Mechanism and kinetics of the synthesis of phenyltrichlorosilane from trichlorosilane and chlorobenzene by gas phase condensation

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HIGHLIGHTS

- A kinetic model for the synthesis of phenyltrichlorosilane was constructed.
- Reaction flux analysis proposed the main pathway of the condensation reaction.
- The mechanisms of formation of phenyltrichlorosilane were proposed.

ARTICLE INFO

ABSTRACT

The mechanism of the synthesis of phenyltrichlorosilane from trichlorosilane and chlorobenzene by gas phase condensation was studied. A kinetic model with 28 species and 56 elementary reactions was established, which was validated by experimental results from a tubular reactor under wide reaction conditions. The mole fraction profiles of the reactants and products from the kinetic model were in good agreement with the experimental results. This gas phase condensation reaction mainly followed an insertion mechanism of dichlorosilylene into the C—Cl bond to form $C_6H_5SiCl_3$. A reaction flux analysis showed that 99% of $C_6H_5SiCl_3$ was generated from the insertion reaction, 74% of $SiCl_3H$ was decomposed into $SiCl_2$ and 91% of $SiCl_2$ was inserted into C_6H_5Cl to form $C_6H_5SiCl_3$. The proposed mechanism and kinetic model are useful for developing and designing commercial reactors to produce phenyltrichlorosilane.

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1. Introduction

Phenyltrichlorosilane is a organosilicon monomer with extensive use in the synthesis of high performance organosilicon polymers [1,2]. The existence of the phenyl group improves the thermostability and ultra-violet light tolerance of the organopolysiloxane as compared with methylpolysilicone [3]. There are mainly three methods to synthesize phenyltrichlorosilane. They are direct catalytic synthesis [4], liquid phase condensation [5] and gas phase condensation [6]. Gas phase condensation has the advantages of high yield and simple technological process, so it has great prospect of industrial production. So far, the preliminary mechanisms of synthesis of phenyltrichlorosilane by gas phase condensation have been studied by several researchers [7,8]. There has been one kinetics study of the gas phase reaction between $SiCl_3H$ and C_6H_5Cl by Davidson et al. [9] who reported that the Arrhenius expression of the main reaction was $k = 10^{7.9} \exp (-26500/RT) \, l \, mol^{-1} \, s^{-1}$. However, there have been no Arrhenius

expressions for the side reactions, which are necessary for predicting the yield and selectivity of the product. Davidson et al. proposed that the initial step was the decomposition of $SiCl_3H$ into $SiCl_3$ and it was followed by the attack of the $SiCl_3$ radical on the aromatic ring to form $C_6H_5SiCl_3$, but this conflicted with subsequent experimental and theoretical studies on the decomposition of $SiCl_3H$ which indicated that $SiCl_3H$ decomposition into $SiCl_2$ was a much more important pathway than $SiCl_3H$ decomposition into $SiCl_3$ [10].

Some kinetic model studies of the decomposition of the reactants (C_6H_5Cl or $SiCl_3H$) are available. Walker has established the mechanisms and kinetics of thermal decomposition of trichlorosilane, which contains of 20 species and 28 elementary reactions [10,11]. The initial step is that HCl removes from $SiCl_3H$ to form $SiCl_2$. Then $SiCl_2$ inserts into the parent molecules to give chlorinated disilanes. The kinetics parameters are obtained by *ab initio* molecular orbital methods [12]. On the other hand, a detailed kinetic model with 39 species and 39 elementary reactions for thermal decomposition of chlorobenzene diluted in H_2 was established by Edward et al. [13]. This work aims to construct a kinetic model for the synthesis of phenyltrichlorosilane from C_6H_5Cl and $SiCl_3H$ by gas phase condensation based on these existing kinetics and

Nomenclature

A	Arrhenius pre-exponential factor, the basic units are in cm^3, mol, s	R	universal gas constant, in cal/mol K
E	activation energy, in cal/mol	$\Delta H_{f,298}$	enthalpy of formation at 298 K, in kcal/mol
k	rate constant for positive reaction, the units are same with A	S_{298}	entropy at 298 K, in cal/mol·K
		C_p	isobaric hot melt, in cal/mol·K
T	temperature, in K.		

mechanisms of the decomposition of the reactants. It is hoped that the rate constants can be already useful for the design of commercial reactors although it is likely that the proposed model still needs further development.

