

## Kinetics of Hydrolysis Reactions of Phenyltrichlorosilane

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The hydrolysis reactions of  $\text{PhSiCl}_3$  were studied in a tubular flow reactor coupled with an infrared spectrophotometer. Infrared peaks of reaction species including unstable intermediates were identified and used to calculate concentrations for each experiment. A reaction model consistent with  $\text{S}_n2$ -Si substitution was developed and parameters determined which describe concentrations vs. time for experiments over a wide range of reactant and HCl concentrations at  $0^\circ\text{C}$ .

### Introduction

The hydrolysis of halosilanes is of fundamental importance in the manufacture of siloxanes. Many publications have described methods of obtaining various siloxanes from halosilanes, but few have dealt with the kinetics of the hydrolysis reactions. The principal reason for this lack of study is that these hydrolysis reactions are fast and as a result difficult to measure.

The hydrolysis reactions that have been studied are principally those of the monohalosilanes. These reactions are generally slower and less complex than those of the di- or trihalosilanes. Recent studies of these reactions include those of Milishkevick et al. (1971), Allen and Modena (1957), and Chipperfield and Prince (1963).

Shaffer and Flanigen (1957) investigated the hydrolysis of alkyl and aryl chlorosilanes using conductometric titration. This method is limited to following only the disappearance of water or the generation of HCl. Therefore, only the limiting step of the combined hydrolysis and condensation reactions can be studied. The reactions were studied in solutions containing high concentrations of HCl, which markedly suppressed the hydrolysis reactions. Half-lives of from 20 to 41,000 sec were observed for the various reactions.

This paper reports a kinetic study of the hydrolysis of phenyltrichlorosilane. Here, the individual hydrolysis products were followed using a continuous flow tubular reactor coupled with an infrared spectrophotometer. This allowed the reaction rate expressions along with the various kinetic parameters for the individual hydrolysis reactions

to be determined. The reactions were studied at  $0^\circ\text{C}$  using 1,2-dimethoxyethane (Ansol Ether 121, Ansol Co., Marinette, Wis.) as a solvent. Different concentrations of HCl were added to the initial concentrations of reactants to determine the effect of HCl upon the reaction.

### Experimental Section

**Apparatus.** The apparatus designed for the hydrolysis experiment is shown in Figure 1. The driving force for the flow system is a tank of compressed nitrogen. The reactants flow through the rotameters, the constant temperature bath and into the reactor. The silane solvent mixture enters the reactor at its base and the water solvent mixture enters through a small tube inserted in the reactor at various lengths. Figure 2 illustrates the reactor and its surrounding heat exchanger. The reactants flow from the reactor into an infrared cell where their concentrations are measured.

The spectrophotometer employed for this study was a dual-beam Perkin-Elmer Model 337. Thallium bromide-iodine (KRS-5) cells were used in order to monitor the infrared region characteristic of the Si-Cl vibration ( $400\text{--}650\text{ cm}^{-1}$ ). The infrared cell and cell holder are shown in Figure 3. A cell path length of 0.01 cm was employed in all experiments.

**Temperature Control.** The reactants were cooled to  $0^\circ\text{C}$  using a constant temperature bath containing distilled water and ice. In order to maintain a constant temperature in the reactor, the concentrations of reactants used were less than 0.1 M for the silanes and 0.4 M for water. These small concentrations limited the temperature rise due to the heat of reaction. The reactor was surrounded by a heat exchanger which contained water recirculating from the ice

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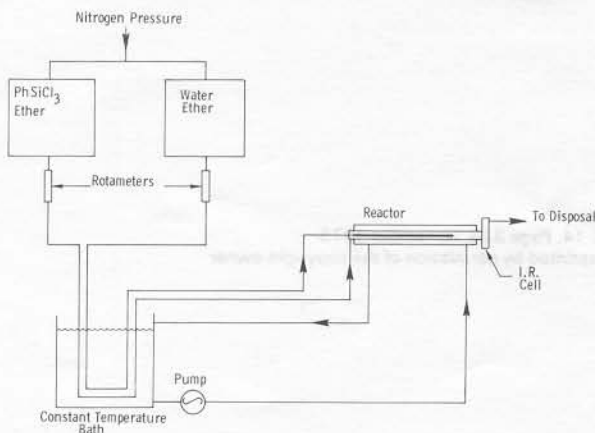


Figure 1. Reactor apparatus.

