p. 90-91°/30 mm, n_D^{20} 1.5240, d_4^{20} 1.1864, MR_D found 49.29, calculated 49.27. Literature data (5): n_D^{20} 1.5240.

2. Interaction of dichlorosilane with *p*-chlorotoluene at 650°. From the condensate obtained (57 g), the following tolylchlorosilanes were isolated by distillation:

a) 12.3 g (34.0%) $p\text{-}CH_3C_6H_4SiHCl_2$—b.p. 86-87°/25 mm, n_D^{20} 1.5240, d_4^{20} 1.1868;

b) 1.8 g (4.0%) $p\text{-}CH_3C_6H_4SiCl_3$—b.p. 90-92°/10 mm, n_D^{20} 1.5265. Literature data (6): b.p. 103-105°/15 mm, n_D^{20} 1.5261;

c) 3.7 g (7.0%) $(p\text{-}CH_3C_6H_4)_2SiCl_2$—b.p. 170-172°/10 mm, n_D^{20} 1.5735, d_4^{20} 1.1810, MR_D found 78.53, calculated 78.14. Literature data (7): b.p. 225-226°/50 mm.

3. Interaction of dichlorosilane with chlorobenzene at 650°. From the condensate obtained (51 g), the following phenylchlorosilanes were isolated by distillation:

a) 5.0 g (15.5%) $C_6H_5SiHCl_2$—b.p. 182-182.5°/754 mm, n_D^{20} 1.5246, d_4^{20} 1.2115, MR_D found 44.77, calculated 44.84. Literature data (1): b.p. 181.5°/750 mm, n_D^{20} 1.5246.

b) 4.0 g (10.5%) $C_6H_5SiCl_3$—b.p. 197.5-198°/754 mm, n_D^{20} 1.5225, d_4^{20} 1.3244, MR_D found 48.76, calculated 48.84. Literature data (1): b.p. 195-196°/743 mm, n_D^{20} 1.5222.

c) 4.1 g (9.0%) $(C_6H_5)_2SiCl_2$—b.p. 155-156°/16 mm, n_D^{20} 1.5820, d_4^{20} 1.2268, MR_D found 68.88, calculated 68.88. Literature data (1): b.p. 141-141.5°/5 mm, n_D^{20} 1.5819.

4. Interaction of dichlorosilane with α-chloronaphthalene at 650°. From the condensate obtained (72.6 g), the following naphthylsilanes were isolated by distillation:

a) 14.4 g (29.0%) $C_{10}H_7SiHCl_2$—b.p. 137-139°/6 mm, n_D^{20} 1.6140, d_4^{20} 1.3075, MR_D found 60.57, calculated 60.29. Literature data (5): b.p. 146-149°/10 mm, n_D^{20} 1.6140;

b) 17.8 g (23.0%) $(C_{10}H_7)_2SiCl_2$—b.p. 250-255°/4 mm, m.p. 149-150°. Literature data (8): b.p. 230-235°/3 mm, m.p. 150-151°.

5. Interaction of dichlorosilane with allyl chloride at 600°. The reaction was carried out with 22.6 g (0.22 mole) of dichlorosilane and 34.5 g (0.45 mole) of allyl chloride. From the condensate obtained (51 g), rectification on a 25-t.t. column failed to isolate individual condensation products.

* In all experiments, before the start and at the end of the experiment, the system was purged with dry nitrogen.
** All high-temperature condensation experiments were carried out by an analogous procedure.

6. **Reaction of dichlorosilane with allyl chloride at 640°**. The reaction was carried out with 24.8 g (0.25 mole) of dichlorosilane and 38.3 g (0.5 mole) of allyl chloride. From the condensate obtained (53 g), rectification on a column with 25 theoretical plates did not make it possible to isolate individual substances.

7. **Reaction of dichlorosilane with benzyl chloride at 600°**. The reaction was carried out with 19.7 g (0.19 mole) of dichlorosilane and 49.6 g (0.39 mole) of benzyl chloride. From the condensate obtained (57.8 g), rectification on a column with 25 theoretical plates gave the following substances:

a) 18.4 g of $HSiCl_3 + SiCl_4$ —b.p. 30-58°/754 mm.

b) 24.6 g of $CH_3C_6H_5$ —b.p. 111°/754 mm, n_D^{20}1.4960.

7. **Reaction of dichlorosilane with benzyl chloride at 650°**. The reaction was carried out with 23.0 g (0.23 mole) of dichlorosilane and 30.4 g (0.24 mole) of benzyl chloride. From the condensate obtained (51 g), rectification on a column with 25 theoretical plates yielded:

a) 16.0 g of $HSiCl_3 + SiCl_4$ —b.p. 30-58°/756 mm.

b) 18.0 g of $CH_3C_6H_5$ —b.p. 111°/756 mm, n_D^{20}1.4961.

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