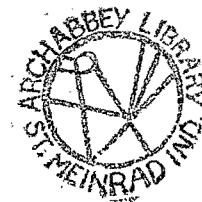


AN ANALYSIS OF THE PRODUCTS
OF THE HYDROLYSIS OF DIETHYLDICHLOROSILANE
AS INFLUENCED BY ACIDS, BASES, AND SOLVENTS,
WITH SPECIAL REFERENCE TO ETHYL ALCOHOL
AS A SOLVENT

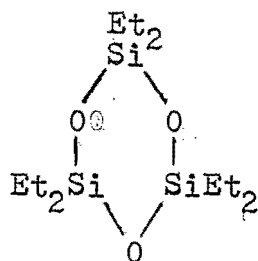
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For the Degree of Bachelor of Science

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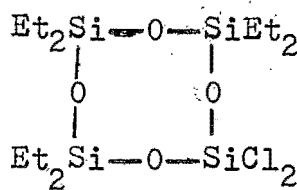


INTRODUCTION

The hydrolysis of diorgano-silicon halides is generally accompanied by dehydration to form complex condensation products containing siloxane linkages (1-8). Although the reports of the hydrolysis of diethyldichlorosilanes, Et_2SiCl_2 , confirm a strong tendency toward the formation of cyclic structures containing silicon-oxygen linkages, there is a lack of consistency toward the amounts of cyclic products produced by the hydrolysis. This lack of clear understanding led Saint Meinrad College to an investigation of the hydrolysis of Et_2SiCl_2 , the results of which are described briefly in the present paper. The cyclic products of primary interest for this study are hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane, which will be referred to as ethyl trimer and ethyl tetramer respectively:



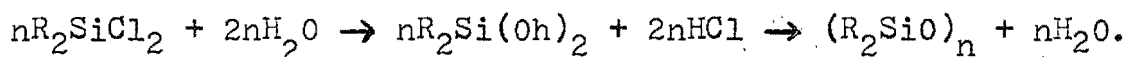
Ethyl Trimer



Ethyl Tetramer.

The water hydrolysis of Et_2SiCl_2 and the related compound, dimethyldichlorosilane, Me_2SiCl_2 , is an

exothermic reaction which yields cyclic products containing silicon-oxygen linkages. Hydrogen chloride is a by-product of the reaction. Various reports (3,9,10) of the water hydrolysis of Et_2SiCl_2 indicate the existence of an intermediate, diethylsilanediol, $\text{Et}_2\text{Si}(\text{OH})_2$, in the formation of these cyclic products. Diethylsilanediol is a white, orthohormic, crystalline solid which melts at 96°C . and boils with decomposition at about 140°C . The existence of such a linear diethylsilanediol intermediate from the water hydrolysis of Et_2SiCl_2 allows the proposed simple reaction path:



Various reports in the literature indicate that a large number of reaction variables influence the proportion of products derived from the water hydrolysis of alkylhalosilanes. These variables include the presence of acid or base medium; the amount of medium; the amount of time the halosilanes react in the medium; the presence of a solvent; the nature and amount of solvent; the reaction temperature and pressure; use of catalyst; and the purity of the dihalide.

It is known that, with nonbulky, substituted dichlorosilanes, such as dimethyldichlorosilane, both linear and cyclic polysiloxanes are obtained on hydrolysis. Complete hydrolysis of Me_2SiCl_2 in various media primarily yields the methyl trimer and methyl tetramer for Patnode

and Wilcock (4). They observed that reducing the pressure reduces the yield of lower-boiling materials (4). With bulkier substituted dichlorosilanes, such as diphenyldichlorosilane, hydrolysis under mild conditions proceeds only to the diphenylsilane-intermediate stage, and cyclic siloxanes are only obtained on usually more drastic conditions (5).

In contrast to the unstable silanol intermediate obtained on hydrolysis of diethyldichlorosilanes, the corresponding bulkier phenyl chlorosilanes gave stable silanols which showed a lower tendency to condense (1). For the lower alkyl homologs, the diol intermediate has been isolated only by special techniques. George, Sommer and Whitmore (10) isolated diethylsilanediol in low yield by means of shortened reaction times and lower temperatures. Andrianov and Sokolov (9) propose that it is the stepwise condensation of the diol intermediate which accounts for the variety of products obtained by the hydrolysis of dialkyldichlorosilanes. They also report (9) that the amount of cyclic products of the hydrolysis of dialkyldichlorosilanes depends on the solubility of the intermediate diol in the medium.

The proposed reaction path, as already described, is altered under certain conditions which favor the production of linear products. Lasocki (11) describes the formation ^{of} $\left[R_2Si(OH) \right]_2 O$ from the reaction of $R_2Si(OH)_2$ in

aqueous dioxane at 25°C. in the presence of hydrogen chloride. Patnode and Wilcock (4) report that chlorine end-blocked linear polysiloxanes are produced from the partial hydrolysis of Me_2SiCl_2 . Shaffer and Flanigen (12), in performing a conductometric hydrolysis of a difunctional chlorosilane system, found that lowering the reaction temperature and increasing the hydrogen chloride concentration suppressed the hydrolysis of Si-Cl bonds and favored the formation of chlorine end-blocked linear siloxanes. However, they identified methylchloropolysiloxanes of the type $\text{Cl Si}(\text{CH}_3)_2 \text{O}_x \text{Si}(\text{CH}_3)_2 \text{Cl}$ (where $x = 1$) which added to the formation of methyl trimer and methyl tetramer.

Solvent Effects

Assuming the formation mainly of cyclic products, the percentage of trimer compared to tetramer also varies according to conditions. An example of this is provided by a comparison of two patents issued to Dobay (13,14). Both patents involve the hydrolysis of Et_2SiCl_2 in methyl alcohol and water. The greater proportion of methyl alcohol in one case favors the formation of the ethyl tetramer, while a greater proportion of water in the other case promotes the production of ethyl trimer.

According to some reports, solvents have little or no effect on the condensation of the silanol groups.

Kuhowski (15) reported that solvents may be inert to organosiloxanes and dissolve silanol groups. He attributed the increased rate of condensation to the increase of temperature.

Other reports indicate that the type and amount of solvent used in the hydrolysis has an effect on the proportion of products. Bentkowska (16) reported that the hydrolysis rate increased with the temperature and water content. The percentage of condensed silanol groups were greater for water than salt solutions. Patnode and Wilcock (4) added 33 moles of the methyl homolog slowly to 66 moles of water at 15-20°C. with stirring and obtained 0.5% methyl trimer and 42.0% methyl tetramer as well as higher boiling products. Following the same general procedure for the hydrolysis of Et_2SiCl_2 and using 0.2 moles excess water, Ostdick (17) obtained 15% ethyl trimer and 30% ethyl tetramer. Ostdick also received a large amount of unreacted Et_2SiCl_2 and a higher-boiling product.

A patent assigned to Kriebble and Elliott (18) describes the hydrolysis of halosilanes by mixing the silanes directly with agitated ice and water. Stirring was used to prevent high local concentration of the acid generated during hydrolysis, so as to reduce the number of silanol groups in the product. Andrianov and

Sokolov (9) obtained 54% cyclic products from the hydrolysis of Me_2SiCl_2 in pure water.

Generally, the amount of cyclic product formed depends on the solubility of the intermediate $\text{R}_2\text{Si}(\text{OH})_2$ in the medium; the better the solubility, the higher the yield of cyclic products. Andrianov and Sokolov (9) reported that the solubility of $\text{Et}_2\text{Si}(\text{OH})_2$ in grams per 100 ml. solvent at 20°C. for pure water is 9.7-10.8; for ethyl alcohol, 67.3-57.5; for 50% ethyl alcohol, 38.8; for 25% ethyl alcohol, 13.3; for methyl alcohol, 111.9; for petroleum ether, 0.35. George Sommer and Whitmore (10) reported that the intermediate $\text{R}_2\text{Si}(\text{OH})_2$ is partly soluble in the presence of benzene.