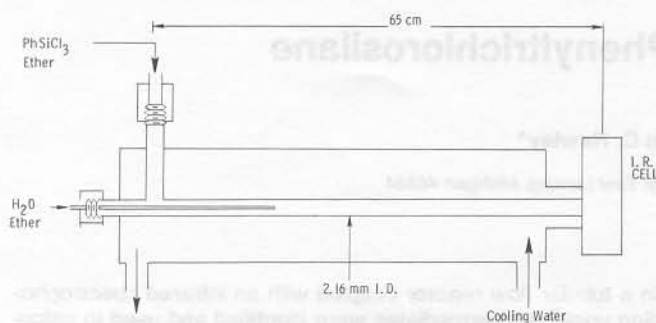


Figure 2. Reactor and surrounding heat exchanger.

bath.

**Reagents.** The ether was dried over  $\text{CaSO}_4$  and distilled from  $\text{KOH}$  in a nitrogen atmosphere. Only the middle fraction of the distillate, that of a constant boiling point, was used. Matheson gaseous  $\text{HCl}$  was used to prepare the  $\text{HCl}$  ether solutions for the runs requiring initial concentrations of  $\text{HCl}$ . The phenyltrichlorosilane was distilled in a nitrogen atmosphere directly in the ether to avoid any contact with atmospheric moisture. The phenyltrichlorosilane solvent mixture was then weighed to calculate the concentration of silane.

### Interpretation of Infrared Spectra

The following assignments were made for the absorption peaks of  $\text{PhSiCl}_3$  and its hydrolysis products:  $\text{PhSiCl}_3$ , 590 and  $517\text{ cm}^{-1}$ ;  $\text{PhSiCl}_2(\text{OH})$ , 572 and  $527\text{ cm}^{-1}$ ;  $\text{PhSiCl}(\text{OH})_2$ ,  $542\text{ cm}^{-1}$ ;  $\text{PhSi}(\text{OH})_3$ ,  $465\text{ cm}^{-1}$ .

The infrared spectrum characteristics of  $\text{PhSiCl}_3$  hydrolysis reaction products and  $(\text{PhSiCl}_2)_2\text{O}$  are shown in Figure 4. These spectra along with spectra of our hydrolysis experiments were used to deduce the species present during the hydrolysis experiments. Kriegsmann and Schowlka (1958) conducted an extensive study of various silanes and assigned the  $590\text{-cm}^{-1}$  peak of the  $\text{PhSiCl}_3$  spectrum to the asymmetric vibration of  $\text{SiCl}_3$  and the  $517\text{ cm}^{-1}$  peak to its symmetric vibration. The  $620\text{-cm}^{-1}$  peak was assigned to the  $\text{Ph-Si}$  bond. Smith (1967) also made these assignments for  $\text{PhSiCl}_3$  and noted that the  $590\text{-cm}^{-1}$  peak has a shoulder at approximately  $583\text{ cm}^{-1}$ .

Preliminary hydrolysis experiments with no initial  $\text{HCl}$  present and with excess water produced spectra similar to that of  $\text{PhSi}(\text{OH})_3$  over the range of from  $380\text{ cm}^{-1}$  to  $740\text{ cm}^{-1}$  at long reactor lengths. At shorter reactor lengths, intermediate bands appeared at 572, 542, and  $527\text{ cm}^{-1}$ . The 572- and  $527\text{-cm}^{-1}$  peaks appeared immediately after the water was added to the system, were well correlated, and

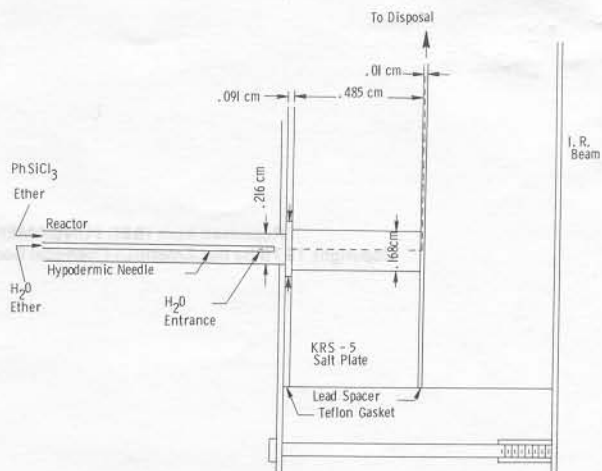


Figure 3. Constant flow infrared cell and cell holder.

