REACTIONS OF THE JOINT PHENYLATION OF TRICHLOROSILANE AND SILICON TETRACHLORIDE

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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REACTIONS OF THE JOINT PHENYLATION OF TRICHLOROSILANE AND SILICON TETRACHLORIDE

The synthesis of phenyltrichlorosilane can be carried out by the interaction of silicon tetrachloride with mercury-, sodium-, and magnesium-organic compounds ([1]), and also by the interaction of trichlorosilane and benzene under pressure according to the scheme

$$HSiCl_3 + C_6H_6 \rightarrow C_6H_5SiCl_3 + H_2. \quad (1)$$

The latter reaction was carried out in the presence of aluminum chloride and boron chloride ([2], [3]), as well as in the absence of catalysts ([4]). However, the maximum yield attained in this reaction does not exceed 40% of theory based on the trichlorosilane reacted ([5]). This is connected with the need to use high temperatures and pressures (300-460° and 150-200 atm), at which, along with reaction (1), disproportionation of trichlorosilane takes place, leading to the formation of silicon tetrachloride (up to 40 mole % of the trichlorosilane reacted), and other side reactions.

Fig. 1

Of great interest is the study of methods for suppressing these side reactions, and also the investigation of the possibility of phenylating the silicon tetrachloride formed. To answer these questions we carried out experiments on the hydrogenation of silicon tetrachloride with hydrogen and found that the reaction proceeds sufficiently intensively according to the scheme

$$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl \quad (2)$$

when the reactants are heated under the conditions under which the phenylation of trichlorosilane is carried out (440-460°, 180 atm). The results obtained

showed the fundamental possibility of phenylating silicon tetrachloride if conditions are provided under which it is first hydrogenated to trichlorosilane and then reacts with benzene. To carry out the first stage of the process, hydrogen formed in reaction (1) and constituting an unused by-product in the phenylation reaction of trichlorosilane was used. For this purpose we heated, at 440° and a pressure of 180 atm, a mixture of silicon tetrachloride, benzene, and trichlorosilane ([6]), varying the molar ratio between trichlorosilane and silicon tetrachloride within the range from 0.25 : 0.75 to 0.85 : 0.15.

Figure 1 presents the results of a series of experiments showing that the yield of phenyltrichlorosilane (in gram-moles per 100 gram-moles of reacted ···

trichlorosilane) with an increase in the content of silicon tetrachloride in the mixture increases sharply. Such an increase cannot be explained only by suppression of the side reaction of disproportionation of trichlorosilane with formation of silicon tetrachloride, since in a number of experiments the yield of phenyltrichlorosilane considerably exceeds 100 g-mol per 100 g-mol of trichlorosilane. This indicates that silicon tetrachloride enters into the phenylation reaction according to the scheme:

$$\begin{gathered} \mathrm{SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl} \\ \underline{\mathrm{HSiCl_3 + C_6H_6 \rightarrow C_6H_5SiCl_3 + H_2}} \\ \mathrm{C_6H_6 + SiCl_4 \rightarrow C_6H_5SiCl_3 + HCl} \end{gathered}$$

The use of elevated hydrogen pressure facilitates the course of the first stage of phenylation of silicon tetrachloride—the hydrosilylation stage. In this connection, the yield of the final product, phenyltrichlorosilane, calculated on silicon tetrachloride, proved to be considerably higher than when a mixture of benzene with silicon tetrachloride was passed through a heated tube at atmospheric pressure.

Thus, it has been shown experimentally that the reaction of phenylation of silicon tetrachloride by benzene can proceed in the absence of organometallic compounds with sufficient yields, provided that conditions are ensured for hydrogenation of silicon tetrachloride by hydrogen and its conversion into the intermediate reaction product, trichlorosilane, according to equation (2). The latter reacts with benzene with formation of phenyltrichlorosilane and regeneration of hydrogen.

Experimental Part

Hydrogenation of silicon tetrachloride

Into an autoclave of 20 l capacity, 4.00 kg of silicon tetrachloride was charged and hydrogen was pumped in to a pressure of 52 atm. The autoclave was heated over 6 hours to a temperature of 440° and kept at this temperature for 4 hours, during which a gradual increase in pressure to 180 atm was observed. After

cooling the autoclave to room temperature, the residual pressure (47 atm) was released and 3.36 kg of reaction products was discharged from the autoclave. On distillation of the mixture from a flask with a dephlegmator, 697 g of a fraction with b.p. 30–55° was obtained. On repeated distillation of this fraction on a rectification column with an efficiency of 45 theoretical plates, 266 g of a fraction with b.p. 31–32° was isolated.

Found, %: H 0.74; 0.73; Cl 79.0; 78.9
$HSiCl_3$. Calculated, %: H 0.74; Cl 78.6

Phenylation of trichlorosilane and silicon tetrachloride

Into an autoclave of 0.6 l capacity, a mixture of 90 g benzene, 17 g trichlorosilane, and 68 g silicon tetrachloride was charged. After 4 hours of heating at 460° (pressure increase to 170 atm), the residual pressure (10 atm at room temperature) was released and 168 g of reaction products was discharged from the autoclave. On rectification of the mixture on a column with an efficiency of 45 theoretical plates, the following were obtained:

Fraction	B.p. temp., °C	Yield, %	Chlorine content, %
1	34–55	2.7	83.0
2	55–57	28.6	83.3
3	57–79	1.8	56.1
4	79–80	39.2	1.5
5	185–190	7.6	49.9
6	190–200	11.5	50.2
Still residue		1.9	40.2

Fractions 1 and 2 consist of silicon tetrachloride (in fraction 1, traces of trichlorosilane); fraction 3 is intermediate; fraction 4 is benzene with traces of silicon tetrachloride; fractions 5 and 6 are phenyltrichlorosilane (in fraction 5 with an admixture of benzene). The yield of phenyltrichlorosilane is 130 g-mol per 100 g-mol of charged trichlorosilane.

Fig. 1 presents data from a series of experiments carried out by an analogous procedure with different ratios between trichlorosilane and silicon tetrachloride.

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