Other reports indicate that the solvent has peculiar effects on the intermediate $\text{R}_2\text{Si}(\text{OH})_2$. Kurlova, et. al. (19) noted that Et_2SiCl_2 in amine and organic solvents added to tetraorganodisiloxane-1,3,-diol yields organocyclosiloxanes. Karlin, et. al. (20) conducted the hydrolysis of organochlorosilanes in the presence of ethylene oxide with cooling; the subsequent treatment of the organosiloxane mixed with water at 100°C. gave simultaneous preparation of ethylene chlorhydrin and siloxanes. Nitzsche, et. al. (21) hydrolyzed Me_2SiCl_2 with methyl alcohol and active charcoal, obtaining almost exclusively polymeric dimethylsiloxanes.

Acid-Base Effects

Periodical and patent references indicate that ^{the} use of various acidic and basic media influences the relative proportions of cyclic products. Andrianov and Izmailov (22) report that hydrolysis of R_2SiCl_2 in dilute HCl forms cyclic and linear products, while in concentrated HCl with regeneration of HCl gas the reaction leads to cyclic products exclusively. The reactions were run in mixtures of ethyl ether with aqueous HCl at 20°C. Karlin and Mitrofanov (23) noted an increase in the number of OH groups in the products of hydrolysis of compounds of the type R_2SiCl_2 when the HCl concentration in the aqueous phase was increased, and attributed this increase to the increased yield of linear polysilanol. Patnode and Wilcock (4) found that in general, hydrolysis in a strongly acidic medium increased the proportion of low molecular weight material as does the use of a water miscible solvent, while hydrolysis in a strongly basic medium reduces the proportion of low boiling weight material. Rodziejewicz and Bertkowska (24) reported that the hydrolysis of Et_2SiCl_2 in the presence of $CuSO_4$ produced 14% ethyl trimer and 86% ethyl tetramer. The comparison of such cyclic structures indicate that $CuSO_4$ broke the siloxane bonds to yield linear polymers of higher molecular weight.

Kipping and Martin (25) performed a hydrolysis of

Et_2SiCl_2 in pure water obtaining linear polymers of molecular weight 530-694. However, Hyde and DeLong (1), in a similar hydrolysis obtained first fraction of molecular weight 297 and found the molecular weight of the residue to be 519-534. Young and co-workers (26) obtained 62% volatile products in the hydrolysis of Et_2SiCl_2 in ether using ice, as compared with 27% when no solvent was used, and 22% when boiling water was the hydrolyzing agent. Miller (27) hydrolyzed Et_2SiCl_2 with ether in pure water and obtained 70.3% volatile material, while Anzlovar (28) hydrolyzed Et_2SiCl_2 in pure water and obtained 32.5% volatile material. Anzlovar (28) and Mulhern (29) studied the hydrolysis of Et_2SiCl_2 in the presence of HCl with and without organic solvent. They found that the amount of cyclic volatile material was greater in the case where organic solvent was used.

George, Sommer and Whitmore (10) report that 15 ml. of Et_2SiCl_2 added to 20 ml. concentrated HCl results in 50% hydrolysis with the main product being sym-tetraethyl-dichlorodisiloxane. In related experiments, they found that the addition of previously prepared diethylsilanediol to concentrated HCl at 0°C. resulted in rapid polymerization, although the same diol appeared to be quite stable in a slightly basic solution at room temperature. The results of Miller (27), Grisley (30), Kirner (31) and

Verbish's (32) hydrolysis of Et_2SiCl_2 with ether in various concentrations of acid and base at $72.0^\circ\text{--}142.0^\circ\text{C}$.

indicated no signs of crystalline products, diethylsilane-diol or sym-tetraethyldichlorodisiloxane. However, as will be shown later in this paper, different concentrations of acid or base are vital factors in the mechanisms of forming ethyl trimer and ethyl tetramer based on the reports of these workers.

Various literature reports indicate that acid and base concentrations in the presence of alcohols have a definite effect on the hydrolysis of Et_2SiCl_2 . Ponomarev, et. al. (33) reported that in a circulating reactor operated at 300°C ., Me_2SiCl_2 in the presence of methyl alcohol gave no methyl chloride as long as HCl was absent. Dobay's (13,14) reports indicate that the hydrolysis of Et_2SiCl_2 in methyl alcohol and water produces maximum yield of ethyl trimer when excess water is present in the hydrolysis, and gives maximum yield of ethyl tetramer when a deficit of water compared to ethyl alcohol is present in the hydrolysis. Rush (34) performed a limited study of the effect of low concentrated hydrochloric acid and high concentration of sodium hydroxide with ethyl alcohol on the hydrolysis of Et_2SiCl_2 using strictly controlled conditions. Rush (34) found that the proportion of trimer to tetramer was greater in HCl than in NaOH .

Literature reports indicate that the hydrolysis in the presence of an acid or base depolymerizes polyorganosiloxanes to trimer or tetramer. The reports of Wenske, Berwald and Teischmann (35) indicate that the vapor reaction of Me_2SiCl_2 hydrolyzate with KOH under a vacuum at 100-200°C. formed methyl tetramer upon depolymerization. Sobolevskii, Nazarova and Lotarev (36) reported that polyorganosiloxanes were prepared by hydrolytic condensation of respective chlorosilanes followed by catalytic rearrangement in the presence of H_2SO_4 .

Kinetics

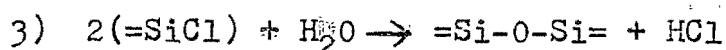
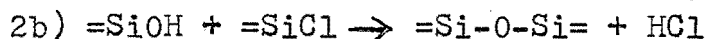
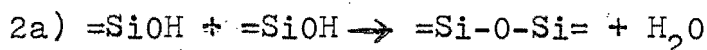
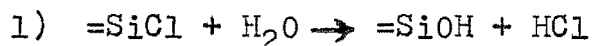
Many reports indicate that the rate of condensation of $\text{Et}_2\text{Si}(\text{OH})_2$ in the presence of an acid is of the second order kinetics. Lasocki and Mickalska (37) reported that the rate of condensation of $\text{Et}_2\text{Si}(\text{OH})_2$ in the presence of water or higher concentrations of alcohols with an acid follows the second order kinetics. Later, Lasocki and Mickalska (38) reported that the addition of salts had a pronounced effect on the rate of condensation when in the presence of HCl. Shaffer and Flanigen (2) found that the hydrolysis rate in ethylene glycol-dimethyl ether changes appreciably with 8M HCl due to the fact that above this concentration there is more than one HCl molecule per solvent molecule, and therefore the rate of hydrolysis of Et_2SiCl_2 with excess HCl increases as the concentration

of HCl increases. Anzlovar (28) and Mulhern (29) studied the hydrolysis of Et_2SiCl_2 in the presence of HCl with or without organic solvent. They found that the amount of cyclic distillable material was less in the case where organic solvent was not present.

Bragin and Karapethyants (39) found a temperature dependence of the vapor pressure of cyclodimethylsiloxanes $(\text{Me}_2\text{Si})_2\text{O}$ by calculations resembling Henglein's equation $\log T_1 = A \log T_2 + B$. They have calculated a relationship between temperature and pressure for cyclodimethylsiloxanes. Lasocki (11) had found the rate coefficient to be 0.091 for the reaction $2\text{Et}_2\text{Si}(\text{OH})_2 \rightarrow [\text{Et}_2\text{Si}(\text{OH})]_n + \text{H}_2\text{O}$ when performed in aqueous dioxane at 25°C . with HCl.

Proposed Mechanisms

Shaffer and Flanigen (12) propose the following reactions for the formation of Si-O-Si linkages for the hydrolysis of Me_2SiCl_2 in the presence of hydrochloric concentrations with ether:



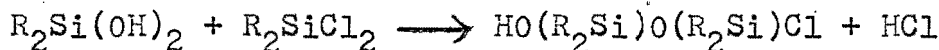
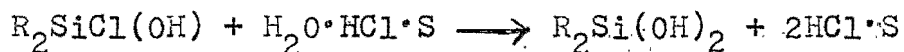
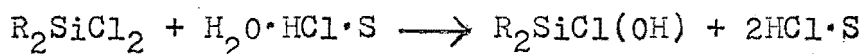
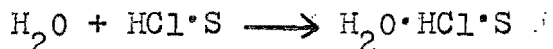
Lasocki and Mickalska (37) generalized the mechanism for the condensation of silanols:



These seem to give the hydrolysis reaction mechanism which describes the part played by hydrochloric acid in the condensation of the silanediol.