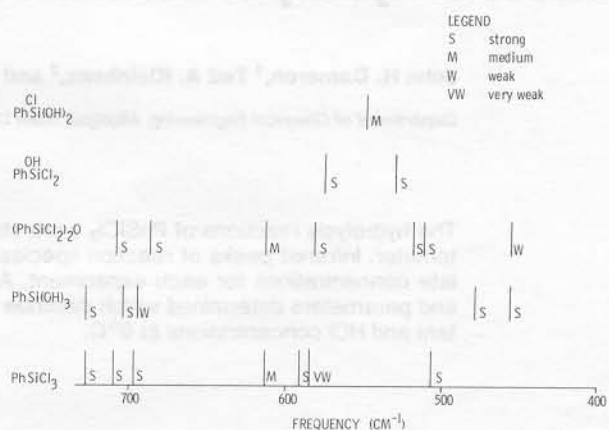
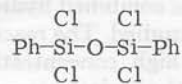


Figure 4. Infrared spectrum of  $\text{PhSiCl}_3$  hydrolysis reaction products and  $(\text{PhSiCl}_2)_2\text{O}$ .

decreased as the reactor length was increased. The  $572\text{-}$  and  $527\text{-cm}^{-1}$  peaks were present and similar in appearance during all runs. For  $\text{Ph}_2\text{SiCl}_2$ , the symmetric and asymmetric peaks of  $=\text{SiCl}_2$  occur at 540 and  $572\text{ cm}^{-1}$ , respectively. Therefore, the  $572\text{-cm}^{-1}$  peak was assigned to the asymmetric vibration of  $\text{SiCl}_2$  in  $\text{PhSiCl}_2(\text{OH})$  and the  $527\text{-cm}^{-1}$  peak was assigned to the symmetric vibration. At all times the  $542\text{-cm}^{-1}$  peak was quite small and somewhat obscure due to the absorption of a solvent peak at  $547\text{ cm}^{-1}$  as seen in Figure 5. Although a dual-beam spectrophotometer was used in this study, the strong absorption of the solvent at  $547\text{ cm}^{-1}$  decreased the accuracy of quantitative measurements near this peak.

The absorption spectrum, Figure 4, characteristic of



was not seen during the experiment. Also a separate experiment showed that the condensation reaction was considerably slower than the hydrolysis reaction at low concentrations of  $\text{HCl}$ .

### Condensation Reaction

To determine the effect of the condensation reaction, the reaction between  $\text{PhSiCl}_3$  and  $\text{PhSi}(\text{OH})_3$  was studied under two different conditions: (a) with no initial concentration of  $\text{HCl}$  and (b) with  $\text{HCl}$  present initially. When  $\text{PhSiCl}_3$  and  $\text{PhSi}(\text{OH})_3$  were mixed in the reactor with no

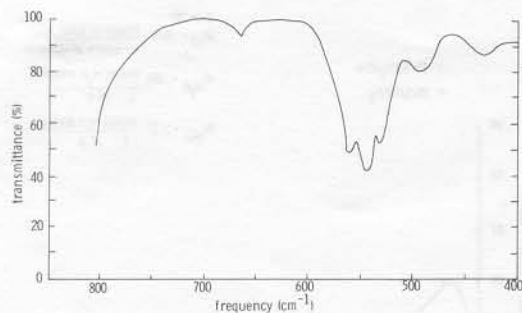


Figure 5. Infrared spectrum of 1,2-dimethoxyethane.

initial concentration of HCl, no reaction was observed over the time of the hydrolysis reaction, approximately 1 sec. However, when  $\text{PhSiCl}_3$  and  $\text{PhSi(OH)}_3$  were mixed with an initial concentration of HCl, a reaction was detected by a decrease in both the  $\text{PhSiCl}_3$  and  $\text{PhSi(OH)}_3$  peaks.

The reaction of  $\text{PhSi(OH)}_3$  and  $\text{PhSiCl}_3$  with HCl present was carried out at  $0^\circ\text{C}$  and the following concentrations:  $\text{HCl} = 0.390\text{ M}$ ,  $\text{PhSiCl}_3 = 0.105\text{ M}$ ,  $\text{PhSiCl}_2(\text{OH}) = 0.053\text{ M}$ , and  $\text{PhSi(OH)}_3 = 0.064\text{ M}$ . In the hydrolysis reactions with no initial concentration of HCl, the concentration of HCl reaches approximately  $0.3\text{ M}$  at the end of the reaction. At this time, the trichloro and dichloro species have reacted leaving principally phenylsilanetriol. Hence, the conditions of the condensation reaction study with HCl initially present were considerably harsher than those encountered during the hydrolysis experiments with no initial concentration of HCl.

