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Abstract

Full Text

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ON THE THERMAL CONDENSATION OF DICHLOROSILANE WITH CHLOROBENZENE

It has been noted in the literature that, in the thermal condensation of dichlorosilane with chlorobenzene, phenyldichlorosilane is formed in a yield of about 30% ([1]). In studying this reaction we were able to establish that the interaction of dichlorosilane with chlorobenzene proceeds in a complex manner. Along with the formation of phenyldichlorosilane by the reaction

$$H_2SiCl_2 + C_6H_5Cl \rightarrow C_6H_5SiHCl_2 + HCl \tag{1}$$

there also occurs replacement of the second hydrogen atom at silicon by a phenyl group; in addition, at the high temperatures at which the thermal condensation is carried out, one should expect a new reaction—the replacement of a hydrogen atom at silicon by a chlorine atom. As a result of this complex course of the process, the reaction products, simultaneously with phenyldichlorosilane, contain diphenyldichlorosilane, phenyltrichlorosilane, benzene, and trichlorosilane.

As our investigations have shown, the yield of the reaction products depends, first of all, on the temperature. From Fig. 1 it is seen that the yield of phenyldichlorosilane increases up to a temperature of about 640-660° (the optimum temperature for reaction 1), reaching 41.7%; at the same time the yield of phenyltrichlorosilane increases to 18.3%. With a further increase in temperature to 700° the yield of phenyldichlorosilane decreases to 12%, whereas the yield of phenyltrichlorosilane continues to increase and reaches 26%. Simultaneously, as the temperature is raised, the yield of diphenyldichlorosilane first increases (to 12.4% at 660°), but at 700° it falls to 2.5%.

Fig. 1. Dependence of the yield of products of the thermal condensation on temperature.
I $-C_6H_5SiHCl_2$, *II* $-C_6H_5SiCl_3$, *III* $-(C_6H_5)_2SiCl_2$, *IV* $-C_6H_6$, *V* $-HSiCl_3$.

These circumstances indicate that, with increasing rate, the reaction of dichlorosilane with chlorobenzene proceeds; therefore silane or chlorosilane was practically absent from the reaction products, and the evolution of hydrogen during the decomposition of dichlorosilane alone was not detected.

$$C_6H_5SiHCl_2 + C_6H_5Cl \rightarrow (C_6H_5)_2SiCl_2 + HCl, \tag{2}$$

as well as side reactions of chlorination of hydridochlorosilanes:

$$H_2SiCl_2 + C_6H_5Cl \rightarrow HSiCl_3 + C_6H_6 \tag{3}$$

and

$$C_6H_5SiHCl_2 + C_6H_5Cl \rightarrow C_6H_5SiCl_3 + C_6H_6. \tag{4}$$

It is quite probable that part of the phenyltrichlorosilane is formed according to the scheme

$$HSiCl_3 + C_6H_5Cl \rightarrow C_6H_5SiCl_3 + HCl. \tag{5}$$

The rates of reactions (3), (4), and (5) increase much more rapidly than the rate of reaction (2), and at 680° the rates of formation of phenyltrichlorosilane become close.

The formation of trichlorosilane and phenyltrichlorosilane can hardly be explained in any other way, for example by disproportionation reactions

$$2H_2SiCl_2 \rightarrow HSiCl_3 + H_3SiCl \tag{6}$$

or by decomposition of dichlorosilane

$$3H_2SiCl_2 \rightarrow Si + 2HSiCl_3 + 2H_2, \tag{7}$$

Similarly, the formation of benzene is difficult to explain by reaction schemes other than (3) and (4), for example, at the expense of pyrolysis of chlorobenzene in a reducing medium. We carried out experiments on the pyrolysis of chlorobenzene, in which the yield of benzene did not exceed 9% (pyrolysis in a hydrogen medium) and 2.2% (pyrolysis in a silane medium), as against 55-60% in experiments on obtaining phenyldichlorosilane. The insignificant role of pyrolysis processes in obtaining phenyldichlorosilane is also indicated by the small yield of high-boiling products—still residues (2-4%).