Shaffer and Flanigen (2) propose the following mechanism for the total hydrolysis reaction of dialkyl-dichlorosilanes including some solvent effects:

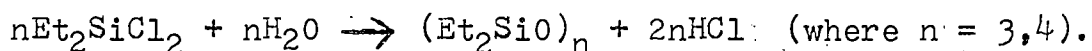
S = solvent



Condensation of the silanediol is also affected by ion exchange resins. Kunowski (15) reported that the condensation of organosilanediols in the presence of ion exchange resins leads to organosiloxanes practically free of the silanol group.

DISCUSSION

In this study, a conjecture about the results of the hydrolysis of Et_2SiCl_2 with ethyl alcohol as solvent in both acidic and alkaline media will be attempted. The percentage results of Miller (27), Grisley (30), Kirner (31), Verbish (32), Mulhern (29), Anzlovar (28), and Rush (34) in Tables I and II will be reanalyzed. Table II contains the percentage yields of the fractions and the percentages of loss as calculated from the reaction:



Product Trends of the Hydrolysis With Solvent

Trimer. As noted in Chart 1, when the water hydrolysis of Et_2SiCl_2 is performed with diethyl ether as solvent in the presence of HCl or NaOH, the percentages of ethyl trimer range between 19.6% and 40.2% obtainable product. As the HCl concentration increases, the percentage of ethyl trimer generally decreases. And also, as NaOH concentration increases, the percentage of ethyl trimer generally decreases.

It appears that when more points on the curve pertaining to ethyl alcohol are determined experimentally, the shape of that curve may well be similar to that pertaining to ethyl ether. This conjecture is reasonable

Table I: Percentage of Each Fraction to the Total Amount of Distillable Product

Acid or Base Concentration	% Forerun	% Trimer	% Inter-mediate	% Tetramer	% A	% B	Tetramer/Trimer	Solvent	Data Source
37% HCl	0.0	41	19	24	85	15	0.59	ether	Miller
37% HCl	0.0	42	12	0	54	46	0	none	Mulhern
24% HCl	0.0	46	14	26	87	13	0.57	ether	Miller
21% HCl	0.0	46	17	28	91	9	0.61	ether	Grisley
21% HCl	0.0	34	31	0	66	34	0	none	Anzlovar
21% HCl	19.6	45	6.2	29.3	97	3	0.65	alcohol	Rush
6.2% HCl	0.0	58	8	19	78	22	0.33	ether	Grisley
pure water	3	57	14	8	81	19	0.14	ether	Miller
pure water	0.0	39	17	16	73	27	0.41	none	Anzlovar
14.2% NaOH	0.0	67	16	12	96	4	0.18	ether	Kirner
14.2% NaOH	0.0	29	13	26	67	33	0.90	none	Mulhern
28.3% NaOH	0.0	56	38	3	98	2	0.05	ether	Kirner
53.6% NaOH	0.0	52	46	0	98	2	0	ether	Verbish
53.6% NaOH	0.0	43	38	5	99	1	0.12	none	Anzlovar
53.6% NaOH	29	21.6	14.2	27.8	92.6	7.4	1.29	alcohol	Rush
62.0% NaOH	0.0	42	53	0	96	4	0	ether	Verbish

A: Cyclic Distillable Material = the sum of forerun, trimer, intermediate, and tetramer.

B: Non-Distillable Material = material not distillable above 220-280°C. at 1.5-2.6 mm.

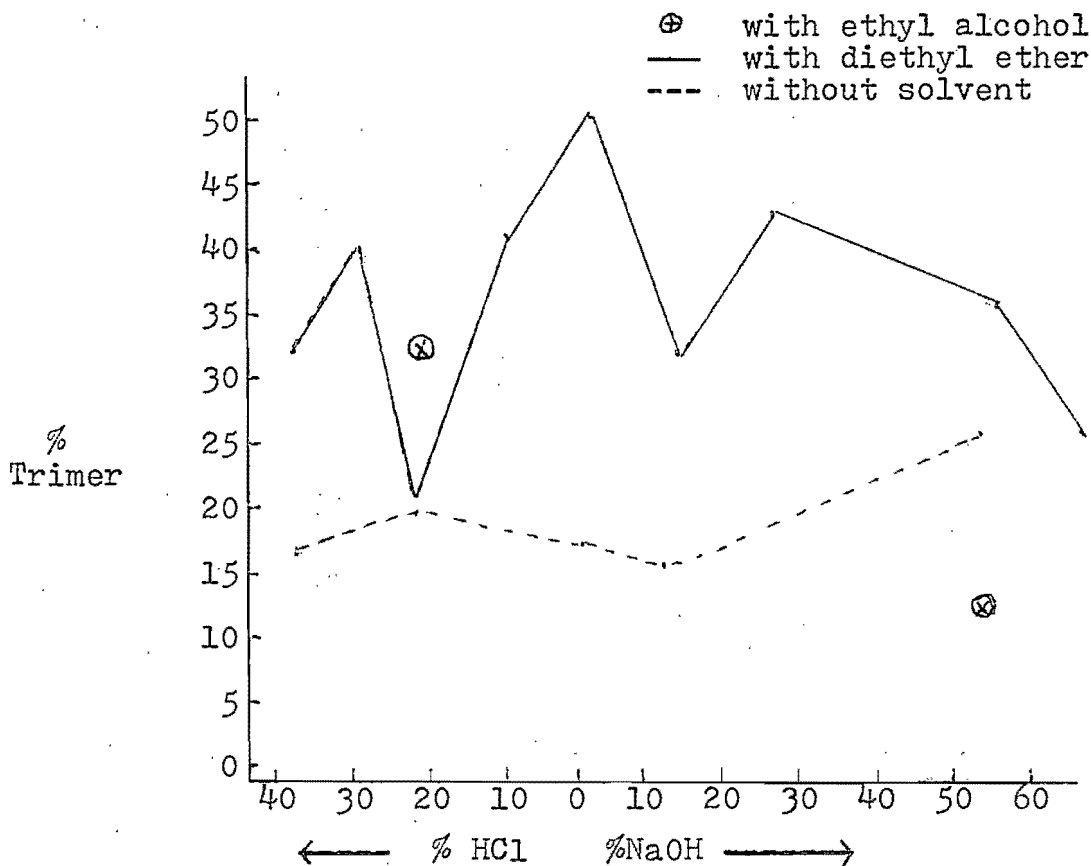
Table II: Percent Yield of Each Fraction and Percent Loss, Based of
the Total Theoretical Yield of Et_2SiO

Acid or Base Concentration	Solvent	% Trimer	% Inter- mediate	% Tetramer	% A	% B	% Loss (100 - (A+B))	Data Source
37% HCl	ether	32.8	15.4	19.3	67.5	11.9	20.5	Miller
37% HCl	none	17.9	5.4	0.0	23.3	19.9	56.8	Mulhern
24% HCl	ether	39.6	11.5	22.4	73.4	11.0	15.6	Miller
21% HCl	ether	19.6	7.3	11.6	38.5	3.8	57.7	Grisley
21% HCl	none	19.6	18.0	0.0	37.6	19.4	43.0	Anzlovar
21% HCl	alcohol	31.7	16.0	20.6	68.3	2.2	29.5	Rush
6.2% HCl	ether	40.2	6.8	15.3	62.3	17.6	20.2	Grisley
pure water	ether	49.7	14.1	6.5	70.3	16.5	13.2	Miller
pure water	none	17.5	7.5	7.5	32.5	12.0	55.5	Anzlovar
14.2% NaOH	ether	32.5	7.9	5.8	46.2	1.9	51.9	Kirner
14.2% NaOH	none	16.1	7.2	14.5	37.8	18.6	43.6	Mulhern
28.3% NaOH	ether	42.6	28.9	2.5	74.0	1.5	24.5	Kirner
53.6% NaOH	ether	34.7	29.6	0.0	64.3	1.3	34.3	Verbish
53.6% NaOH	none	25.1	27.9	2.8	57.4	0.6	42.0	Anzlovar
53.6% NaOH	alcohol	11.7	23.4	15.1	50.2	4.0	45.8	Rush
62.0% NaOH	ether	24.2	30.5	0.0	54.7	2.3	43.0	Verbish