The half-life of  $\text{PhSi(OH)}_3$  in the condensation study with HCl initially present was approximately  $0.5\text{ sec}$ , based on the initial rate of reaction. In run 13K, the half-life of  $\text{PhSiCl}_3$  is approximately  $0.0015\text{ sec}$  and that of  $\text{PhSiCl}_2(\text{OH})$  is  $0.1\text{ sec}$ . Therefore, in examining the spectra of the hydrolysis reaction with no HCl initially present, condensation does not appear to be a significant factor. However, for the hydrolysis reactions with an initial HCl concentration greater than  $1\text{ M}$ , the condensation effect can be seen at long reaction times where the amount of  $\text{PhSi(OH)}_3$  present falls below that predicted by the model.

#### Calculation of Concentrations

It was experimentally determined, using infrared spectrophotometry, that the difference of the absorption of  $\text{PhSiCl}_3$ ,  $A$ , and the corresponding base line absorption,  $A_0$ , was proportional to the product of the concentration,  $c$ , of  $\text{PhSiCl}_3$  in the ether solution and the infrared cell path length,  $d$  (i.e., the Beer's law relationship is applicable).

$$A_0 - A = \epsilon dc \quad (1)$$

It was assumed that the same relation was valid for each reaction species being monitored. Here,  $\epsilon$  is the extinction coefficient or proportionality constant.

The base-line technique was used to measure the absorption of each peak. The extinction coefficient,  $\epsilon$ , for the  $465\text{-cm}^{-1}$  peak of  $\text{PhSi(OH)}_3$  was found by the reaction of  $\text{PhSiCl}_3$  with an excess of water at long reaction times. The  $517\text{-cm}^{-1}$  peak was used to determine the concentration of  $\text{PhSiCl}_3$  and the  $527\text{-cm}^{-1}$  peak was used for  $\text{PhSiCl}_2(\text{OH})$ . The extinction coefficients for these peaks were determined using a least-squares fit for absorption data obtained at different reaction times when reacting  $1\text{ mol}$  of  $\text{PhSiCl}_3$  with  $\frac{1}{2}\text{ mol}$  of water. The extinction coefficients obtained are  $\epsilon_{517} = 446\text{ (M cm)}^{-1}$ ,  $\epsilon_{527} = 390\text{ (M cm)}^{-1}$ , and  $\epsilon_{465} = 237\text{ (M cm)}^{-1}$ . To determine the cell length,  $d$ , the empty sample cell transmittance was measured and a num-

Table I. Summary of Run Conditions (Initial Chlorosilane-Water Conditions)<sup>a</sup>

Run	Concn of $\text{PhSiCl}_3$ , M	Concn of $\text{PhSiCl}_2(\text{OH})$ , M	Concn of total silane, M	Concn of water, M	Concn of HCl, M
13K	0.0836	0.0154	0.099	0.328	0.0
18K	0.0672	0.0326	0.0998	0.3096	0.0
20	0.0379	0.0351	0.073	0.215	1.21
21	0.0672	0.0278	0.095	0.291	1.463
22	0.0849	0.00712	0.0918	0.242	0.338
24	0.0329	0.0447	0.0776	0.259	0.0
26	0.061	0.0242	0.0852	0.0807	0.0

<sup>a</sup> Concentrations are based on mixed reactants.

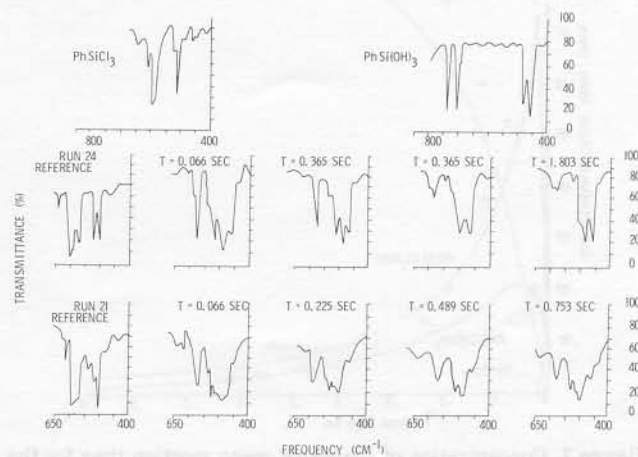


Figure 6. Spectra of  $\text{PhSiCl}_3$ ,  $\text{PhSi(OH)}_3$  plus sample of spectra obtained during runs 21 and 24.

ber of interference bands obtained (Smith, 1944).

