



Catalysis, Kinetics and Reaction Engineering

Effect of chloralkanes on the phenyltrichlorosilane synthesis by gas phase condensation



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ABSTRACT

To enhance the process of phenyltrichlorosilane synthesis using gas phase condensation, a series of chloralkanes were introduced. The influence of temperature and chloralkane amount on the synthesis was studied based on the product distribution from a tubular reactor. The promoting effect of chloralkane addition was mainly caused by the chloralkane radicals generated by the dissociation of C–Cl bond. The promoting effect of the chloromethane with more chlorine atoms was better than those with less chlorine atoms. Intermediates detected from the reactions with isoprene and bromobenzene demonstrated that both trichlorosilyl radical and dichlorosilylene existed in the reaction system in the presence of chloralkanes. A detailed reaction scheme was proposed.

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1. Introduction

Phenyltrichlorosilane ($C_6H_5SiCl_3$) is an important organosilicon monomer used as a silane coupling agent and a precursor of siloxane polymers [1–7]. Industrially, phenyltrichlorosilane is mainly produced through thermal gas phase condensation with trichlorosilane ($HSiCl_3$) and chlorobenzene (C_6H_5Cl) as reactants [8,9]. However, the conversion of trichlorosilane is poor at lower temperature (<400 °C), while byproducts increase at higher temperature. In order to improve the yield of phenyltrichlorosilane, an initiator or catalyst which can enhance the reaction at lower temperature would be invaluable. Goetze *et al.* reported that alkanes, diazenes and organodisilanes can be used as a free radical initiator in the synthesis of organosilanes [10]. Krasnova investigated the pyrolysis of trichlorosilane in the presence of chloroform ($CHCl_3$) and concluded that chloroform enhanced the conversion of trichlorosilane and the yield of desired products [11]. However, few researches have reported the role of chloroform and other chloralkanes in this process. In this investigation, the synthesis of phenyltrichlorosilane in the presence of a chloralkane, such as CH_2Cl_2 , $CHCl_3$ and CCl_4 , was studied. The influence of temperature and chloralkane amount on the product distribution was analyzed.

In this reaction system, there are two major reactions, namely, the condensation reaction [Eq. (1)] and the reduction reaction [Eq. (2)] [8, 9], which give four main products. With respect to the reaction mechanism, most researchers believe that the initial step is the pyrolysis

of trichlorosilane. The trichlorosilyl radical ($\bullet SiCl_3$) and dichlorosilylene ($:SiCl_2$) are the main intermediates formed in this step [12–15]. Regarding the role of these two active species, Heinicke reported that dichlorosilylene can be generated at above 670 °C *via* the combination of two trichlorosilyl radicals and that α -elimination from hexachlorodisilane and direct α -elimination from $HSiCl_3$ required a high temperature [14]. Heinicke concluded that without a free radical initiator, the trichlorosilyl radical was the main intermediate. Krasnova [11] reported that the introduction of chloroform favored the generation of dichlorosilylene. It is dubious whether dichlorosilylene serves as another important intermediate. In this work, the role of dichlorosilylene in the mechanism of phenyltrichlorosilane synthesis and the promoting effect of chloralkanes were discussed.



2. Experimental

2.1. Materials

All reagents used in this study were of analytical grade. Trichlorosilane and chlorobenzene were purchased from Hycegas Co., Ltd. and Beijing Modern Eastern Fine chemical Co., Ltd., respectively. All the chloralkanes and benzene used were from Beijing Modern Eastern Fine Chemical Co.,

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Ltd. Isoprene used to trap dichlorosilylene was purchased from Alfa Aesar Co., Ltd. and bromobenzene and fluorobenzene were purchased from Sinopharm Chemical Reagent Co., Ltd. For the product analysis, chromatographically pure phenyltrichlorosilane was bought from TCI Chemical Industry Co., Ltd.

2.2. Experimental apparatus

The phenyltrichlorosilane synthesis is performed in a quartz tube reactor with inner diameter of 20 mm and length of 300 mm, as illustrated in Fig. 1. The reactor is composed of four sections: feeding and vaporizing system, reacting and quenching system, condensing and collecting system, and pressure stabilizing system. Trichlorosilane and chlorobenzene are pumped into the vaporizers, respectively. The flow rate of the feedstock is controlled to fit the value of space time and the molar ratio of trichlorosilane and chlorobenzene (always 1:1 unless otherwise emphasized). The promoter chloralkane is pre-mixed with chlorobenzene. High purity nitrogen is used to dilute the vapor of the reaction gas, to quench the outlet mixture and also to purge the system to avoid the blockade of the vaporizer and reactor. The outlet gas is water-cooled to below 20 °C and most of the products are condensed. Some light components such as trichlorosilane are subsequently condensed by a cold trap. Afterward, the non-condensable gas is vented through a pressure transmitter and an electromagnetic valve, so as to maintain the system pressure.