A: Cyclic Distillable Material

B: Non-Distillable Material

Chart 1: % Trimer vs. Acid-Base Concentrations

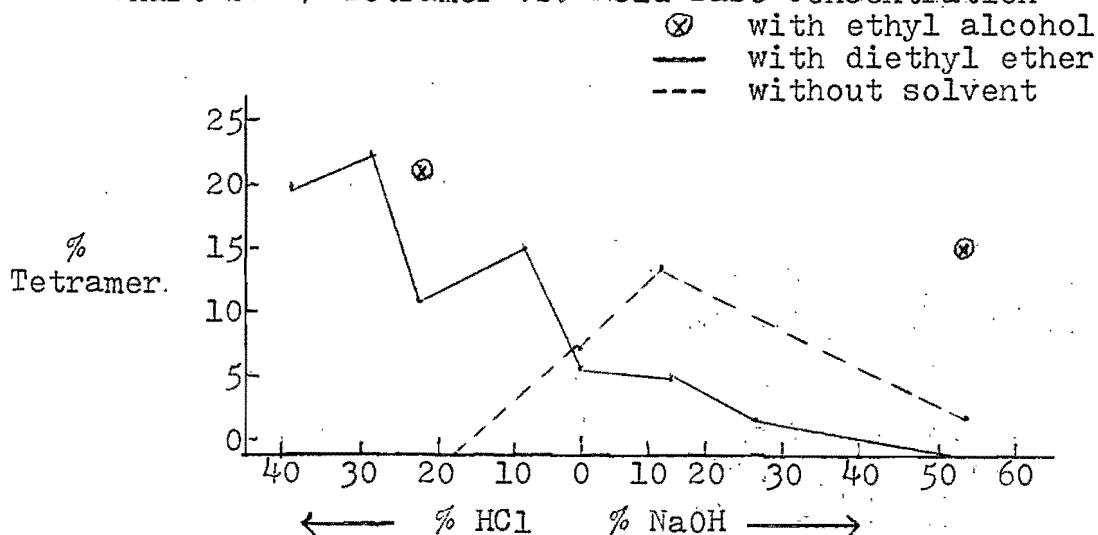


for two reasons. (1) As mentioned earlier, Lasocki and Mickalska (37) reported that when Et_2SiCl_2 is hydrolyzed in the presence of HCl with alcohol as solvent, the condensation of $\text{Et}_2\text{Si}(\text{OH})_2$ follows second order kinetics. There is every reason to believe that it will be the same with diethyl ether as solvent. (2) Ponomarev, et. al. (33) reported that in a circulating reactor operated at 300°C ., when Me_2SiCl_2 reacted with HCl and methyl alcohol, some methyl chloride was produced. It is well-known that methyl chloride and methyl alcohol

can react to produce dimethyl ether. Therefore, in a similar context, when ethyl alcohol is present there may also be present a certain concentration of diethyl ether.

Tetramer. As noted in Chart 2, when the water hydrolysis of Et_2SiCl_2 is performed with diethyl ether or ethyl alcohol as solvent in the presence of HCl or NaOH, the percentages of ethyl tetramer range from 22.4% to 0.0%. Using diethyl ether as solvent, the percentage of obtainable ethyl tetramer generally decreases as the medium changes from acid to pure water to base. It is evident that ethyl tetramer is not obtainable when diethyl ether is used in the presence of a high NaOH concentration.

Chart 2: % Tetramer vs. Acid-Base Concentration



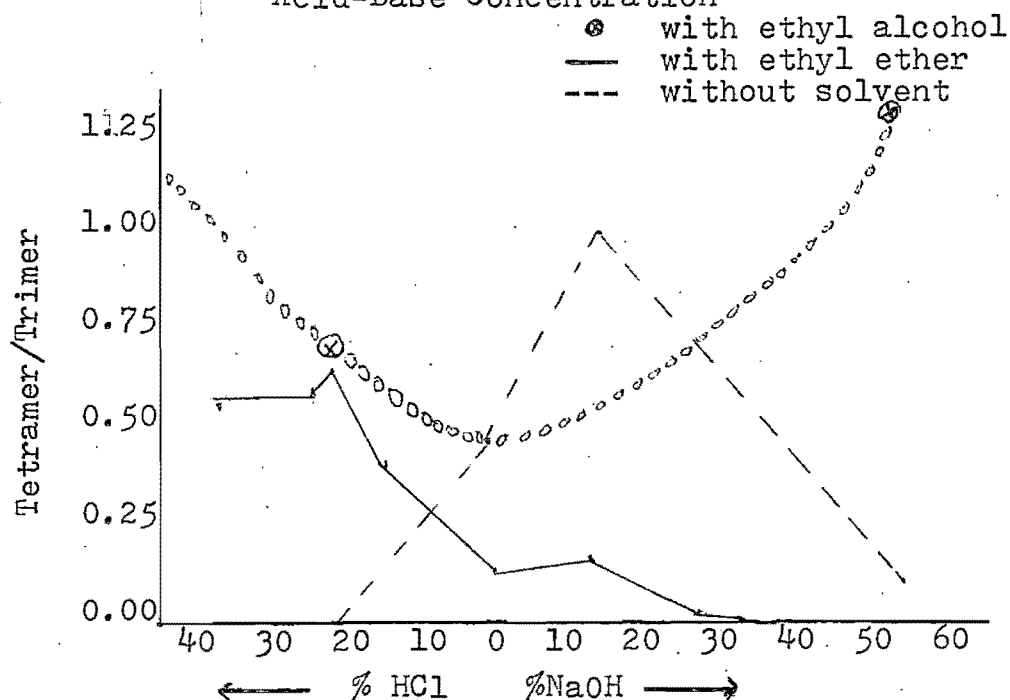
If the proposed conjecture of ethyl alcohol as solvent is true, alcohol in the absence of acid may have a definite effect on the yield of ethyl trimer and ethyl tetramer. It appears that when more points on the curve

pertaining to ethyl alcohol in the presence of NaOH are determined experimentally, ethyl trimer may be obtainable in good yield compared to the case of using diethyl ether as solvent.

Lasocki and Mickalska (38) reported that the addition of salts had a pronounced effect on the condensation rate of the diethylsilanediol intermediate in the presence of HCl and methyl alcohol as solvent. The possible formation of a methyl chloride salt is the main consideration here. It is interesting that the hydrolysis of Et_2SiCl_2 in the presence of 21% HCl concentration and alcohol as solvent yield a greater percentage of ethyl trimer and ethyl tetramer compared to the same hydrolysis with ethyl ether or no solvent.

Tetramer/Trimer Ratio. As noted in Chart 3, when using ethyl ether as solvent, this ratio generally decreases in a regular way from a weak acid concentration to a strong base concentration. It appears that when more points on the curve pertaining to ethyl alcohol are determined experimentally, the ratios may well be exemplifications of the reports of Dolay (13,14). His reports indicate that the hydrolysis of Et_2SiCl_2 yield maximum amounts of ethyl trimer when excess water with methyl alcohol is present in the hydrolysis. The best percentage yield of ethyl tetramer was produced when

Chart 3: Tetramer/Trimer Ratio vs.
Acid-Base Concentration



the hydrolysis was conducted in the presence of excess methyl alcohol with little quantity of original water (13).

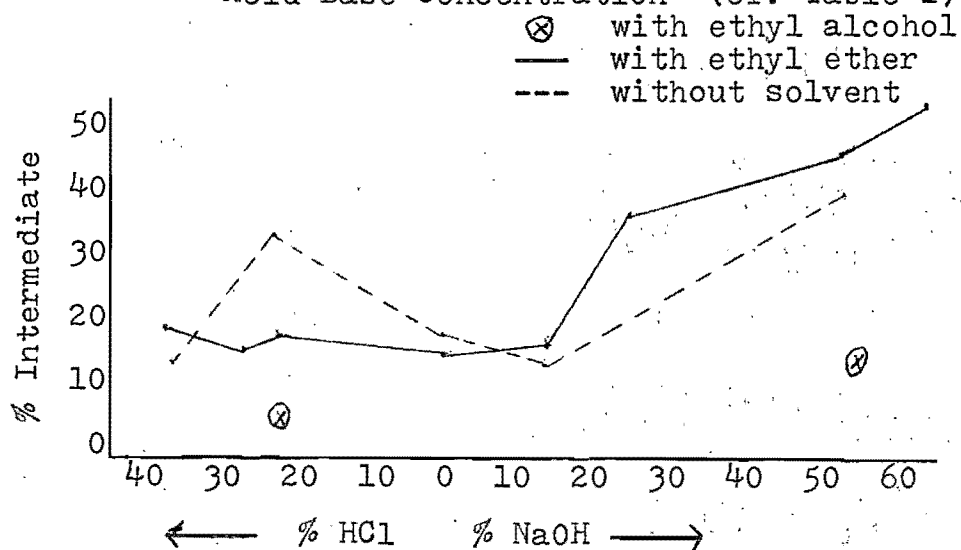
The projective data for ethyl alcohol as solvent can be indicated as drawn in Chart 3. The hydrolysis in the presence of ethyl alcohol increases the production of ethyl tetramer as compared to the same hydrolysis with ethyl ether or pure water as solvent.