2. Experimental

The experimental setup is shown in Fig. 1. The reactants, $SiCl_3H$ and C_6H_5Cl (Fine Chemicals Co., Ltd, Beijing), 99.5% pure, were pumped into preheating evaporators by piston pumps. The evaporating temperature was controlled at 503 K. The decomposition of the reactants is negligible at this temperature. After evaporation, $SiCl_3H$ and C_6H_5Cl were mixed and fed into a steel tubular reactor (type of steel: stainless steel 0Cr18Ni9) with length 300 mm, inner diameter 20 mm. The reaction temperatures and pressures used ranged from 773 K to 953 K and 1 atm to 6 atm, respectively. The reaction product was condensed by water cooling, and the condensates were collected for GC analysis.

The details of the GC analysis are: packed column OV-210 (moderate polarity), detector TCD, carrier gas H_2, column temperature 90 °C, injection port temperature 240 °C, detector temperature 240 °C, programmed temperature from 90 °C to 240 °C at 10 °C/min, injection amount 1 μL, column head pressure 0.8 MPa, and TCD bridge current 120 mA. The species identity of products was calibrated by the retention times of standard samples.

3. Kinetic modeling

The kinetic models previously developed for the thermal decomposition of the reactants, $SiCl_3H$ and C_6H_5Cl, were used as the starting point of our model, which contains three parts,

Table 1
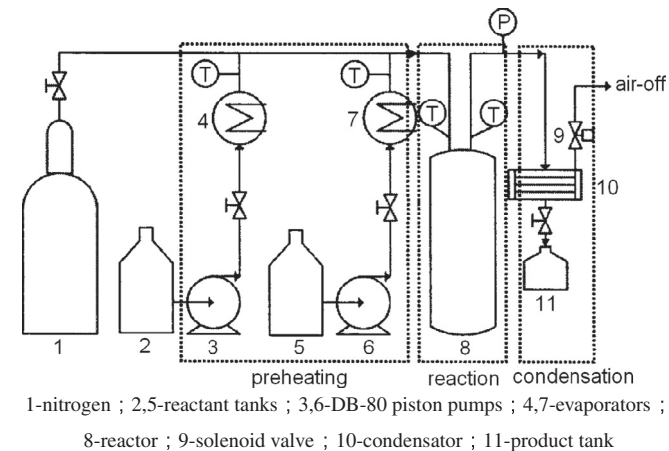Rate constants of the reactions for the synthesis of phenyltrichlorosilane.

