KINETICS OF THE HYDROLYSIS OF DIPHENYLDICHLOROSILANE

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ABSTRACT

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by

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The rate constants for the hydrolysis of diphenyldichlorosilane were determined from concentration data for Ph_2SiCl_2 and $Ph_2Si(OH)_2$ in a tubular reactor of various lengths. The data were analyzed assuming plug flow in the reactor system and that the reactions proceed in a stepwise, irreversible manner. The rate constants were determined based on a steady-state approximation for the intermediate $Ph_2Si(OH)$.

The second order rate constants for the hydrolysis of the first and second chlorine atoms were 2.1 and 20 l. $mole^{-1}$ sec^{-1}, respectively at 27°C.

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Alan R. Bond

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I. INTRODUCTION

The objective of this work was to study the hydrolysis of diphenyldichlorosilane. The rate constants, k_1 and k_2, for the hydrolysis reactions were determined from concentrations of reactive species at various lengths in a tubular flow reactor.

The experimental system used in this study is the one that was tested and used in a previous study of phenyltrichlorosilane.[1] Fast reactions (those with second order rate constants $\geq$ 2000 M^{-1} sec^{-1}) may be studied in the flow system used for this study. The rate constants for hydrolysis of most chlorosilanes are of such magnitude as to consider them fast when compared to those determined in conventional batch studies. A continuous flow tubular reactor was used in conjunction with an infrared spectrometer as a detector to monitor and characterize intermediates and products at various reaction times. Our work demonstrates that this novel system can be used for accomplishing our major objective, determining the rates of hydrolysis of diphenyldichlorosilane, and in addition it has general applicability for determining rate constants for other chlorosilane reactions.

Early work on the rate of hydrolysis of chlorosilanes has involved conductometric experiments. Prince[2] monitored the hydrolysis of triphenylchlorosilane and triphenylchlorostannane in a flow system conductometrically; no intermediate hydrolysis products formed are analysed.

In the work reported by Prince[2], the rate constants for pseudo-unimolecular hydrolysis were calculated; these constants depended on the initial water concentrations.

Schaffer and Flanigen[3,4] studied the conductrometric titration of chlorosilanes. They observed both hydrolysis and condensation in their batch experiments. Later, Prince[5], and more recently Prince and Timm[11,12,13], studied the solvolysis of mono-silicon, germanium and tin chlorides and acetates. However, these experiments were not designed to determine a stepwise hydrolysis of a multifunctional species.

We were able to follow the rapid, step-wise hydrolysis of phenyldichlorosilane, using the continuous flow tubular reactor system. The reactions were carried out in dimethoxyethane at 27°C and 43°C. This solvent has no major absorption bands in the 800-400 cm^{-1} region and kept the reaction homogeneous. Steady-state conditions in the flow system enabled us to record complete infrared spectra for the 800-400 cm^{-1} region. The absorbance data for each species at differing reactor lengths were analyzed as a function of time.

The conversion of reactor length to time requires analysis of the flow in our tubular reactor. Hawley and Kleinhenz[15] have reported on the "Plug Flow Approximation of Laminar Flow Tubular Reactor". They found that the reaction velocity constants determined by assuming a plug flow model even for experiments involving laminar flow, gave reasonably good estimates of the actual constants. The plug flow model was used in this work with no corrections.

II. PREVIOUS WORK

The hydrolysis of Group IV halides has been studied by several workers[1-13]. However, these conductometric and titrimetric methods follow the hydrolysis of all species present. Our method, like that of Kleinhenz et al[1], follows the hydrolysis of the individual species present in the reaction.

Prince[2] and Shaffer and Flanigen[3,4] employed conductometric methods for following hydrolysis. Results of the study by Shaffer and Flanigen[3] of the hydrolysis of alkyl and aryl chlorosilanes were that the products indicated by the conductometric end-points are chlorine end-blocked siloxane hydrolysis intermediates. However, diphenyldichlorosilane gave only diphenylsilanediol as the hydrolysis product for 1,2-dimethoxyethene at 0°C. They indicated the possible presence of $Ph_2SiCl(OH)$ in this system.

They then studied the rates and mechanisms of hydrolysis in homogeneous solutions in the presence of excess HCl[4]. The kinetics of the reaction of water with chlorosilanes was expressed as:

$$\frac{d(2H_2O)}{dt} = k(H_2O)^m(\equiv SiCl)^n(HCl)^p$$

Values of m and n were determined, but not p. The value for m in all cases is one, first order for the first 0.01 to 0.02 mole of chlorosilane is two in $RSiCl_3$ systems.

Prince[2] developed an apparatus for the study of fast hydrolysis reactions of organometallic halides under both constant and plug-flow conditions. The reactions were followed by conductivity change. The first order rate constant for Ph_3SiCl (1.9×10^{-3} M) with H_2O (2.10 M) in $Me_2CO + Et_2O$ (1.6:1 v/v) is 2.64 sec^{-1} in a constant flow experiment. There also was a "marked effect of water concentration on hydrolysis rate..."[2].

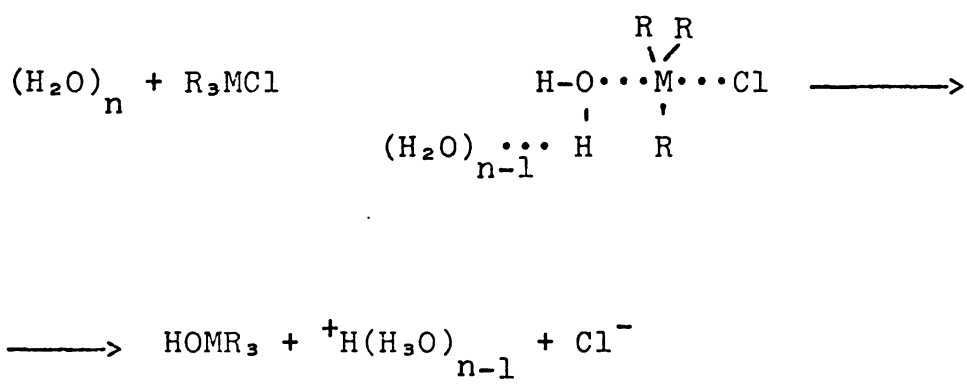
Prince[5] studied the solvolysis of organotin and silicon chlorides. The solvolysis of triisopropylsilyl chloride in propan-2-ol "has abnormally low steric factor and is catalyzed by pyridine"[5]. Hydrolysis in Me_2CHOH is second order and is not catalyzed by pyridine. "Data are consistent with a synchronous displacement of tin and silicon in which steric effects are important in determining reactivity"[5]. The second-order rate constant for triisopropylchlorosilane is 2.5×10^{-2} $l\ mole^{-1}\ sec^{-1}$.

Chipperfield and Prince[6] used rapid reaction techniques[2] to follow hydrolysis of chlorotriphenyldermane and chlorotriphenylsilane. The silane was faster than the germane; e.g., in acetone the first-

order rate constants are: $k_{Ge} = 0.02$, $k_{Si} = 4.0\ sec^{-1}$ at 25°C 2M aqueous solution.

The same authors[7] used a rapid reaction technique[2] in studying the rates of hydrolysis in organic solvents of a series of halides R_3MCl, where M = Si or Ge and R is alkyl or aryl. Also the mechanism of the hydrolysis is discussed. In acetone, with excess water (2M) there was a first order dependence of the hydrolysis rate on the halide concentration over the rage studied (10^{-4} - 10^{-2} M).

At 25°C the first-order rate constnat equals 4.03 sec^{-1}. They concluded that their data favor the following hydrolysis mechanism[8].



Many of the later papers deal with the mechanism of nucleophilic displacements on organosilicon halides. This work deals with the hydrolysis of silicon halides with alcohols (solvolysis)[9,10] and hydrolysis of silicon

acetates[11,12,13] Sommer[14] details various mechanisms in his book, including the hydrolysis of the silicon-chlorine bond with water in ether which is described as proceeding via a Sn_2-Si mechanism.

We have shown, Kleinhenz, et al[1], that the hydrolysis of $PhSiCl_3$ in 1,2-dimethoxyethene proceeds by the stepwise breaking of each SiCl bond. The second-order rate constants were found to be 1500, 77.5, and 1000 $l.mole^{-1}$-sec^{-1} for the first, second and third chlorines, respectively. A tubular flow reactor system was used.

III. EXPERIMENTAL

A. Reagents

Diphenyldichlorosilane (Ph_2SiCl_2) was obtained from Dow Corning Corporation. The IR spectrum of this material indicated no siloxane species, a purity of 95% or better (See Figure 1). 1,2-Dimethoxyethane (DME) was used as a solvent and was obtained from the Ansul Corporation. The solvent, as received, contained 3-4% water, as well as inhibitors. These were removed by shaking the solvent over potassium hydroxide pellets and then distilling it under dry nitrogen while in contact with potassium hydroxide pellets. Only the middle cuts, b.p. 84.0 - 84.5°C, were used.

Diphenylsilanediol was obtained from Dow Corning Research Department. An infrared spectrum, obtained on a nujol mull, indicated a purity of $\geqslant$90% since there was no siloxane absorption (Figure 2). The IR spectrum of this compound was compared with the spectra of the hydrolysis products of Ph_2SiCl_2. This identified the major species a $Ph_2Si(OH)_2$.