Intermediate. The intermediate indicated in Tables I and II are not the intermediate-diols spoken of in Chapter I. Instead, this intermediate is simply the middle run between the distilled pure ethyl trimer and tetramer.

As noted in Chart 4, when using ethyl ether or ethyl

alcohol as solvent in the presence of HCl or NaOH concentrations, the percentage yield of the distilled intermediate ranges between 19% and 53% product. As HCl concentration increases, the percentage yield of intermediate increases. Ironically, it seems that the minimum amount of distilled intermediate precedes the maximum amount of pure ethyl tetramer. In the same manner, the maximum amount of distilled intermediate precedes the minimum amount of ethyl tetramer.

Chart 4: % Intermediate vs.
Acid-Base Concentration (cf. Table I)

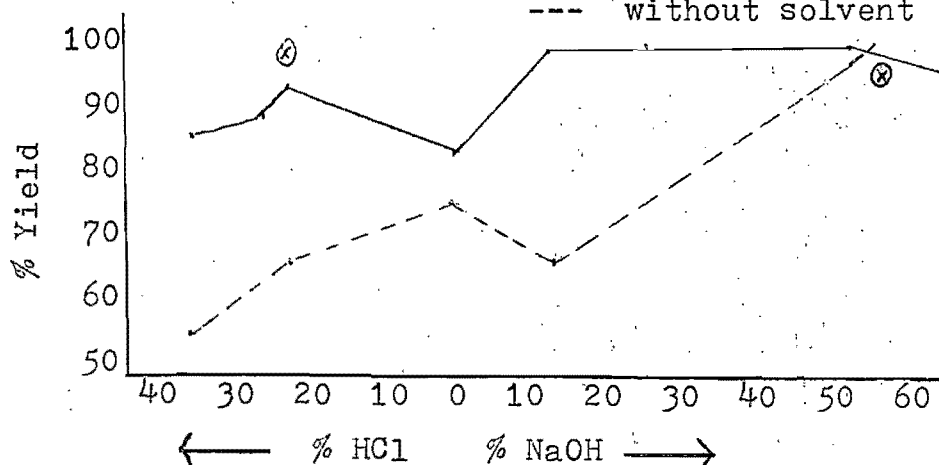


In using ethyl ether or ethyl alcohol as solvents in the presence of HCl concentrations, the yield of pure tetramer exceeds the yield of intermediate. In using either solvent in the presence of NaOH concentrations, the yield of intermediate exceeds the yield of pure tetramer. An experimentally controlled analysis of the

distilled intermediate material should be conducted so as to understand the types and amounts of organocyclosiloxanes that may comprise the distilled intermediate materials.

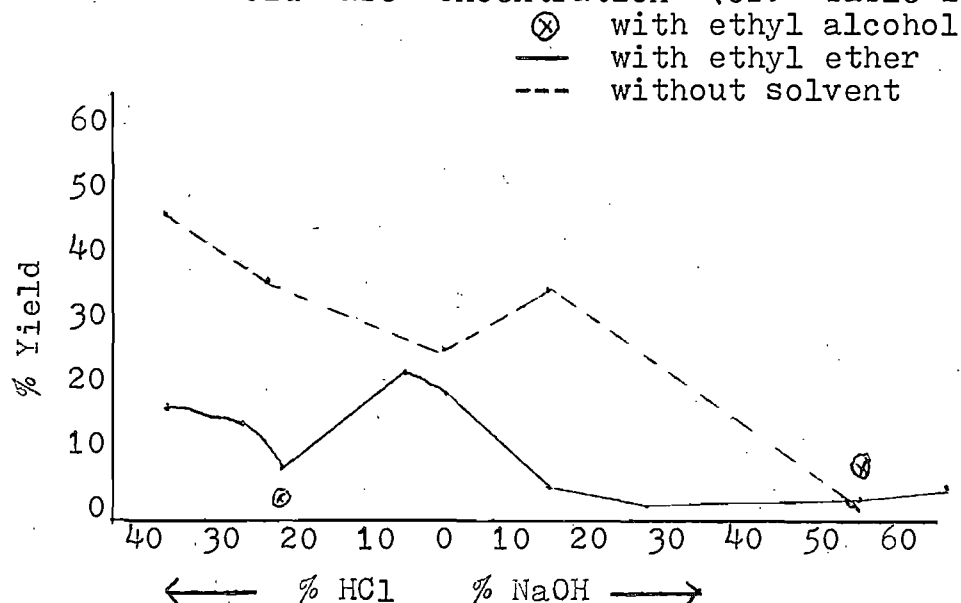
Total Cyclic Distillable Material and Non-Distillable Material. As depicted in Chart 5, the hydrolysis with ethyl ether as solvent in the presence of a base medium yields a greater percentage of cyclic distillable material than in the presence of an acid medium of the same concentration. As indicated in Chart 6, the opposite trends of acid and base mediums occur in the comparison of non-distillable materials.

Chart 5: % Cyclic Distillable Yield vs.
Acid-Base Concentration (cf. Table I)
⊗ with ethyl alcohol
— with ethyl ether
--- without solvent



The hydrolysis in the presence of an acidic medium with ethyl alcohol as solvent yields the greatest percentage of cyclic distillable material as compared to

Chart 6: % Non-Distillable Yield vs.
Acid-Base Concentration (cf. Table I)



the same hydrolysis with ethyl ether or no solvent.

However, the hydrolysis in the presence of a base medium with ethyl alcohol as solvent yields the lowest percentage of cyclic distillable material as compared to the same hydrolysis with ethyl ether or no solvents. The percentage yield of non-distillable material is extremely small when ethyl alcohol is used as solvent in the presence of an acid or base medium.

Emphasis on the Relation Between Table I and Table II. The titles of Charts 7 and 8 indicate the sources of the data portrayed in the Charts. The Charts also establish the definition of the term, Subdivision. Subdivision by subdivision, the curves in the two Tables are not necessarily similar. Within Chart 7 the curves

Chart 7: % Hydrolysis Products vs. Acid-Base Concentration, in Presence of Ethyl Ether (cf. Table I), Based on the Total Amount of Distillable Product.