2.3. Analytical method

A Techcomp 7890II gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) was used to analyze the condensed mixture from the water-cooler and the cold trap. According to the composition of condensate, the yield of phenyltrichlorosilane (Y) was defined as the ratio of the flow rate (F) of phenyltrichlorosilane produced to that of trichlorosilane in the feed:

$$Y = F_{C_6H_5SiCl_3,p} / F_{HSiCl_3,c} \quad (3)$$

The selectivity of phenyltrichlorosilane S was defined as the ratio of the flow rate of phenyltrichlorosilane in the condensate to the flow rate of trichlorosilane converted:

$$S = F_{C_6H_5SiCl_3,p} / F_{HSiCl_3,c} \quad (4)$$

In the case of trapping experiment, a GC–MS system (Agilent 6890 GC and 5973N MS) was used to identify the products whose standard samples were hard to obtain.

3. Results and Discussion

3.1. Effects of chloralkanes in the low temperature region

When a chloralkane is added to the reacting system, its effects on the yield and selectivity of phenyltrichlorosilane below 400 °C (low temperature region) are different from those above 500 °C (high temperature region). This suggests that the promoting mechanisms of chloralkanes are different in the two temperature regions.

In the low temperature region, as the reaction temperature is increased from 240 to 400 °C, the yield and selectivity of phenyltrichlorosilane increase monotonically. The reaction initiates beyond the threshold of 240 °C as illustrated in Fig. 2.

The effects of chloralkanes can be correlated to the number of chlorine substituent, n . The more chlorine atoms in the chloromethane, $CH_{4-n}Cl_n$, the higher yield of phenyltrichlorosilane is obtained. As the temperature is increased, the difference between the chloromethanes becomes more obvious. As shown in Table 1, the bond dissociation energy of the C–Cl bond D_{C-Cl} is much lower than that of the C–H, chemical bond D_{C-H} , and the former decreases with increasing n [16]. So, it can be concluded that the increased yield of phenyltrichlorosilane is due to the dissociation of the C–Cl bond in the chloromethanes. As compared with the Si–Cl bond in trichlorosilane, the homolytic cleavage of the C–Cl bond in chloromethanes is easier, generating the chlorine radical $\cdot Cl$. As a matter of fact, chloromethanes are used as free radical initiators in this reaction system. However, the chloromethanes favor not only the synthesis of phenyltrichlorosilane, but also the generation of side products, such as tetrachlorosilane and benzene, leading to the decreased selectivity to phenyltrichlorosilane. Only $CH_{4-n}Cl_n$ with $n > 1$ was considered because methyl chloride ($n = 1$) was in gas phase at room temperature [17].

The chloromethanes participated in the phenyltrichlorosilane synthesis reaction. It experienced dechlorination and hydrogenation process, and its amount decreased during this reaction. Take tetrachloromethane as an example. The chloromethane distribution in the product after adding tetrachloromethane ($\tau = 60$ s) is listed in Table 2. Tetrachloromethane is first converted into chloroform and then dichloromethane.

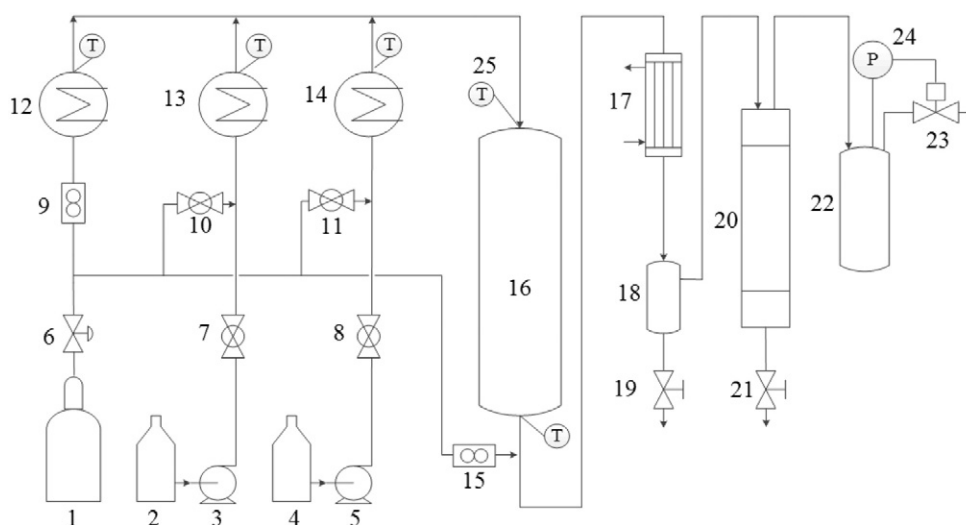


Fig. 1. Schematic of the experimental apparatus. 1—high purity nitrogen; 2,4—feed tank; 3,5—single cylinder plunger pump; 6—pressure reducing valve; 7,8,10,11—one way valve; 9,15—mass flow controller; 12,13,14—vaporizer; 16—tubular oven and tube reactor; 17—water-cooler; 18—product collection tank; 19,21—corrosion resistance valve; 20—cold trap; 22—buffer tank; 23—electromagnetic valve; 24—pressure transmitter; 25—thermocouple.

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