B. Reactor

Figure 3 is a sketch of the tubular reactor connected to the infrared cell. The reactor was constructed of 2.16 mm. inside diameter stainless steel tubing, which was jacketed

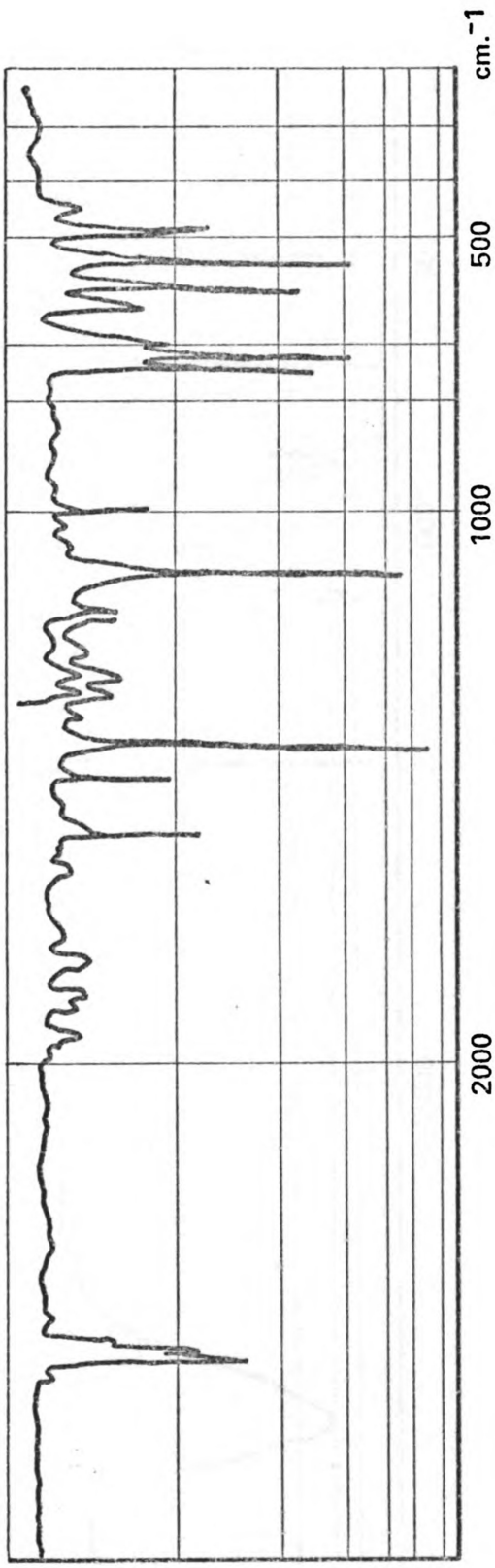


FIGURE 1. INFRARED SPECTRUM OF Ph_2SiCl_2

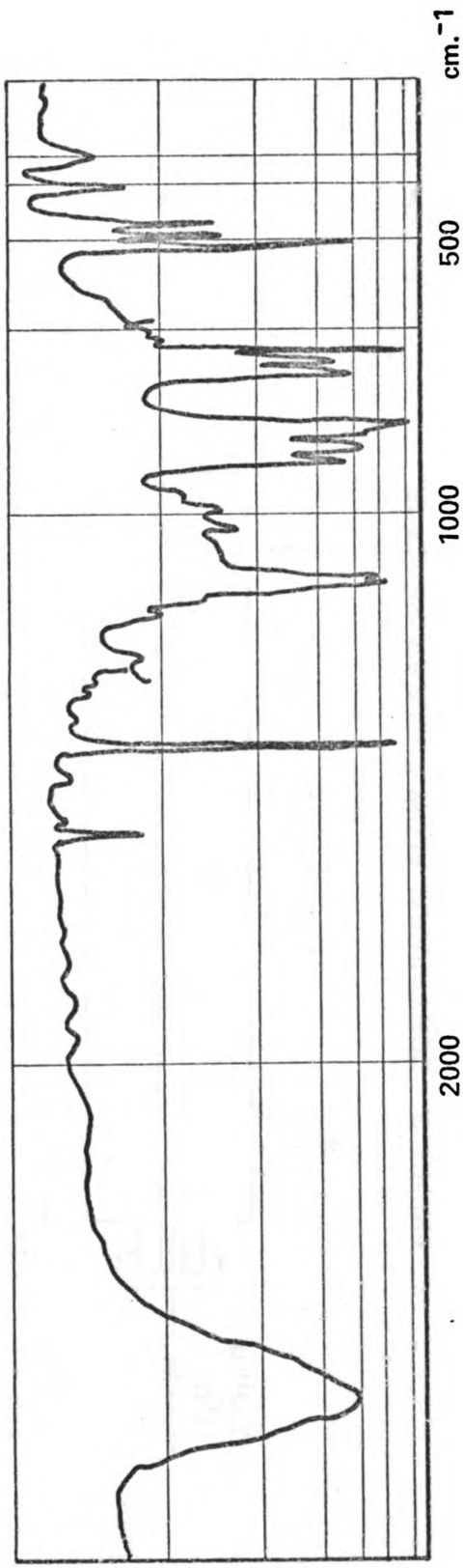


FIGURE 2. INFRARED SPECTRUM OF $Ph_2Si(OH)_2$

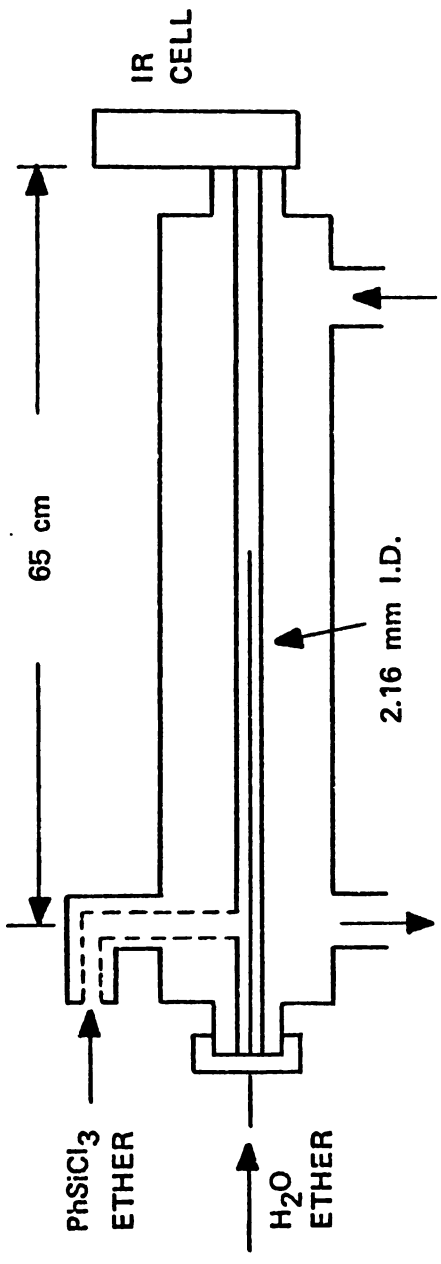


FIGURE 3. CONTINUOUS FLOW TUBULAR REACTOR.

with a one inch copper tube. Water was added to the reactor through a stainless steel hypodermic needle; the end of the needle was closed and the water was forced through two radial holes near the end of the needle. The length of the reactor could be varied merely by changing the position of the water inlet. The windows of the infrared cell were thallium iodide-bromide. The sample chamber was 0.1 mm. thick, 25 mm. high and 10 mm. wide. The cell was connected to the reactor so that the flowing fluid had to make a 30° turn before passing through the cell.

C. Apparatus

Figure 4 is a schematic of the flow system used for this experimentation. The Ph_2SiCl_2 and 1,2-dimethoxyethane were mixed in one of the stainless steel tanks while water mixed with 1,2-dimethoxyethane was contained in the other. Nitrogen pressure was used as the driving force to cause flow. Rotameters were calibrated and used to monitor the flow of the water and the chlorosilane solvent mixture. The temperature of the reaction was controlled by circulating water or other controlled temperature fluid from a constant temperature bath through the jacket of the reactor.

The infrared cell was connected to the end of the reactor. This was specially constructed to allow for the connection of the reactor to the normal sample area of a