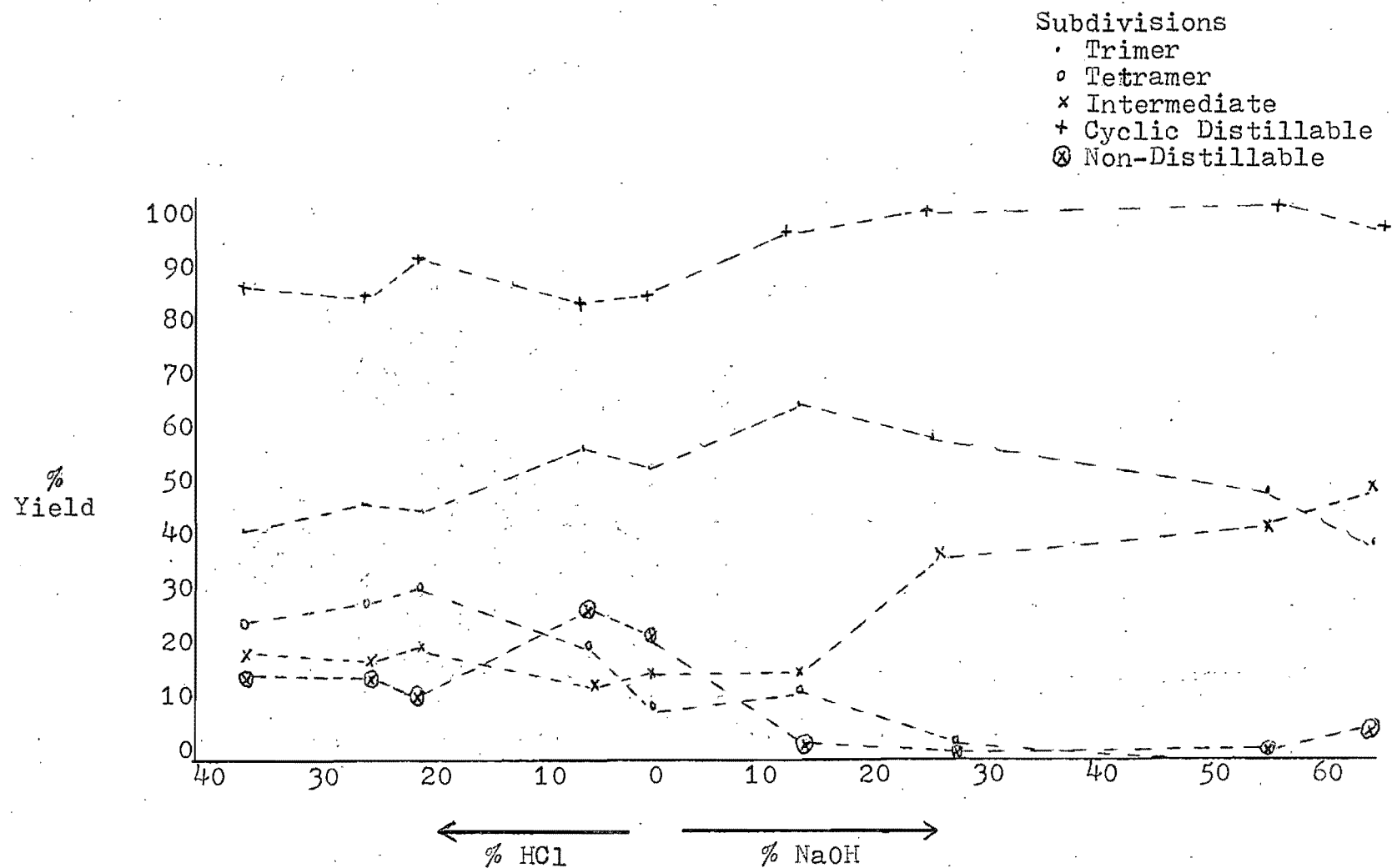
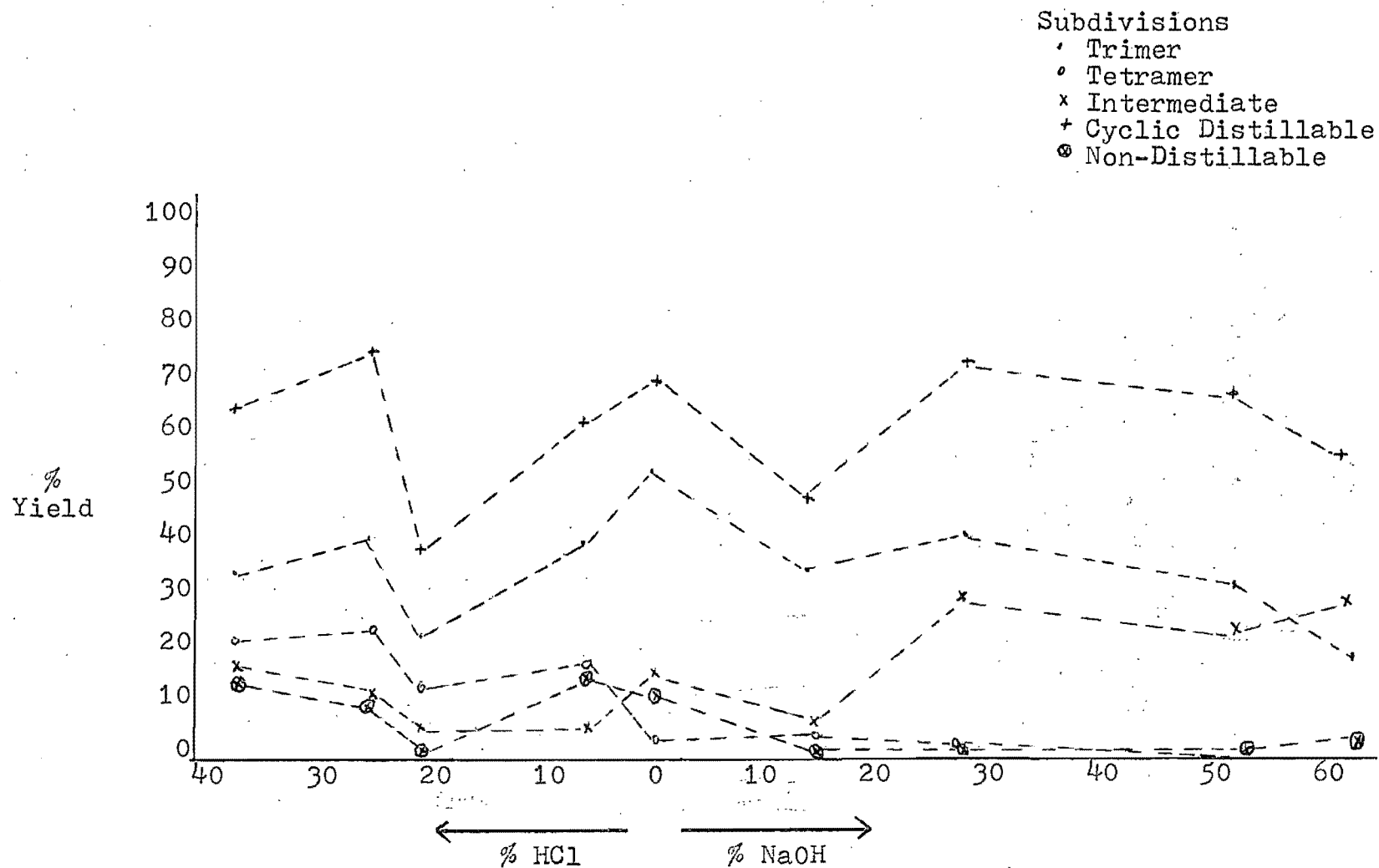


Chart 8: % Hydrolysis Products vs. Acid-Base Concentration, in Presence of Ethyl Ether (cf. Table II), Based on the Total Theoretical Yield of Et_2SiO .



for the percentages of cyclic distillable material and non-distillable material are shown to be reflections of each other. Within Chart 8 the corresponding curves are not reflections of each other, but instead reproductions. Considering Charts 7 and 8, the two curves for percentage of non-distillable material are quite similar. Because of the variation in these relationships, it is difficult to draw any firm conclusions.

Comparison of Earlier Work Without Solvent

Trimer. As is clear from Chart 1, for all acid and base concentrations the yield of trimer is less when no solvent is present than in the corresponding concentrations when ethyl ether was used as a solvent. The absence of solvent in all acid and base hydrolyses restricts the yield of trimer to a 9 point range of 16.1% to 25.1%.

Tetramer. As depicted in Chart 2, the absence of solvent in all acid and base concentrations restricts the yield of tetramer to 14.5% or less. For the hydrolysis without solvent, the greatest yield of tetramer is found in low concentrations of NaOH. No tetramer was found for the hydrolysis without solvent in HCl concentrations.

Tetramer/Trimer Ratio. As shown in Chart 3, without solvent, the tetramer/trimer ratio is 0.0 in concentrated

acid, increases to a maximum of 0.9 near the theoretical neutral point (40), and decreases to 0.1 in concentrated base. The shape of this curve is identical to that of the tetramer yield from the hydrolysis without solvent.

Intermediate. With or without solvent, as depicted on Chart 4, the percentage of intermediate increases with increasing NaOH concentration. With or without solvent, the increase is at about the same rate.

Without solvent, the percentage of intermediate tends to decrease with increasing HCl concentration. On the other hand, with ethyl ether, the percentage of intermediate generally increases with increasing HCl concentration. Since the conjecture indicates that ethyl alcohol may follow the same pattern as ethyl ether in concentrated HCl, the percentage of intermediate may generally increase with increasing HCl concentration in ethyl alcohol.