Selected reactions	A	n	E	Ref.
Reactions of the thermal decomposition of $SiCl_3H$				
1 $SiCl_3H + M = SiCl_2 + HCl + M^d$	2.5E+10[*]	0.000	30,050[*]	
2 $SiCl_3H = H + SiCl_3$	9.2E+20[*]	0.000	92,900[*]	[10]
3 $SiCl_3 = SiCl_2 + Cl$	3.2E+15	0.000	66,800	[10]
4 $Cl + SiCl_3H = HCl + SiCl_3$	3.2E+10	0.000	2000	[10]
5 $SiCl_3 + SiCl_3H = SiCl_4 + SiHCl_2$	3.2E+08	0.000	15,000	[10]
6 $SiHCl_2 = H + SiCl_2$	1.6E+15	0.000	49,300	[10]
7 $H + SiCl_3H = H_2 + SiCl_3$	3.2E+10	0.000	7000	[10]
8 $SiCl_3 + SiCl_3 = Si_2Cl_6$	1.0E+10	0.000	0	Est.[a]
9 $Si_2Cl_6 = SiCl_4 + SiCl_2$	1.0E+14	0.000	52,500	Est.[a]
10 $SiHCl_2 + SiHCl_2 = HCl_2SiSiCl_2H$	1.0E+10	0.000	0	Est.[a]
11 $HCl_2SiSiCl_2H = SiCl_3H + HSiCl$	1.0E+14	0.000	52,500	Est.[a]
12 $HCl_2SiSiCl_2H = SiCl_2H_2 + SiCl_2$	2.0E+13	0.000	48,300	[10]
13 $SiHCl_2 + SiCl_3 = Cl_3SiSiHCl_2$	1.0E+10	0.000	0	Est.[a]
14 $SiHCl_2 + SiCl_3H = SiCl_2H_2 + SiCl_3$	3.2E+08	0.000	15,000	Est.[b]
15 $SiCl_2 + SiCl_2 = Cl_2SiSiCl_2$	4.0E+15[*]	0.000	0	
16 $Cl_2SiSiCl_2 + M => SiCl_4 + Si(S) + M$	2.0E+21[*]	0.000	15,000[*]	
17 $SiCl_2 + SiCl_3H = Cl_3SiSiHCl_2$	1.5E+08	0.000	17,400	[10]
18 $Cl_3SiSiHCl_2 = SiCl_4 + HSiCl$	6.3E+13	0.000	52,500	[10]
19 $HSiCl + SiCl_3H = Cl_3SiSiH_2Cl$	9.1E+08	0.000	7500	[10]
20 $Cl_3SiSiH_2Cl = SiCl_2H_2 + SiCl_2$	2.0E+13	0.000	48,300	[10]
21 $Cl_3SiSiH_2Cl = SiCl_4 + SiH_2$	1.0E+14	0.000	54,000	[10]
22 $SiH_2 + SiCl_3H = HCl_2SiSiH_2Cl$	6.2E+09	0.000	3100	[10]
23 $HCl_2SiSiH_2Cl = SiCl_2H_2 + HSiCl$	6.3E+14	0.000	52,500	[10]
24 $SiCl_2H_2 = SiCl_2 + H_2$	8.3E+14	0.000	78,000	[10]
25 $SiCl_2H_2 = HSiCl + HCl$	6.9E+14	0.000	75,800	[10]
26 $SiHCl_2 + H = SiCl_2H_2$	1.0E+17	0.000	0	Est.[c]
27 $SiCl_3 + Cl = SiCl_4$	1.0E+17	0.000	0	Est.[c]
Reactions of the thermal decomposition of C_6H_5Cl				
28 $C_6H_5Cl = C_6H_5 + Cl$	3.0E+15	0.000	95,500	[13]
29 $C_6H_5Cl = C_6H_4Cl + H$	1.3E+16	0.000	110500	[13]
30 $C_6H_5Cl + H = C_6H_6 + Cl$	1.5E+15[*]	0.000	7500	[13]
31 $C_6H_5Cl + H = C_6H_5 + HCl$	1.0E+13	0.000	11,300	[13]
32 $C_6H_5Cl + H = C_6H_4Cl + H_2$	2.0E+13	0.000	18,600	[13]
33 $C_6H_4Cl + C_6H_5Cl = C_6H_5C_6H_4Cl + Cl$	2.6E+12	−0.130	4430	[13]
34 $C_6H_5C_6H_4Cl = C_6H_5 + C_6H_4Cl$	1.9E+16	0.000	117000	[13]
35 $C_6H_4Cl + C_6H_4Cl = C_6H_4ClC_6H_4Cl$	1.8E+13	0.000	0	[13]
36 $C_6H_4Cl + C_6H_5Cl = C_6H_4ClC_6H_4Cl + H$	5.4E+15	−1.390	3850	[13]
37 $C_6H_4Cl + C_6H_6 = C_6H_5C_6H_4Cl + H$	9.9E+37	−5.480	19,970	[13]
38 $C_6H_5 + C_6H_5Cl = C_6H_5C_6H_4Cl + H$	4.5E+49	−10.65	33,300	[13]
39 $C_6H_5 + C_6H_5Cl = C_6H_5C_6H_5 + Cl$	2.6E+12	−0.120	4500	[13]
40 $C_6H_5 + C_6H_6 = C_6H_5C_6H_6 + H$	1.6E+45	−9.390	31,000	[13]
41 $H + C_6H_6 = C_6H_5 + H_2$	2.0E+13	0.000	18,600	[13]
42 $C_6H_5C_6H_5 = C_6H_5 + C_6H_5$	5.0E+16	0.000	117000	[13]
43 $C_6H_6 = C_6H_5 + H$	1.7E+16	0.000	111500	[13]
44 $Cl + C_6H_5Cl = HCl + C_6H_4Cl$	1.0E+13	0.000	12,500	[13]
45 $Cl + C_6H_6 = HCl + C_6H_5$	1.1E+13	0.000	12,500	[13]
46 $Cl + H_2 = HCl + H$	4.8E+13	0.000	5000	[13]
47 $H + H = H_2$	1.0E+18	0.000	0	[13]
48 $Cl_2 = Cl + Cl$	7.7E+08	0.000	55,600	[13]
49 $H + Cl_2 = Cl + HCl$	7.9E+13	0.000	1200	[13]
50 $H + Cl = HCl$	1.0E+17	0.000	0	[13]
Reactions of the interaction of C_6H_5Cl and $SiCl_3H$				
51 $C_6H_5 + SiCl_3H = C_6H_6 + SiCl_3$	3.0E+14[*]	0.000	7500	[13]
52 $SiCl_3 + C_6H_5 = C_6H_5SiCl_3$	1.0E+17	0.000	0	Est.[c]
53 $SiCl_2 + C_6H_5Cl = C_6H_5SiCl_3$	1.0E+14[*]	0.000	17,400	[10]

(continued on next page)

1-nitrogen ; 2,5-reactant tanks ; 3,6-DB-80 piston pumps ; 4,7-evaporators ;

8-reactor ; 9-solenoid valve ; 10-condensator ; 11-product tank

Fig. 1. Schematic of the apparatus for preparing phenyltrichlorosilane by gas phase condensation.