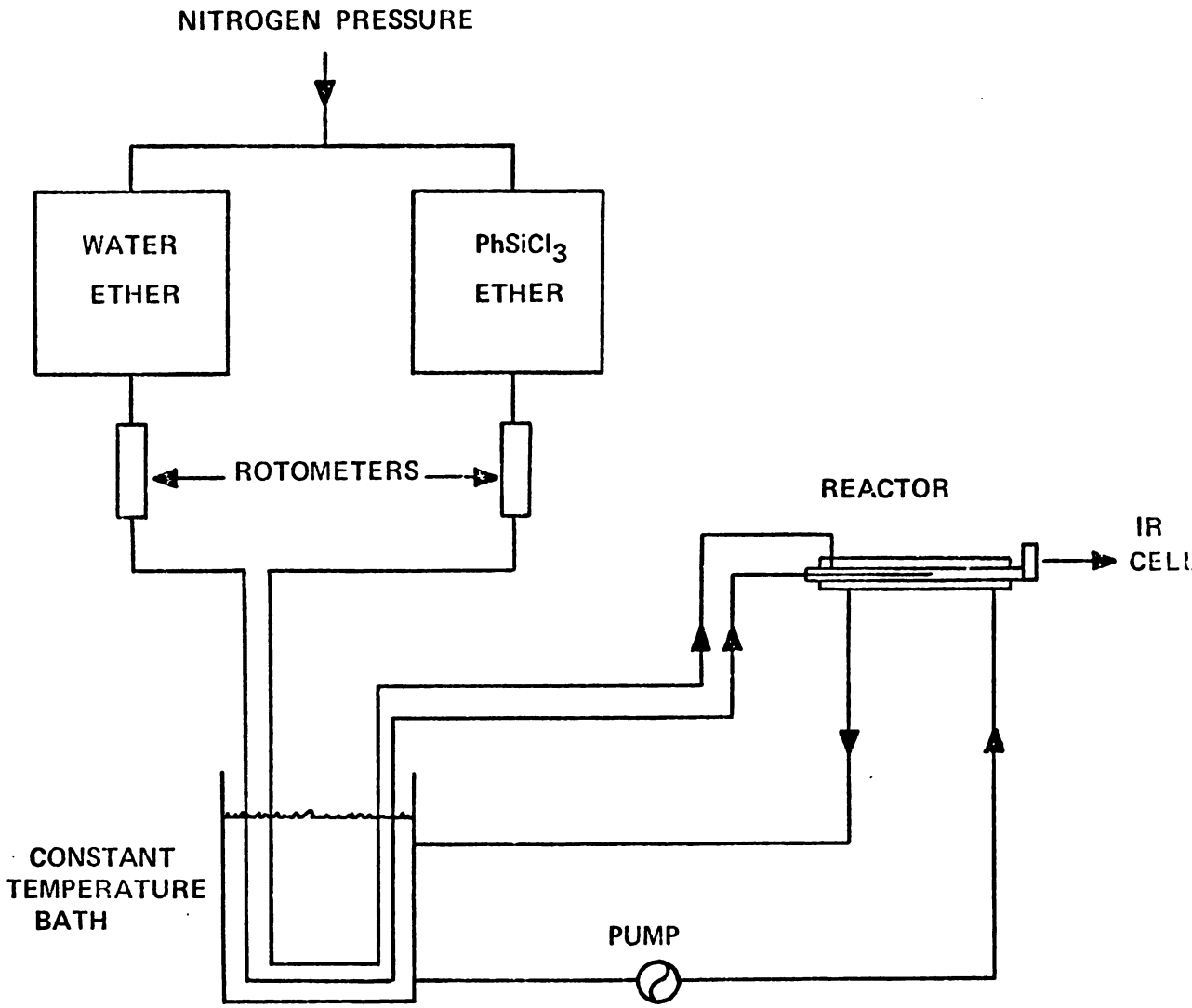


FIGURE 4. HYDROLYSIS EXPERIMENTAL FLOW SYSTEM.

Perkin Elmer 337 infrared spectrometer. A diagram of the cell is shown in Figure 5; the cell was constructed of stainless steel for added strength. Therefore, the reactor could be attached directly.

The P.E. 337 spectrometer is a grating instrument. The gain and drift were checked before each run to optimize performance. A 0.1 mm. reference cell was used to compensate for minor absorptions by the solvent, 1,2-dimethoxyethene.

Values of absorbance versus reactor length were obtained at various flow rates of water and Ph_2SiCl_2. The absorbance data were converted to concentrations. Reaction times were calculated from the flow rates and the reactor lengths. Finally, from these data the rate constants were obtained.

Temperature was controlled by means of a water bath through which the reactants flowed before entering the reactor. Heat exchange was accomplished by means of two helical stainless steel coils, 0.25 in OD. Water from the water bath was also pumped through the reactor jacket.

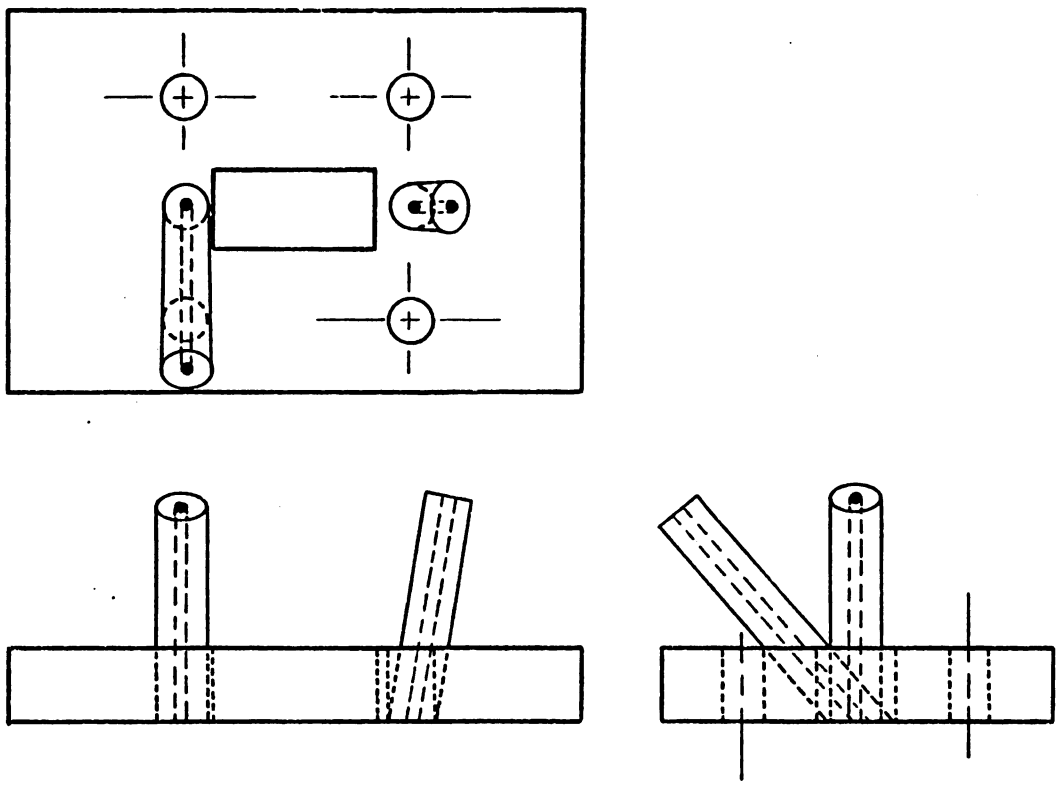


FIGURE 5. INFRARED CELL MOUNT
(STAINLESS STEEL)

IV. EXPERIMENTAL CONDITIONS

The hydrolysis of Ph_2SiCl_2 was carried out at 27°C in one run, and 42°C in three runs. The desired reactant concentrations were obtained by controlling flow rates of the reactants, as shown by rotameter readings. Time was varied by changing the length of the reactor; this was accomplished by changing the axial position of the hypodermic needle which introduced the water-solvent mixture (See Figure 3).

The reaction model was developed from concentrations of reaction quantities at various times and initial concentrations. A summary of the initial concentrations of chlorosilane and water for the experiments is given in Table 1.

The initial molar ratios of water to chlorosilane varied from 1.44 to 3.87. These high molar ratios were needed to drive the reaction to completion. At a water to chlorosilane ratio of about 1:1 a small but relatively constant amount of monochloro intermediate was detected.

TABLE 1

EXPERIMENTAL CONCENTRATION

INITIAL CHLOROSILANE–WATER CONDITIONS				REACTANT FLOW RATES			
RUN	CONC. OF Ph_2SiCl_2 MOLES/l.	CONC. OF WATER MOLES/l.	TEMPERATURE °C	WATER/ SILANE	SILANE SOLVENT CC/MIN.	WATER SOLVENT CC/MIN.	TOTAL FLOW RATE CC/MIN.
1.1	0.20	0.33	26±1	1.65	44	8.4	52.4
2.1	0.16	0.23	41±1	1.44	44	4.7	48.7
2.2	0.15	0.42	41±1	2.80	44.5	9.6	54.1
2.3	0.15	0.53	40±1	3.54	41	11.7	52.7
2.4	0.15	0.58	43±1	3.87	34	10.9	44.9

V. INTERPRETATION OF IR SPECTRA

Our results are based on comparisons of the infrared spectra of reacting mixtures with the spectra of the hydrolysis products of Ph $SiCl_2$. This provided a unique examination of individual hydrolysis species. The following assignments were made for Ph_2SiCl_2 and its hydrolysis products.

Ph_2SiCl_2	620, 590, 520 cm^{-1}
$Ph_2SiCl(OH)$	550 - 520 cm^{-1} (postulated)
$Ph_2Si(OH)_2$	510 cm^{-1}

Diphenyldichlorosilane and diphenylsilanediol are stable compounds and their spectra are well documented[12] (Figures 1 and 2). The infrared absorptions of phenylsilanes have been described by A. L. Smith[18]. The strong bands in the 500-600 cm^{-1} region are due to silicon-chlorine stretching. The 580-590 bands are due to the asymmetric Si-Cl stretch and the 520 band in Ph_2SiCl_2 is due to the symmetric SiCl stretch. The band at 510 cm^{-1} is the Si-O symmetric stretch. Also present in this region are some bands due to the aromatic ring. These are generally weak; they occur below 500 cm^{-1}.

During the hydrolysis experiments, no new band was found for a $Ph_2SiCl(OH)$ type of species. It is expected that a band in the region of 550-520 cm^{-1} would occur for a mono-chloro intermediate. The fact that there was

no large change in the ratio of the 580 cm^{-1} band to the 535 cm^{-1} abs ption suggested that if the monochloro species existed, it was only at very low concentration and was assumed to be in steady state. In the earlier work of Kleinhenz, et al[1], the concentration of the $PhSiCl(OH)_2$ species was found to be low. No specific PhSiCl(OH) species was observed.

To test the stability of the silanol species, a sample of $Ph_2Si(OH)_2$ was allowed to react at room temperature with concentrated HCl in 1,2-dimethoxyethane. No change was observed in the IR spectrum of the $Ph_2Si(OH)_2$.