#### Conditions for $\text{PhSiCl}_3\text{-H}_2\text{O}$ Reaction

The reactants were drawn into the holding tanks by first flushing the reactor system with dry nitrogen and then evacuating it. This prevented any contact between the reactants and atmospheric moisture.

A reference spectrum of the silanes before any water had been added to the system was obtained. This allowed the calculation of the initial concentrations. The  $\text{PhSiCl}_3$  concentration was determined using the  $517\text{-cm}^{-1}$  peak and correcting the concentration for the absence of the  $\text{H}_2\text{O}$ -solvent mixture. All other silane present was assumed to be  $\text{PhSiCl}_2(\text{OH})$ .

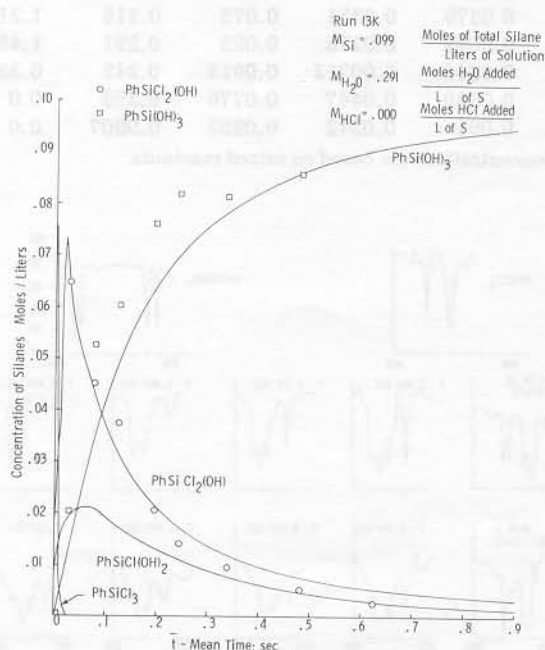
The initial HCl concentration was determined by electrolytically titrating the HCl solvent solutions before the  $\text{PhSiCl}_3$  and  $\text{H}_2\text{O}$  were added. The initial HCl concentration was then calculated using the HCl added with each solution.

The desired flow rates were set using the rotameters and needle valves. The flow rates were then maintained at a constant setting during each run and the residence time was controlled by varying the position of the hypodermic needle. At each desired holding time, the ir spectrum from  $650\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  was scanned.

The initial concentrations of several runs are given in Table I. Since a major object of this study was the HCl effect, the HCl concentration was varied from 0 to  $1.46\text{ mol/l}$ . During each run, approximately  $0.3\text{ mol/l}$  of HCl was produced. The total silane present was varied from  $0.072$  to

**Table II. Kinetic Parameters and Standard Deviations**

Parameters	Linear estimate of std dev
$K_1 = 220.0$	121.0
$K_2 = 16.5$	1.05
$K_3 = 40.6$	4.90
$n = -0.612$	0.0809



**Figure 7.** Concentration of silanes vs. mean reaction time for the hydrolysis of PhSiCl<sub>3</sub>.

0.099 mol/l. and the initial H<sub>2</sub>O concentration from 0.0807 to 0.328 mol/l. for the various runs.

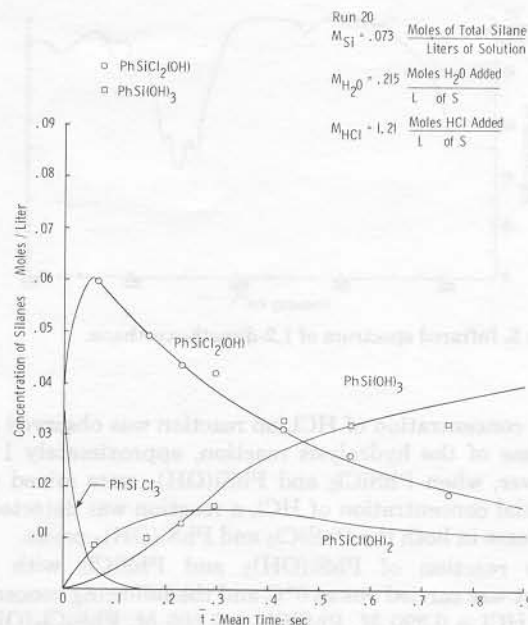
Figure 6 shows the spectra of PhSiCl<sub>3</sub>, PhSi(OH)<sub>3</sub>, and spectra obtained during two different hydrolysis experiments. The spectrum of PhSiCl<sub>3</sub> is a reference spectrum of the silane solvent mixture obtained before any water has been added to the system. The spectrum compares closely with those of Kriegsmann et al. (1958) and Smith (1967). To obtain the spectrum of PhSi(OH)<sub>3</sub>, crystals of PhSi(OH)<sub>3</sub> were dissolved in 1,2-dimethoxyethane. The PhSi(OH)<sub>3</sub> crystals were produced from the hydrolysis of phenyltrimethoxysilane using a procedure similar to Tyler (1955).