Fig. 2. Dependence of the yield of products of thermal condensation on contact time. *I*—$C_6H_5SiHCl_2$; *II*—$C_6H_5SiCl_3$; *III*—$(C_6H_5)_2SiCl_2$.

Fig. 3. Dependence of the yield of products of thermal condensation on the molar ratio of dichlorosilane to chlorobenzene (a). *I*—$C_6H_5SiHCl_2$; *II*—$C_6H_5SiCl_3$; *III*—$(C_6H_5)_2SiCl_2$.

Figure 2 gives experimental data on the dependence of the yields of phenyldichlorosilane, phenyltrichlorosilane, and diphenyldichlorosilane on contact time; Fig. 3, on the ratios of the reacting components. Under optimal conditions, the total yield of these compounds is 74.6%.

Experimental Part*

1. Condensation of dichlorosilane with chlorobenzene.

A mixture of calculated amounts of dichlorosilane and chlorobenzene was fed from a dropping funnel, cooled with dry ice, into a quartz tube 24 mm in diameter and 75 mm long, equipped with electric heating. The reaction products were condensed successively in a water condenser, an ice-cooled trap, and a trap cooled with a dry ice-acetone mixture. Before the start of the experiment, the tube was purged with a stream of dry nitrogen. Separation of the liquid reaction products was carried out by rectification in three stages. First, on a low-temperature packed column with an effective—

* S. A. Platonova and T. A. Klochkova took part in the experimental work.

with an efficiency of 37 theoretical plates, unreacted dichlorosilane (b.p. 8-10°) and trichlorosilane (b.p. 30-32°) were distilled off. The residue was then rectified on a glass packed column with an efficiency of 26 theoretical plates at atmospheric pressure, with isolation of benzene (b.p. 78-80°), chlorobenzene (130-132°), phenyldichlorosilane (180-185°), and phenyltrichlorosilane (192-199°). The still residue was distilled at a residual pressure of 10 mm with isolation of the residue of phenyltrichlorosilane and also diphenyldichlorosilane (b.p. 146-150°). The composition of the intermediate fractions was calculated from their chlorine content. The results of the experiments performed are given in Table 1.

Table 1

Thermal condensation of chlorobenzene with dichlorosilane

No.	Amount of dichlorosilane, g	Amount of chlorobenzene, g	Synthesis temp., °C	Flow, experiment, ml/min	Flow, control, sec	Ratio H_2SiCl_2, C_6H_5Cl, mol.	Yield of liquid products, g	Yield of reaction products based on reacted dichlorosilane, %	Yield of reaction products based on reacted dichlorosilane, %	Yield of reaction products based on reacted dichlorosilane, %	Yield of reaction products based on reacted dichlorosilane, %	Yield of reaction products based on reacted dichlorosilane, %	Yield of high-boiling residues, wt. %
								trichlorosilane	benzene	phenyldichlorosilane	biphenyl	diphenyldichlorosilane	
1	41	50	560-570	140	40	1:1,1	87	21,1	26,4	20,2	6,4	1,4	2,5
2	41	50	580-590	140	39	1:1,1	81	2,0	35,0	27,8	8,3	5,5	2,5
3	30	37	600-610	96	36		56	23,0	53,0	24,2	4,7	6,5	2,0
4	36	43	600-630	120	38	1:1,1	66	17,2	34,0	30,3	1,3	5,8	4,2
5	88	197	640-650	420	37	1:8,0	275	27,4	59,0	41,7	18,0	8,3	3,7
6	54	66	660-670	200	39	1:1,2	115	25,4	58,8	38,0	18,3	13,4	2,1
7	41	48	680-690	150	39	1:1,1	87	16,1	63,2	22,6	21,8	9,5	3,1
8	41	47	700-710	140	36	1:1,0	83	31,6	62,2	11,6	25,7	2,5	4,0
9	33	75	650-660	174	39	1:2,0	104	Not determined	Not determined	33,0	16,9	12,1	2,7
10	30	104	650-660	210	39	1:3,1	120	»	»	13,2	29,7	16,3	1,9
11	53	64	600-610	108	21	1:1,1	90	»	»	10,7	7,1	4,6	3,8
12	30	38	600-610	168	60	1:1,1	61	»	»	25,9	1,2	3,1	3,4
13	30	38	600-610	300	111	1:1,1	59	»	»	20,5	16,6	7,0	4,1

* The yield of gaseous reaction products is 70 mol. (0.75 mol. % calculated as silane).