VI. CALCULATION OF CONCENTRATIONS

The bands at 580 cm^{-1}, ($PhSiCl_2$) and at 510 cm^{-1}, {$Ph_2Si(OH)_2$} were measured using a "beer stick", a log ruler, by placing infinity on I_o and measuring the peaks by the baseline technique. The concentrations were obtained from experimentally obtained Beer's law plots (or ε values) of the respective species. The values of the concentration C, were corrected for the path length of the infrared cell by means of this equation:

$$C = A/\varepsilon\ell$$

Where A = absorbance

ε = absorption coefficient

ℓ = path length

The cell was calibrated for each series of runs by running an empty (air) cell and counting the interference fringes,

$$\ell = \frac{\text{(no. of fringes)}}{2(\nu^1 - \nu^2)}$$

where ν^1 and ν^2 are the measured fringes. Absorption coeffecients of the 580 cm^{-1} and 510 cm^{-1} bands are given in Table 2.

TABLE 2

ABSORPTION COEFFICIENTS AND BAND MAXIMA

SPECIES	ν, $cm.^{-1}$	E, $(M\ cm.)^{-1}$
Ph_2SiCl_2	~585	325
$Ph_2Si(OH)_2$	~505	318

Figures 6, 7, 8, 9, and 10 are graphs of mole fraction of total silane (the concentration of silane species divided by the initial silane concentration) versus the residence time in the reactor. Reaction time, t, was determined by dividing the volume of the reactor, V, by the total flow rate, w.

$$V = AL$$

$$t = \frac{V}{w}$$

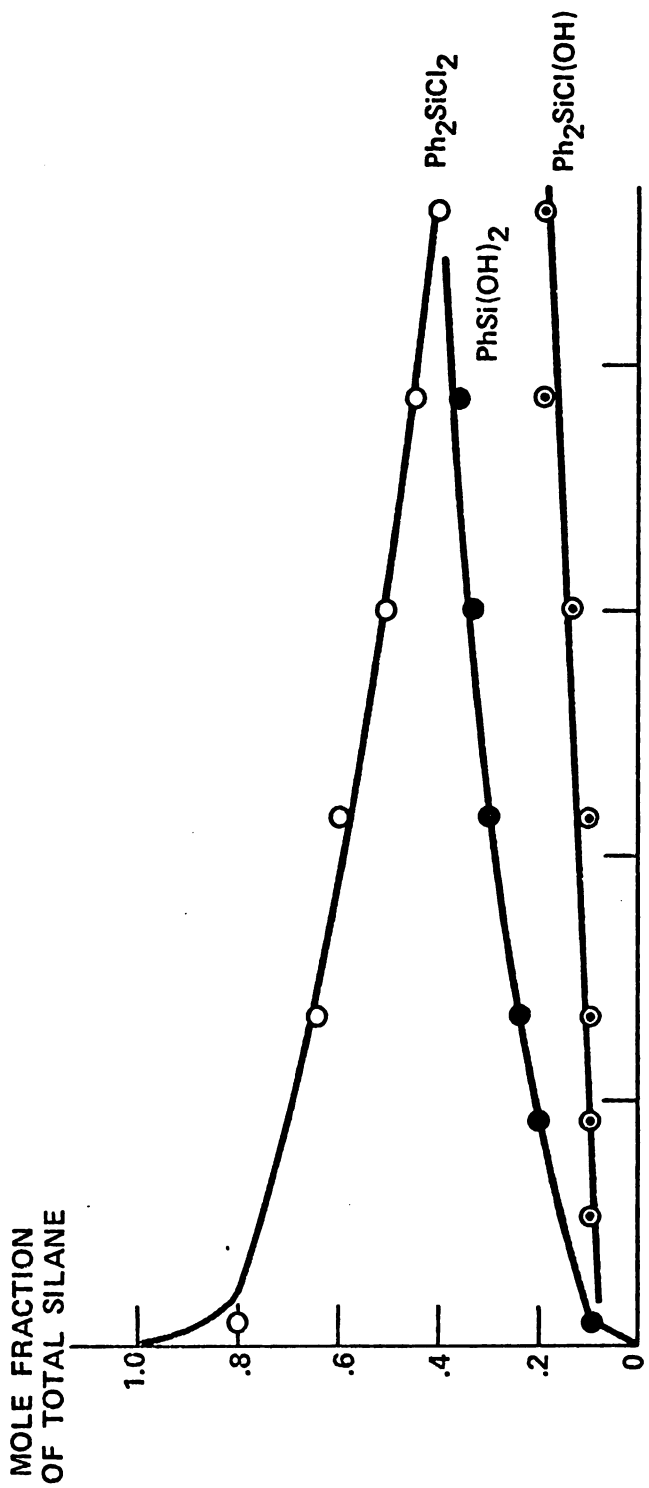


FIGURE 6. MOLE FRACTION OF TOTAL SILANE CHARGE VS. RESIDENCE TIME (RUN 1.1)

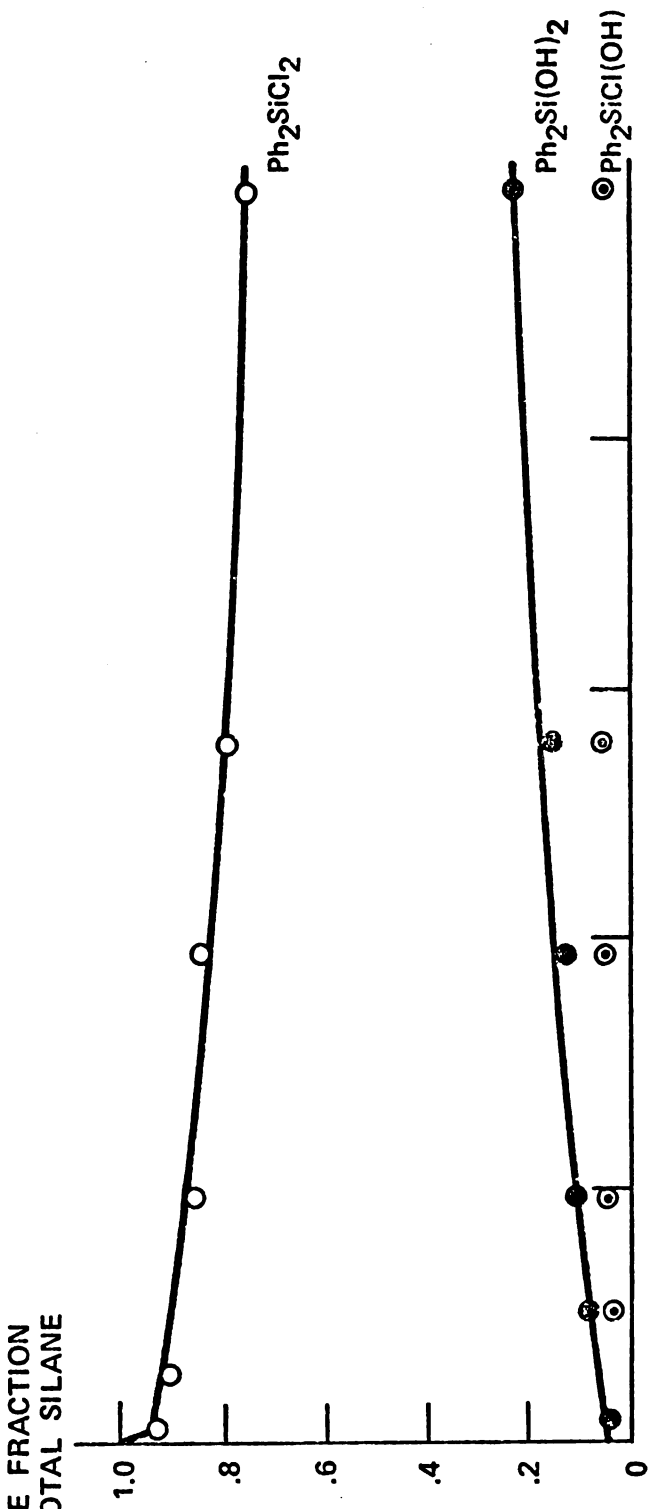


FIGURE 7. MOLE FRACTION OF TOTAL SILANE CHARGE VS. TIME (RUN 2.1)