Some of the spectra obtained during the two hydrolysis experiments, runs 21 and 24, are also shown in Figure 6. These two experiments illustrate the hydrolysis reactions in media both where no HCl is initially present and where a high concentration of HCl is initially present. Run 24 contained no initial concentration of HCl, while run 21 contained 1.46 M HCl initially. At the end of run 24, the spectrum closely approximates that obtained for PhSi(OH)<sub>3</sub>.

Due to the high concentration of HCl, the rate of the hydrolysis reaction in run 21 is considerably slower than run 24. Also the peaks at 485 and 465 cm<sup>-1</sup> are smaller and less distinct than those in run 24. Some condensation does take place in run 21 and this effect can be seen in Figure 9, where the amount of silanes present falls below that predicted by the model.

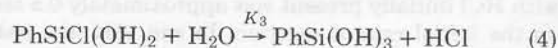
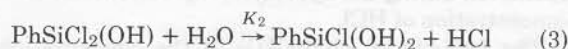
### Results and Discussion

The following reaction steps were used to model the hy-



**Figure 8.** Concentration of silanes vs. mean reaction time for the hydrolysis of PhSiCl<sub>3</sub>.

drolysis of PhSiCl<sub>3</sub>.



Under the conditions used in this study, these reactions were found to be essentially irreversible. It was assumed that the reactions were first order with respect to H<sub>2</sub>O and the silanes. The effect of HCl was incorporated into the rate expression using the term [HCl]<sup>n</sup>. The rate expressions used to describe these reactions are

$$\frac{d[\text{PhSiCl}_3]}{dt} = -K_1[\text{PhSiCl}_3][\text{H}_2\text{O}][\text{HCl}]^n \quad (5)$$

$$\frac{d[\text{PhSiCl}_2(\text{OH})]}{dt} = K_1[\text{PhSiCl}_3][\text{H}_2\text{O}][\text{HCl}]^n - K_2[\text{PhSiCl}_2(\text{OH})][\text{H}_2\text{O}][\text{HCl}]^n \quad (6)$$

$$\frac{d[\text{PhSiCl}(\text{OH})_2]}{dt} = K_2[\text{PhSiCl}_2(\text{OH})][\text{H}_2\text{O}][\text{HCl}]^n - K_3[\text{PhSiCl}(\text{OH})][\text{H}_2\text{O}][\text{HCl}]^n \quad (7)$$

$$\frac{d[\text{PhSi}(\text{OH})_3]}{dt} = K_3[\text{PhSiCl}(\text{OH})_2][\text{H}_2\text{O}][\text{HCl}]^n \quad (8)$$

$$[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 - [\text{PhSiCl}_2(\text{OH})] - 2[\text{PhSiCl}(\text{OH})_2] - 3[\text{PhSi}(\text{OH})_3] \quad (9)$$

$$[\text{HCl}] = [\text{HCl}]_0 + [\text{PhSiCl}_2(\text{OH})] + 2[\text{PhSiCl}(\text{OH})_2] + 3[\text{PhSi}(\text{OH})_3] \quad (10)$$

Here, [HCl]<sub>0</sub> and [H<sub>2</sub>O]<sub>0</sub> are the initial concentrations of HCl and H<sub>2</sub>O respectively.

Increasing the initial HCl concentration had the effect of decreasing the rate of the hydrolysis reaction. Using a least-squares type curve-fitting program, the constants listed in Table II were determined to fit the various data sets. Figure 5-12 are plots of the data points and model (solid lines) for the various runs.