Total Cyclic Distillable Material and Non-Distillable Material. The percentages reported in Chart 5 indicate that the amount of cyclic distillable material generally increases as the medium changes from strong acidic to neutral to strong alkaline conditions without the use of solvent. The curve of percentages depicted in Chart 6 indicate that the amount of non-distillable material is directly opposite to that of cyclic distillable material of the same medium conditions. This is no surprise since

the percentages of the non-distillable material are based on the percentage of the total cyclic distillable amounts.

As indicated from Table II, the amount of cyclic distillable material is less for the hydrolysis without solvent as compared to the same hydrolysis with solvent. The reports of Patnode and Wilcock (4) indicate the same general observation with the hydrolysis of Me_2SiCl_2 . They reported that when the hydrolysis was conducted in 400 cc. ether and 400 cc. water, a yield of 98% distillable cyclic material resulted. However, 57% distillable cyclic material was obtained from the same hydrolysis without solvent in 600 cc. water. Moreover, Patnode and Wilcock (4) indicate that the type of medium in the hydrolysis without solvent has an effect on the total percentage yield of distillable cyclic products.

The St. Meinrad reports (cf. Table II) of the hydrolysis of Et_2SiCl_2 indicate that the presence of ethyl ether with pure water or with a high HCl concentration produced a substantially greater percentage of cyclic distillable products than the same hydrolyses without the presence of a solvent. However, the difference of the percentages of cyclic distillable products is not as great in the comparable hydrolyses with a high NaOH concentration. These results along with Chart 5 indicate that the amount or type of solvent and

the medium conditions have an effect on the hydrolysis.

Emphasis on the Relation Between Table I and Table II. The titles of Charts 9 and 10 indicate the sources of the data portrayed in the Charts. The Charts also establish the definition of the term, Subdivision. Subdivision by subdivision, the curves in the two tables are generally similar. Considering Charts 9 and 10, the two curves for percentages of cyclic distillable material are quite similar with the exception of the hydrolysis conducted in pure water. And also, the two curves for percentages of non-distillable material are quite similar, including the hydrolysis conducted in pure water.

It has already been established, that it is difficult to draw any firm conclusions from the variation of these relationships in Charts 7 and 8. Therefore, it is difficult to draw any firm conclusions on how the medium conditions with the amount or type of solvent have on the effect of the hydrolytic production of the distillable cyclic products.

Mechanism. For the hydrolysis of diethyldichlorosilane to form cyclic products there is definite evidence indicating the existence of a diethylsilanediol intermediate, but beyond that there is little definitive evidence regarding the specific reaction mechanism.

Lasocki (11) has articulated a hydronium ion chain

Chart 9: % Hydrolysis Products vs. Acid-Base Concentration, in Absence of Solvent (cf. Table I), Based on the Total Amount of Distillable Product.

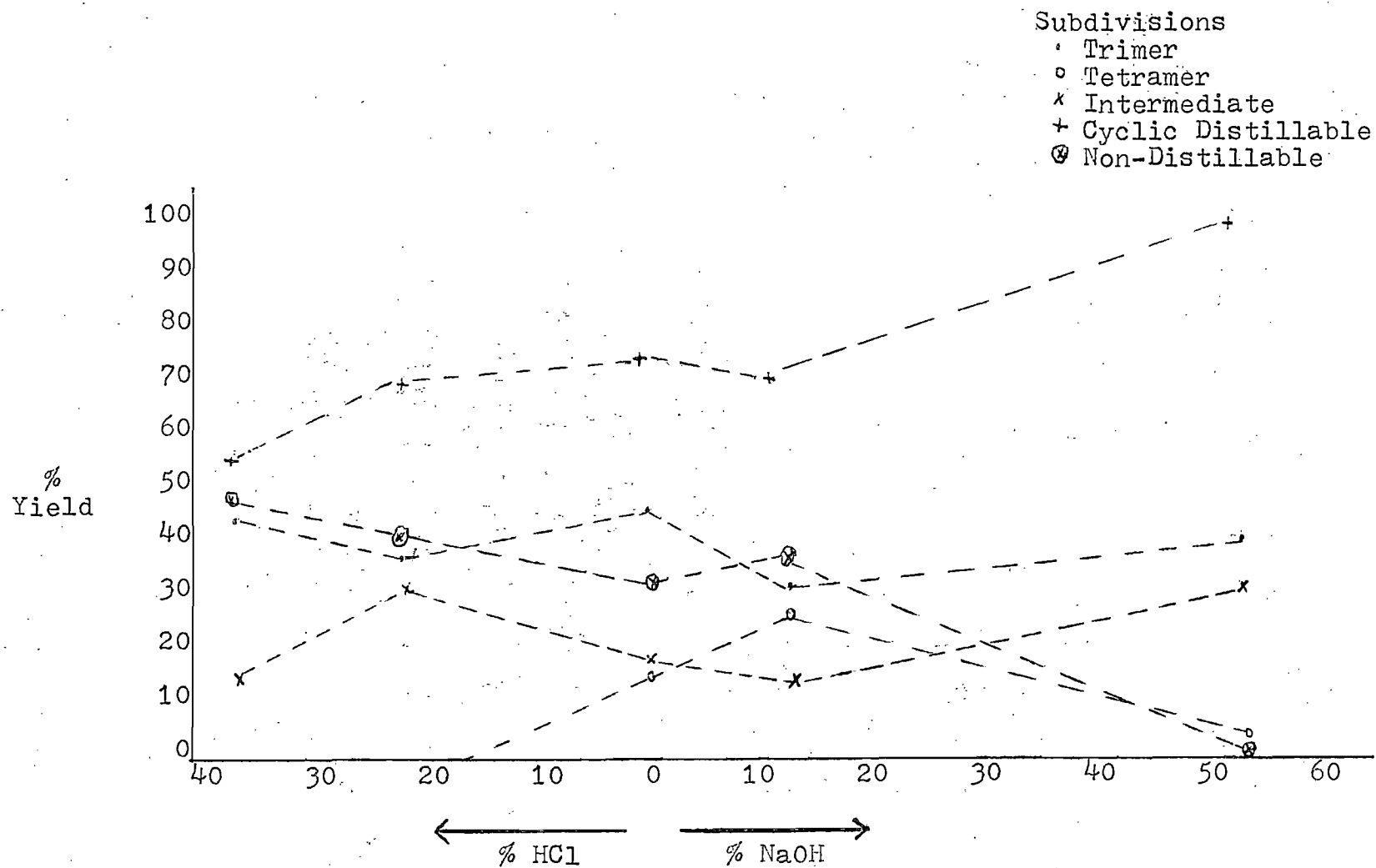
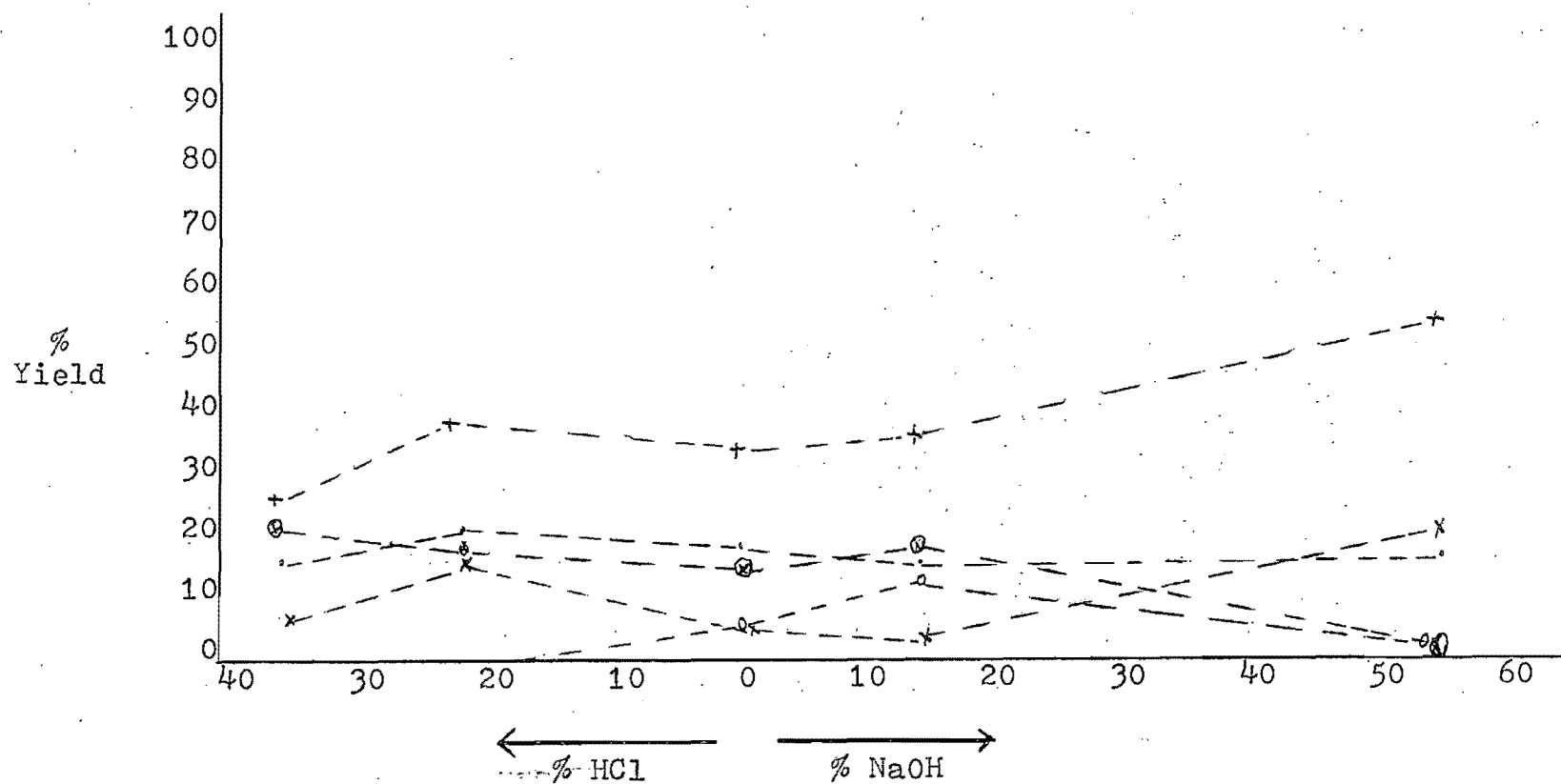
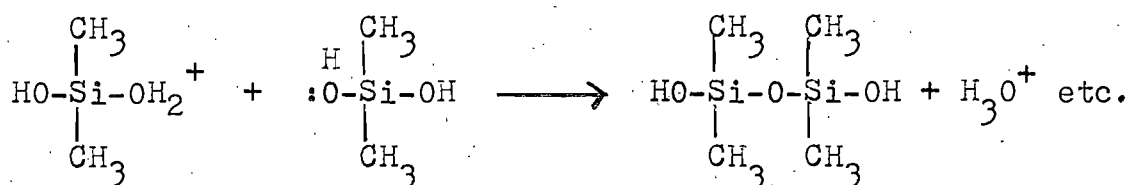
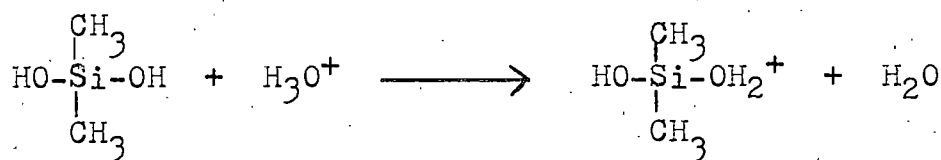