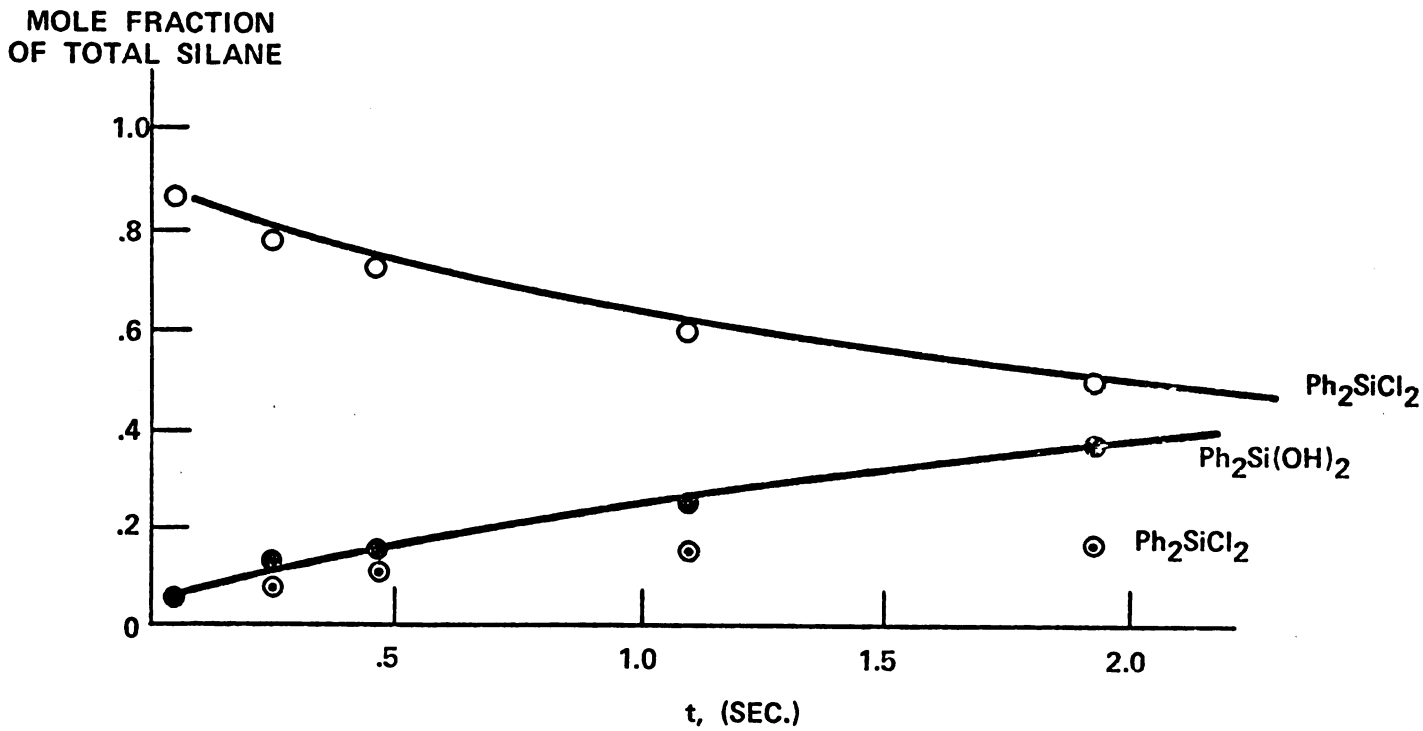


FIGURE 8. MOLE FRACTION OF TOTAL SILANE CHARGE VS. TIME (RUN 2.2)

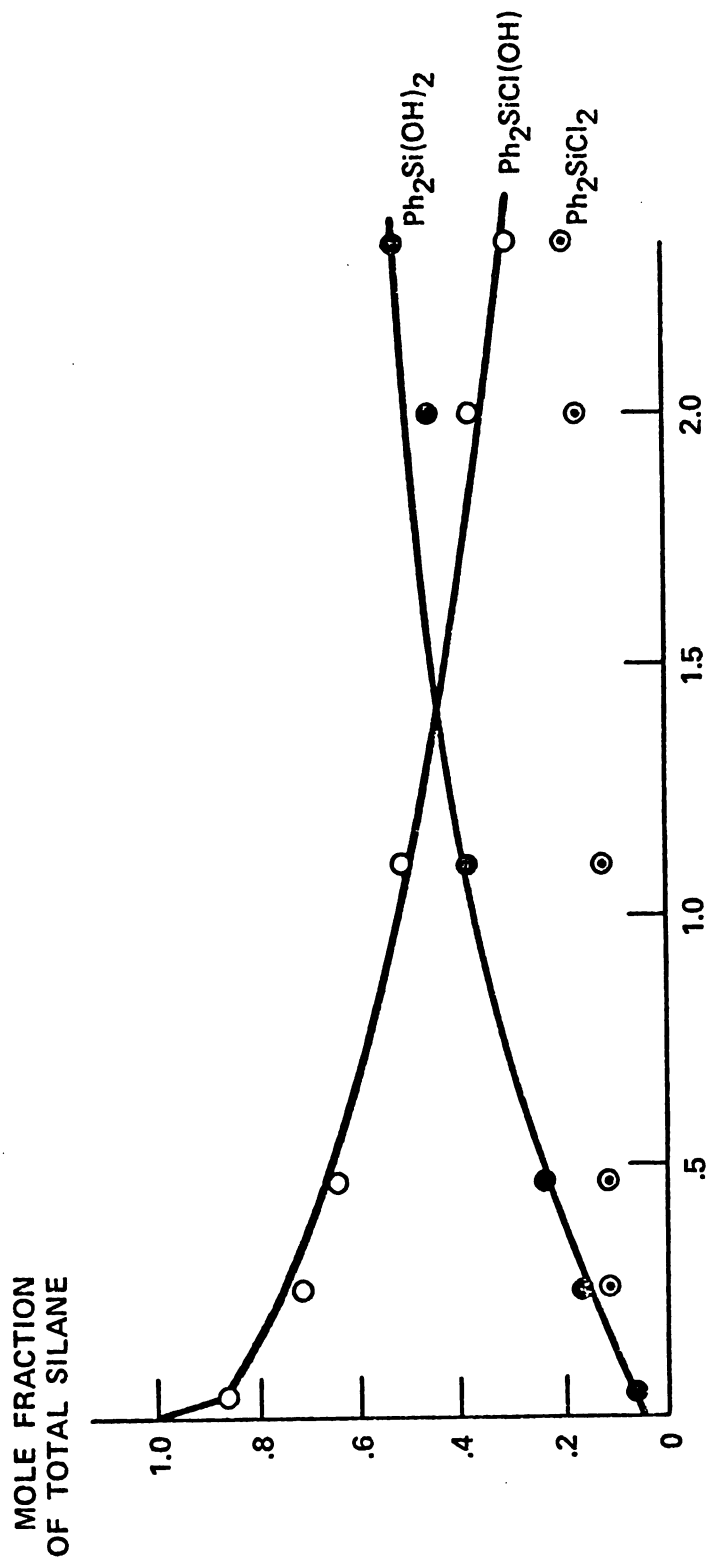


FIGURE 9. MOLE FRACTION OF TOTAL SILANE CHARGE VS. TIME (RUN 2.3)

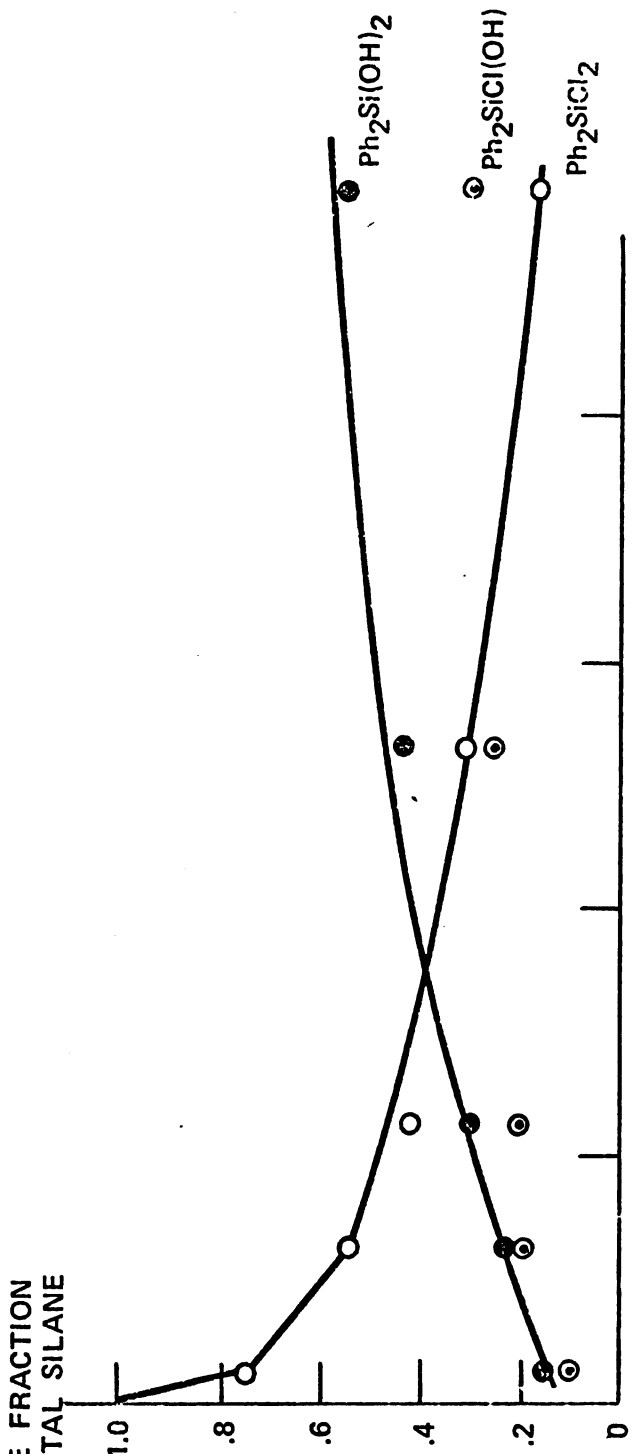


FIGURE 10. MOLE FRACTION OF TOTAL SILANE CHARGE VS. TIME (RUN 2.4)

VII.

MODEL OF Ph_2SiCl_2 HYDROLYSIS AND DETERMINATION OF RATE CONSTANTS

The following reactions were assumed to represent the hydrolysis of Ph_2SiCl_2:

$$Ph_2SiCl_2 + H_2O \xrightarrow{k_1} Ph_2SiCl(OH) + HCl$$

$$Ph_2SiCl(OH) + H_2O \xrightarrow{k_2} Ph_2Si(OH)_2 + HCl$$

It was assumed that the reactions were first order with respect to each reactant, second order overall, and irreversible.