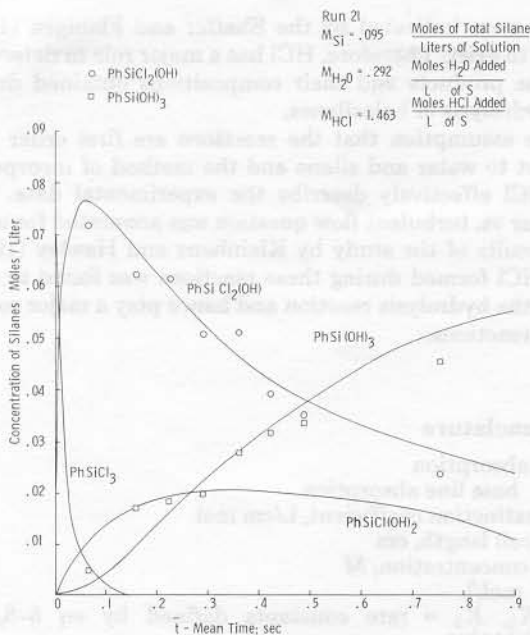


Figure 9. Concentration of silanes vs. mean reaction time for the hydrolysis of  $PhSiCl_3$ .

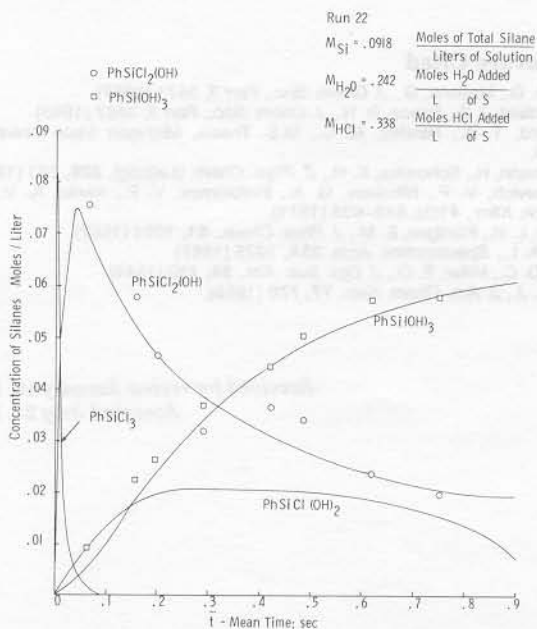


Figure 10. Concentration of silanes vs. mean reaction time for the hydrolysis of  $PhSiCl_3$ .

The kinetic parameters were found assuming that plug flow exists in the system. The effect of this assumption was studied by Kleinhenz and Hawley (1970) for reaction orders between 0 and 3. Their analysis employed an integration of the concentration-velocity product for each model over the flow cross section.

It was concluded that for irreversible first and second order reactions the rate constants determined using a plug flow model would be 15% lower than those determined using a laminar flow model. This produces a bound of 15% between two extremes, that of laminar flow and that of plug flow. In the actual system neither of the models completely describes the situation. Although the Reynolds number for this system is well within the laminar flow region, there is considerable mixing in the system where the reactants are combined and again when the reactor effluent enters the infrared cell. Also, there is a certain amount of

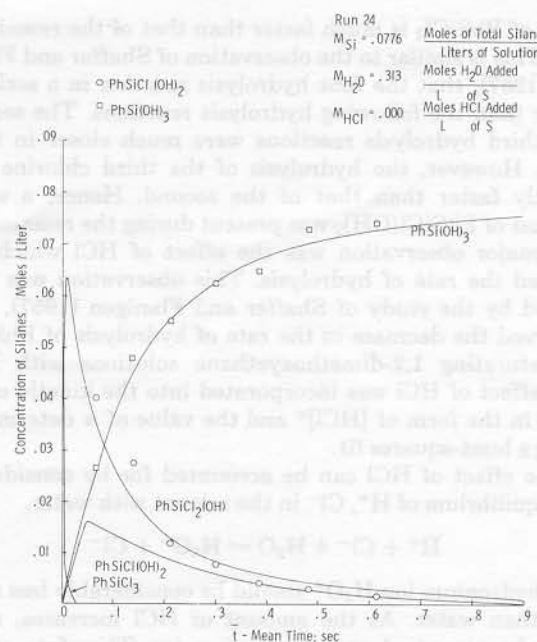


Figure 11. Concentration of silanes vs. mean reaction time for the hydrolysis of  $PhSiCl_3$ .