2. Decomposition of chlorobenzene in a hydrogen medium

A mixture of chlorobenzene and hydrogen was fed into the reaction tube described above at 600–650° in such a ratio that the concentration of chlorobenzene corresponded to its concentration in the experiments on phenylation of dichlorosilane. The reaction products were condensed analogously to item 1, and after completion of the experiment the mixture was distilled on a column with an efficiency of 26 theoretical plates, with isolation of benzene and chlorobenzene (see Table 2).

Table 2

Decomposition of chlorobenzene

No.	Charge of chlorobenzene, g	Hydrogen feed rate, l/h	Nitrogen feed rate, l/h	Charge of silicon hydride, g	Experiment temp., °C	Duration of experiment, min	Contact time, sec	Yield of liquid products, g	Yield of reaction products based on chlorobenzene taken, %	Yield of reaction products based on chlorobenzene taken, %
									benzene	chlorobenzene
1	54,0	3,6	–	–	650	132	37	52,0	8,0	80,0
2	48,0	3,6	–	–	650	120	40	46,0	9,0	79,0
3	25,5	–	2,0	3,1	600	66	37	25,0	2,2	89,0

3. Decomposition of chlorobenzene in the presence of silane

Silane was obtained by the interaction of triethoxysilane with metallic sodium at 80–85° (^{2}) and was fed in a stream of dry nitrogen (2 l/h) into the reaction tube at 600°. Chlorobenzene was fed from a dropping funnel. The reaction products were collected in receivers cooled with ice and with a mixture of acetone and dry ice. The gaseous reaction products passed through 2 traps with alkali solution. The mixture of liquid reaction products was distilled on a column with an efficiency of 26 theoretical plates, with isolation of benzene and chlorobenzene (see No. 3 of Table 2).

4. Disproportionation of dichlorosilane. Dichlorosilane was fed into the reaction tube at 650° in a stream of dry nitrogen (4 l/hr). The reaction products were condensed successively in three traps cooled, respectively, to temperatures of −40°, −80°, and −180°. The gaseous reaction products passed through 3 traps containing a titrated alkali solution and were collected in a gasometer.

Table 3

Disproportionation of dichlorosilane

No.	Dichlorosilane charge, g	Dry nitrogen feed rate, l/hr	Temperature, °C	Duration of experiment, min	Contact time, sec	Yield of liquid products, g	Yield of reaction products based on dichlorosilane taken, %	Yield of reaction products based on dichlorosilane taken, %	Yield of reaction products based on dichlorosilane taken, %	Yield of reaction products based on dichlorosilane taken, %	Yield of reaction products based on dichlorosilane taken, %
No.	Dichlorosilane charge, g	Dry nitrogen feed rate, l/hr	Temperature, °C	Duration of experiment, min	Contact time, sec	Yield of liquid products, g	dichlorosilane	trichlorosilane	silicon tetrachloride	monochlorosilane	hydrogen chloride
1	15.6	4	650	60	42	14.9	14.3	11.0	35.7	11.6	1.9
2	39.0	4	650	150	41	36.0*	9.6	23.3	28.0	21.0	5.4

* The hydrogen content in the gaseous reaction products is 1% or 0.01 g-mol per g-mol of dichlorosilane.

The condensate collected at temperatures of −40° and −80° was rectified and analyzed analogously to the procedure described above. The product collected at −180° was treated with an aqueous alkali solution, and the amount of evolved hydrogen was determined (Table 3).

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