Plug flow was assumed and was shown to be a valid approximation by Kleinhenz and Hawley[15]. Since the rate controlling step was treated as second order and irreversible, the calculated rate constant from the plug flow model should be within 15 percent of values determined from a laminar flow model. The data were analyzed by assuming the following reaction scheme:

$$A + W \xrightarrow{k_1} B + H$$

$$B + W \xrightarrow{k_2} C + H$$

where, $A = Ph_2SiCl_2$

$B = Ph_2SiCl(OH)$

C = $PhSi(OH)_2$

H = HCl

W = water

The rate equations are:

$$-dA/dt = k_1AW \qquad (1)$$

$$dB/dt = k_1AW - k_2BW \qquad (2)$$

$$dC/dt = k_2BW \qquad (3)$$

In the experiments the concentration of B, $[Ph_2SiCl(OH)]$, was always observed to be small. Therefore, the steady-state approximation on B was assumed, i.e., dB/dt = 0. The following equation was used to analyze the data.

$$\frac{2.3}{2A_o-W_o} \log \left[\frac{A(\beta+A_o)}{A_o(\beta+A)}\right] = k_1t$$

where, $\beta = (W_o-2A_o)/(2 + k_1/k_2)$

or, since $k_2 >> k_1$,

$\beta = (W_o-2A_o)/2.$

This equation was derived from the following:

A_o-A = moles of A reacted

W_o-W = moles of W reacted

= moles of A reacted plus moles of C formed.

If $dB/dt = 0$, then from (2):

$$B = k_1A/k_2$$

$$A_o - A = B + C; \quad W_o - W = A_o - A + C = B + 2C$$

$$A_o - A = k_1/k_2 A + C$$

therefore, $$C = A_o - (1 + k_1/k_2)A \qquad (4)$$

$$W_o - W = A_o - A + A_o - (1 + k_1/k_2)A$$

$$= 2A_o - (2 + k_1/k_2)A$$

therefore, $$W = W_o - 2A_o + (2 + k_1/k_2)A \qquad (5)$$

Substitute (5) into (1):

$$dA/dt = -k_1A(W_o - 2A_o + (2 + k_1/k_2)A)$$

$$= -k_1(2 + k_1/k_2)A(\beta + A)$$

$$= -k_1' A(\beta + A) \qquad (6)$$

where, $$k_1' = k_1(2 + k_1/k_2)$$

$$\beta = (W_o - 2A_o)/(2 + k_1/k_2)$$

Integration of (6) by partial fractions:

$$M/A + N/(\beta + A) = 1/A(\beta + A)$$

$$(\beta + A)M + NA = 1$$

$$M + N = 0 \quad M = -N$$

Therefore, $$\beta M = 1 \quad M = 1/\beta$$

$$1/\beta A - 1/\beta(\beta + A) = 1/A(\beta + A)$$

so, $$dA/\beta A - dA/\beta(\beta - A) = dA/A(\beta + A)$$

integrating, $$1/\beta \ln \left[\frac{A(\beta + A_o)}{A_o(\beta + A)}\right] = -k\,t \qquad (7)$$

This gives (8) used to analyze the data:

$$\frac{2.3}{2A_o - W_o} \log \left[\frac{A(\beta + A_o)}{A_o(\beta + A)}\right] = k_1 t \qquad (9)$$

Figure 11 is a plot of (8) for Runs 1.1, 2.3-.4. Table 3 gives the slopes, the calculated rate constants and the initial concentrations.

The rate constant k_2,(20 l mole^{-1} sec^{-1}) can be obtained empirically by plotting C, [$Ph_2Si(OH)_2$] vs. t, and obtaining the initial slope, dC/dt. The slope of a plot of dC/dt versus W, [H_2O] (Figure 12), give k_2 since $dC/dt = k_2BW$; $k_2' = k_2B$. Therefore, from the estimates of B, k_2 was determined; B was obtained by difference, since A and C were known. Figure 13 is a plot of A, B, C versus time. These calculations gave k_1 = 2.1 l mole-sec^{-1} and k_2 = 20 l mole-sec^{-1} (Table 4).

A Runge-Kutta computer solution to the rate expressions was available. The output of this program is a series of concentrations for all reactants at specified times for chosen rate constants. The rate constants found to give the best fit were: $k_1 \sim 1$ and $k_2 \sim 10$ l mole^{-1} sec^{-1}.

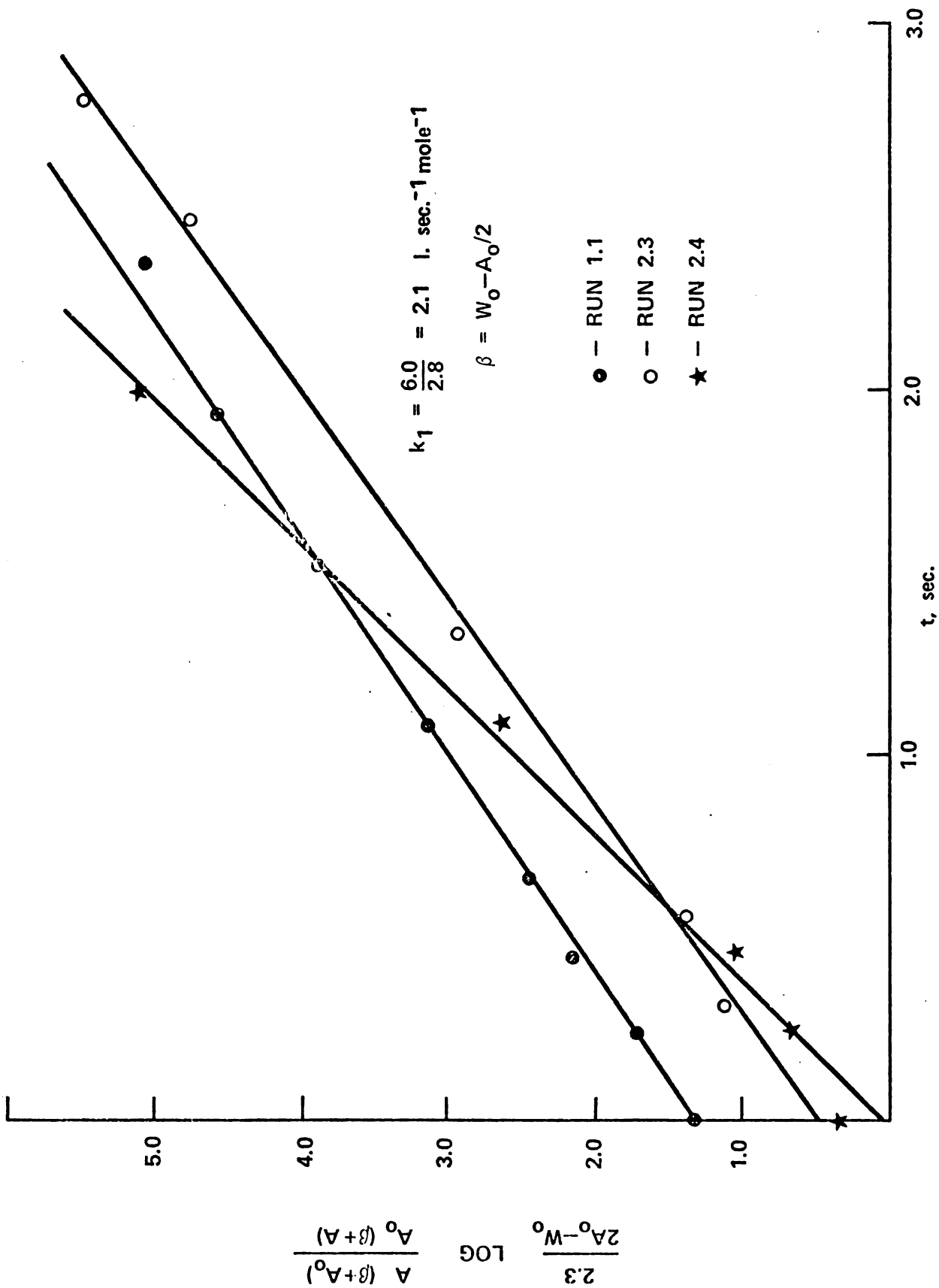


FIGURE 11. PLOT OF $\frac{2.3}{2A_o - W_o}$ LOG $\frac{A\ (\beta + A_o)}{A_o (\beta + A)}$ VS. TIME (RUNS 1.1, 2.1–4)

TABLE 3. STEADY STATE CALCULATIONS

	t, sec.	$\frac{2.3}{2A_o - W_o} \times \log \frac{A(\beta + A_o)}{A_o(\beta - A)}$	β	k_1, l. mol.$^{-1}$sec.$^{-1}$
RUN 1.1				
1	.042	1.30	.07	1.6
2	.25	1.74		
3	.46	2.17		
4	.67	2.44		
5	1.09	3.14		
6	1.51	3.90		
7	1.93	4.56		
8	2.35	5.05		
RUN 2.1		$A_o - W_o \simeq 0$		
RUN 2.2		$A_o - W_o \simeq 0$		
RUN 2.3				
24	.042	0.33	.53	2.5
25	.25	.69		
26	.46	1.08		
27	1.09	2.64		
28	2.00	5.09		
29	2.34	–		
RUN 2.4				
30	.051	.023	.58	1.9
31	.31	1.13		
32	.56	1.41		
33	1.33	2.95		
34	2.46	4.76		
35	2.79	5.48		

$\beta = W_o - A_o/2$

FIGURE 12.