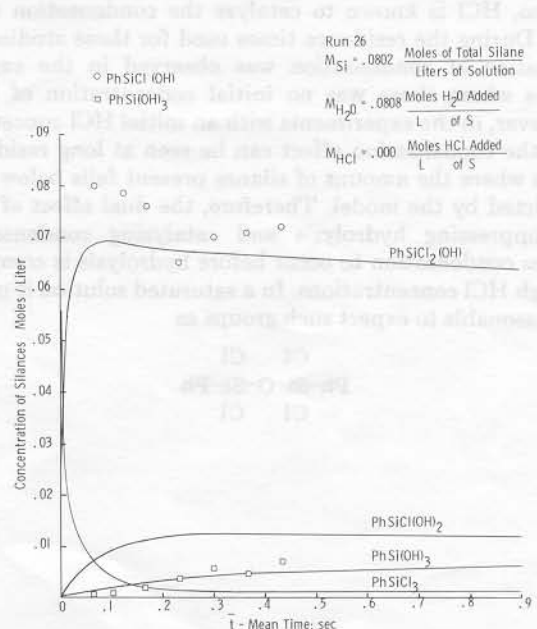


Figure 12. Concentration of silanes vs. mean reaction time for the hydrolysis of  $PhSiCl_3$ .

mixing due to radial diffusion. Therefore, the kinetic parameters determined using the plug flow model are estimated to be within this 15% bound.

The hydrolysis of the first chlorine atom in  $PhSiCl_3$  is extremely fast and near the limit of the system to determine. Therefore, this first rate constant  $K_1$  should only be considered an estimate of its actual value. The parameters  $K_2$ ,  $K_3$ , and  $n$  are well defined based upon the data fit and the linear estimates of standard deviations.

### Concluding Remarks

This study demonstrates the ability of using a flow system and an infrared spectrophotometer to study a fast series of reactions. It enables the infrared spectra of intermediate species to be studied and their concentrations to be determined.

It was found that the hydrolysis of the first chlorine

atom of  $\text{PhSiCl}_3$  is much faster than that of the remaining two. This is similar to the observation of Shaffer and Flanigen (1957), that the first hydrolysis reaction in a series is faster than the following hydrolysis reactions. The second and third hydrolysis reactions were much closer in their rates. However, the hydrolysis of the third chlorine was slightly faster than that of the second. Hence, a small amount of  $\text{PhSiCl}(\text{OH})_2$  was present during the reaction.

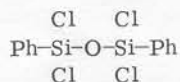
A major observation was the effect of HCl which decreased the rate of hydrolysis. This observation was supported by the study of Shaffer and Flanigen (1957), who observed the decrease in the rate of hydrolysis of  $\text{PhSiCl}_3$  by saturating 1,2-dimethoxyethane solutions with HCl. The effect of HCl was incorporated into the kinetic equations in the form of  $[\text{HCl}]^n$  and the value of  $n$  determined using a least-squares fit.

The effect of HCl can be accounted for by considering the equilibrium of  $\text{H}^+$ ,  $\text{Cl}^-$  in the solvent with water.



The hydronium ion  $\text{H}_3\text{O}^+$  should be considerably less reactive than water. As the amount of HCl increases, more water becomes tied up as hydronium ion. Therefore, an increase in the HCl concentration would suppress the hydrolysis reaction.

Also, HCl is known to catalyze the condensation reaction. During the residence times used for these studies, no indication of condensation was observed in the experiments where there was no initial concentration of HCl. However, in the experiments with an initial HCl concentration the condensation effect can be seen at long residence times where the amount of silanes present falls below that predicted by the model. Therefore, the dual effect of HCl of suppressing hydrolysis and catalyzing condensation causes condensation to occur before hydrolysis is complete at high HCl concentrations. In a saturated solution it might be reasonable to expect such groups as



which were indicated by the Shaffer and Flanigen (1957) study to exist. Therefore, HCl has a major role in determining the products and their compositions obtained during the hydrolysis of halosilanes.

The assumption that the reactions are first order with respect to water and silane and the method of incorporating HCl effectively describe the experimental data. The laminar vs. turbulent flow question was accounted for using the results of the study by Kleinhenz and Hawley (1970). The HCl formed during these reactions was found to suppress the hydrolysis reaction and hence play a major role in these reactions.

### Nomenclature

- A = absorption
- $A_0$  = base line absorption
- $\epsilon$  = extinction coefficient, l/cm mol
- d = cell length, cm
- C = concentration, M
- M = mol/l.
- $K_1, K_2, K_3$  = rate constants defined by eq 5-8, (l/mol)<sup>1+n/sec</sup>
- n = power to which the HCl concentration is raised in the kinetic model

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Received for review January 16, 1975  
 Accepted July 24, 1975