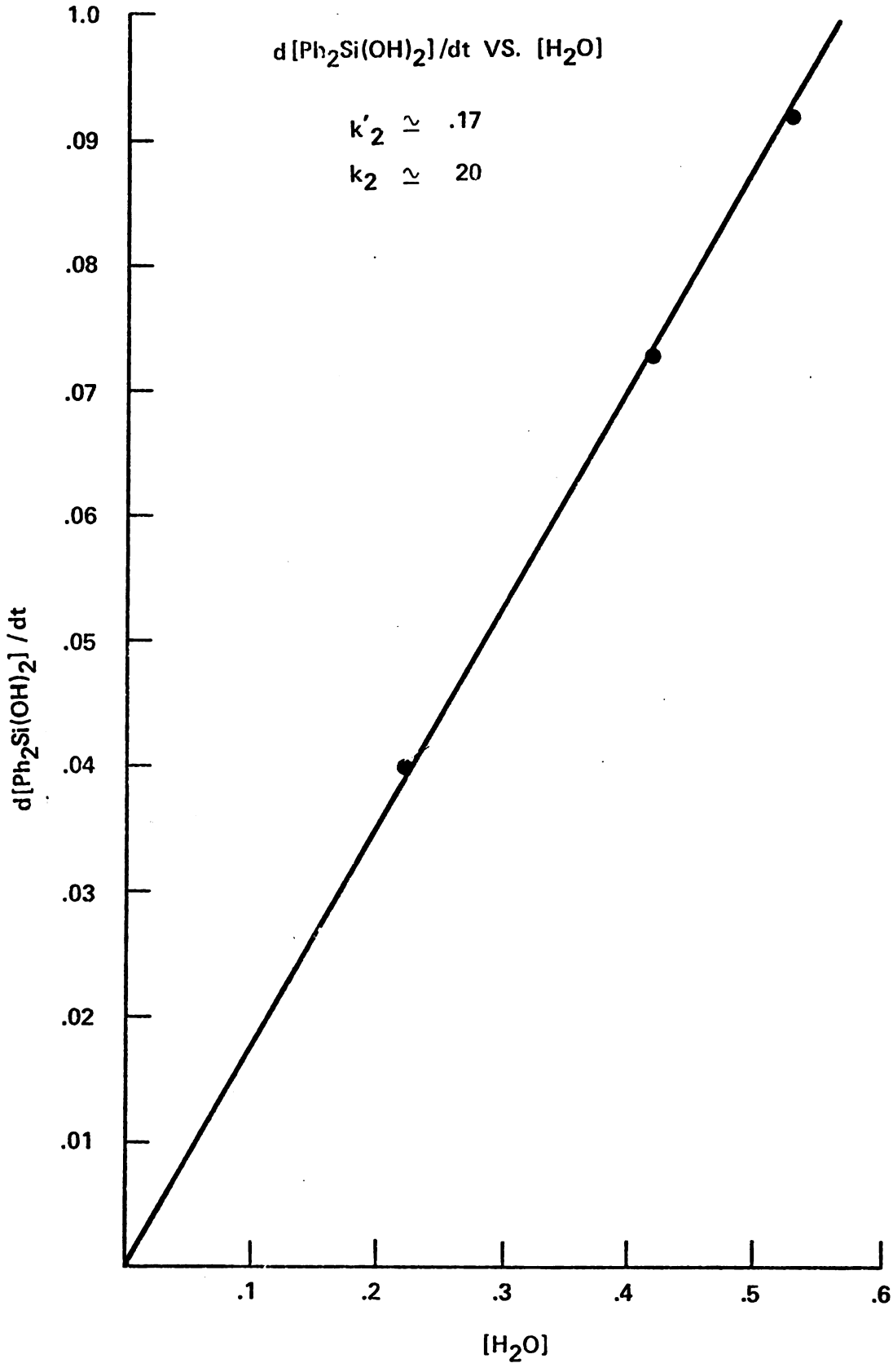

d [Ph2Si(OH)2] /dt VS. [H2O]
k'2 ≃ .17
k2 ≃ 20
1.0
.09
.08
.07
.06
.05
.04
.03
.02
.01
d[Ph2Si(OH)2] /dt
.1
.2
.3
.4
.5
.6
[H2O]

FIGURE 13. PLOT OF A, B, C VS. TIME (RUN 2.4)

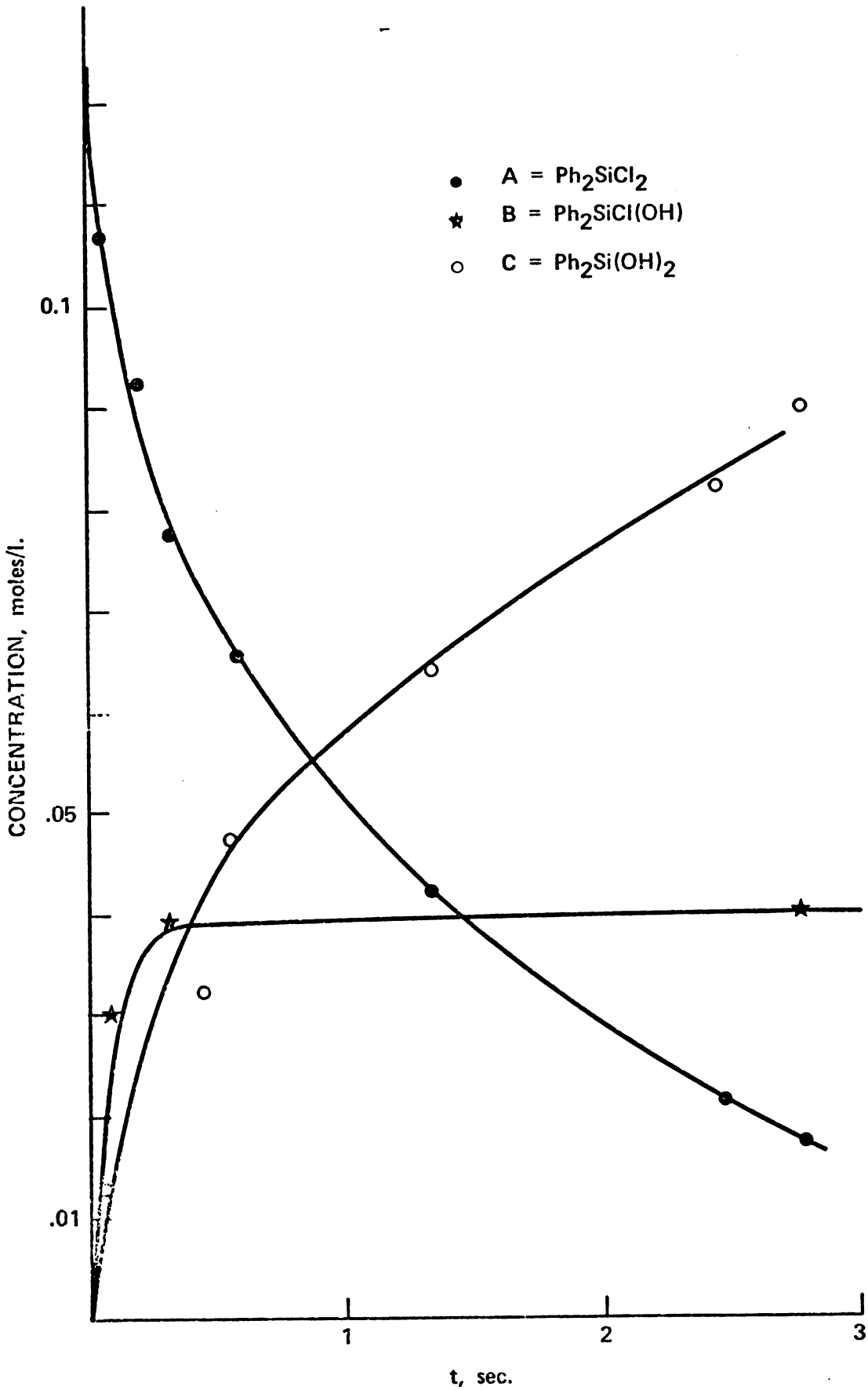


TABLE 4. RATE CONSTANTS AND CALCULATED RESIDENCE TIME, RUNS 1.1, 2.1–4.

RUNS	k_1 (1/mole-sec.)	k_2'	k_2 (1/mole-sec.)	Wo/Ao
1.1	1.6	0.17	20	1.65
2.1		0.17	20	1.44
2.2		0.17	20	2.80
2.3	2.5	0.17	20	3.54
2.4	1.9	0.17	20	3.87

$k_1 \sim$ 1/mole-sec.

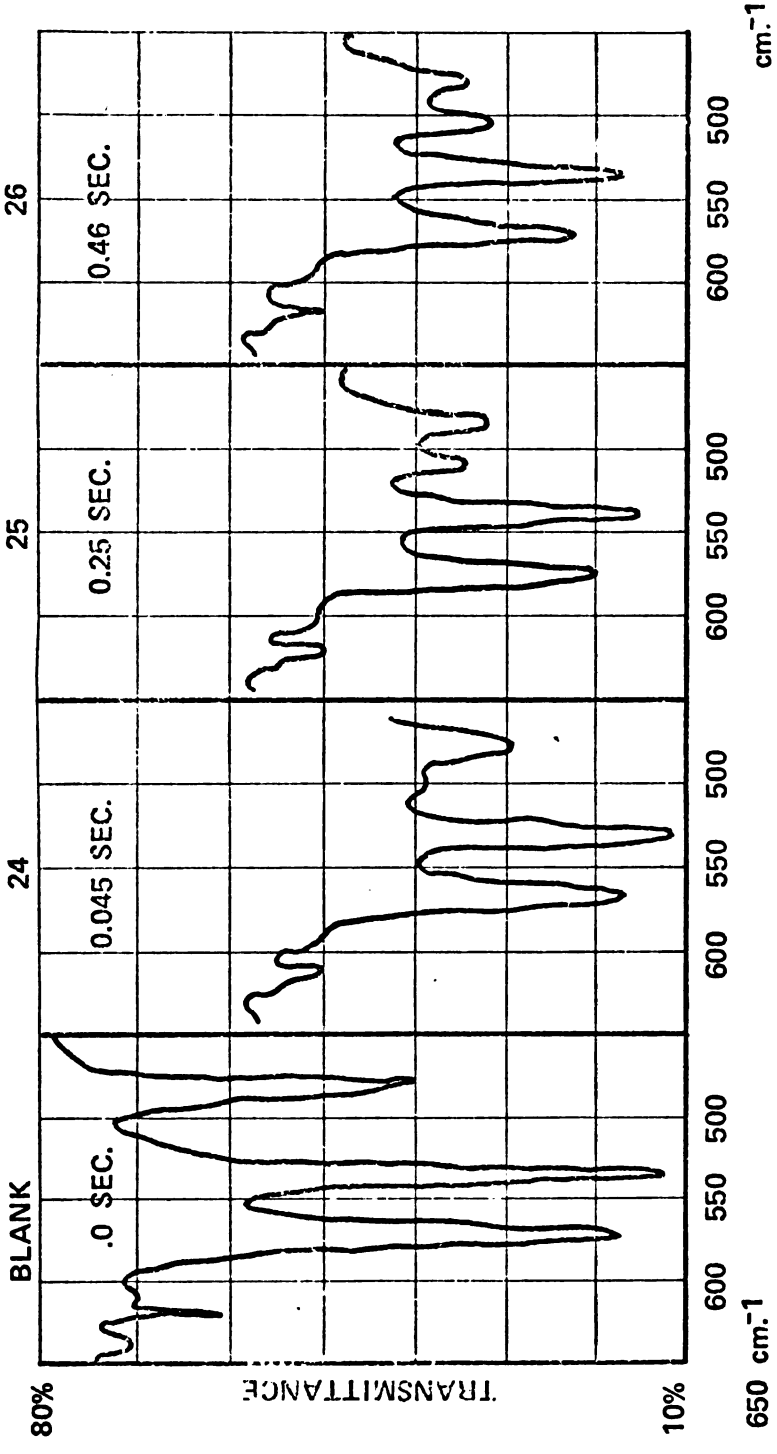
RUN 1.1	t, sec.	2.1	t, sec.	2.2	t, sec.	2.3	t, sec.	2.4	t, sec.
1	.042	13	.045	19	.042	24	.042	30	.051
2	.25	14	.27	20	.25	25	.25	31	.31
3	.46	15	.49	21	.46	26	.46	32	.56
4	.67	16	.94	22	1.09	27	1.09	33	1.33
5	1.09	17	1.39	23	1.92	28	2.00	34	2.46
6	1.51	18	2.52			29	2.34	35	2.79
7	1.93								
8	2.35								

Our statement that there is no silanol condensation of intermediate, or condensation product (monochlorodisiloxane), is very low is valid since the reaction time is very short for our experiment. It was expected that condensation did not occur. Also the data indicate that two moles of water are consumed per mole of diphenyldichlorosilane. Finally, the infrared spectra show no indication of tetraphenyldichlorodisiloxane when compared with a reference spectrum.

VIII. EXAMPLE

Spectra of Run 2.3 are shown in Figure 14. The reference spectrum was determined before addition of water. The spectra show changes due to hydrolysis at varying reactor lengths. Throughout a run, the silane-solvent and water-solvent flow rates were held constant. Time was varied by changing the reactor volume. This was accomplished by withdrawing the hypodermic needle from about 1 to 60 centimeters as described.

The absorptions of the two species, Ph_2SiCl_2 and $Ph_2Si(OH)_2$ are given in Table 2. The molar concentrations were calculated from the cell thickness and the absorption coefficient taken from Figure 11. The concentration of $Ph_2SiClOH$ was calculated by means of the mass balance since the concentration of two species was determined and a step-wise hydrolysis was assumed.



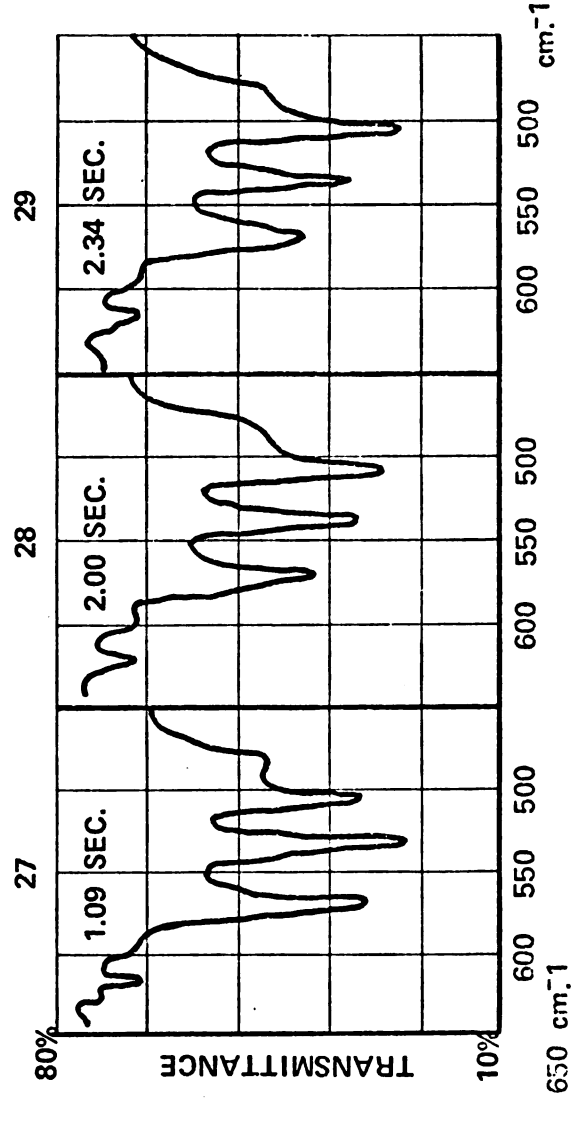


FIGURE 14. SPECTRA FROM RUN 2.3

IX. RESULTS AND CONCLUSIONS

It was demonstrated that the hydrolysis of Ph_2SiCl_2 could be followed by means of infrared spectroscopy. This study again demonstrates our novel flow system and the usefulness of an infrared spectrometric detection system.

The hydrolysis reactions of the individual chlorines of Ph_2SiCl_2, in 1,2-dimethoxyethane, were followed at 0°C. Reaction times of 0.05 to 3 seconds could easily be measured. Silanol condensation reactions generally require more time than this.

The hydrolysis reactions are adequately modeled as first order with respect to each species and second order overall; the reactions are irreversible. To minimize flow problems, the flow rates of each silane and of water were kept constant. Both steady state approximation and direct analysis were found to give values in agreement with the rate constants obtained from a Runge-Kutta computer solution of the rate experssions. The reaction velocity constants were determined to be as follows:

$k_2 \approx 2.0$ l mole^{-1} sec^{-1} and

$k_2 \approx 20$ l mole^{-1} sec^{-1}

The fact that our plot of the second order expression goes through zero substantiates our model.

X. LIST OF REFERENCES

1. Hawley, M.G., Larson, W.D., Bond, A.R., Dow Corning Report No. 605, 1968.

2. Prince, R.H., Trans. Farady Soc., 54, (G) 835 (1958).

3. Shaffer, L.H., and Flanigen, E.M., J. Phys. Chem., 61, 1591, (1957).

4. Shaffer, L.H., and Flanigen, E.M., J. Phys. Chem., 61, 1595, (1957).

5. Prince, R.H., J. Chem. Soc, 1783 (1959).

6. Prince, R.H. and Chipperfield, J.R., Proc. Chem. Soc., 385, (1960).

7. Chipperfield, J.R. and Prince, R.H., J. Chem. Soc., 3657, (1963).

8. Sommer, L.H., Angew. Chem. (Internat. Ed.), 1, 143 (1962).

9. Petersen, R.C. and Ross, S.D., J.Am. Chem. Soc. 85, 3164 (1963).

10. Sommer, L.H., Parker, G.A., Lloyd, N.C., Frye, C.L. and Michael, K.W., J.Am. Chem. Socl, 89, 857 (1967).

11. Prince, R.H. and Timms, R.E., Inorg. Chim. Acta, 129 (1967).

12. Prince, R.H. and Timms, R.E., Inorg.Chim. Acta, 257 (1968).

13. Prince, R.H. and Timms, R.E., Inorg. Chim. Acta, 260 (1968).

14. Sommer, L.H., "Stereochemistry, Mechanism and Silicon", Mcgraw-Hill, New York, 1965.

15. Kleinhenz, T.A., and Hawley, M.C., Engineering Research Report, M.S.U. (1970).

16. Hawley, M.C., Larson,W.D., and Bond,A.R., "Variable Length Reactor", Patent Applied for 1970.

17. Tyler, L.J., J.Am. Chem. Soc., 770 (1959).

18. Smith, A.L., Spectrochimica Acta, 1075, (1967).

19. Gill, R.K., IBM-FSP, Dow Corning Corp., (1968).