Chart 10: % Hydrolysis Products vs. Acid-Base Concentration, in Absence of Solvent (cf. Table II), Based on the Total Theoretical Yield of Et_2SiO .

Subdivisions
 · Trimer
 ○ Tetramer
 × Intermediate
 + Cyclic Distillable
 ⊙ Non-Distillable

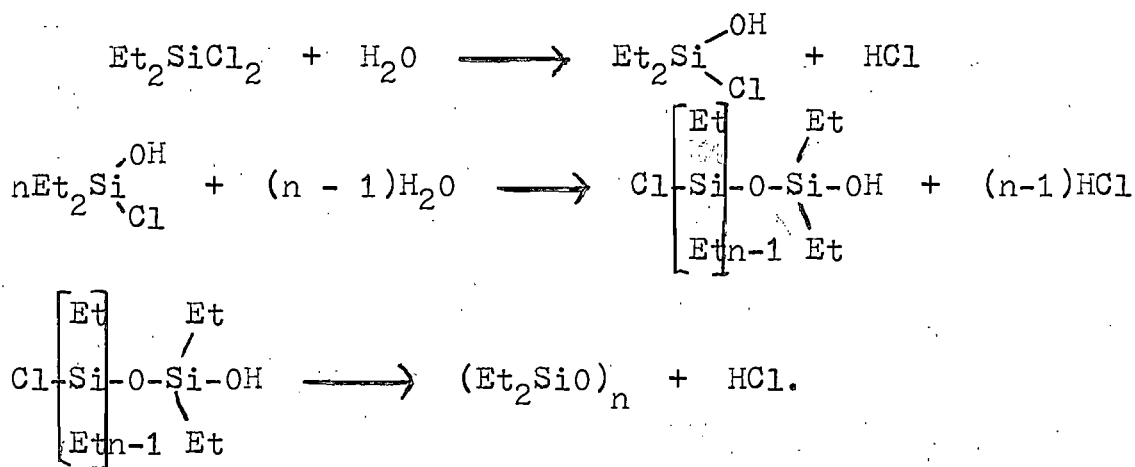


mechanism for the condensation of $\text{Me}_2\text{Si}(\text{OH})_2$:



Lasocki (11) does not mention the cyclization of the longer chains, but it would seem feasible that the longer chains could form cyclic products by splitting out H_2O .

Anzlovar (28) has suggested that a chlorosilanol-intermediate mechanism is compatible with observed data:



When the hydrolysis was conducted in 21% hydrochloric acid with ethyl alcohol as solvent, the results indicates (cf. Table II) that a higher percentage of cyclic distillable material was obtained than in the same hydrolysis with ethyl ether or no solvent. On the other hand, when the hydrolysis was conducted in 53.6% NaOH

with ethyl alcohol as solvent, the results indicate a lower percentage of cyclic distillable material than in the same hydrolysis with ethyl ether or no solvent.

Andrianov and Sokolov (9) state that the amount of cyclic product formed depends on the solubility of the intermediate, diethylsilanediol, in the medium; the better the solubility, the higher the yield of cyclic product. Following Andrianov and Sokolov (9), Anzlovar (28) conjectured that the amount of cyclic distillable product produced is dependent on the solubility of the chlorosilanol intermediate.

If either Andrianov, et. al. (9) or Anzlovars' (28) statement is universal, then it could well be that the silanol intermediates are more soluble in the presence of sodium hydroxide than in the presence of hydrochloric acid. The results mentioned in Table II indicate such a possibility. However, when more experimental data with ethyl alcohol is obtained, the silanol intermediates could well be found to be more soluble in the presence of hydrochloric acid with ethyl alcohol as solvent than in the same hydrolysis with ethyl ether or no solvent. Or, the silanol intermediates could well be less soluble in the presence of sodium hydroxide concentrations with ethyl alcohol as solvent than in the same hydrolysis with ethyl ether or no solvent.

A definitive statement of mechanism for these reactions require, among other things, that the relationship between solvent effect and media concentration be more clearly established for a wider range of solvents and media. Such information seems necessary before a more thorough investigation into the kinetics of the reactions can be undertaken.

SUMMARY OF PROJECTIONS

It has already been mentioned that the relationship between solvent effect and media concentrations ^{should} be more clearly established for a wider range of solvents and media. This paper proposes that two more hydrolyses should be conducted in the presence of ethyl alcohol as solvent; (1) with the presence of 37% HCl, and (2) with the presence of 14.2% NaOH. The percentage results that might be expected are as follows:

Trimer. Lasocki and Mickalska (37) reports that the addition of salts has a pronounced effect on the rate of condensation of diethylsilanediol intermediate in the presence of HCl and methyl alcohol as solvent. The possibility of methyl chloride salt is the main consideration here. The hydrolysis of Et_2SiCl_2 in the presence of 37% HCl concentration and alcohol as solvent should yield a greater percentage of diethyl trimer compared to the same hydrolysis in the presence of diethyl ether or no solvent.

Based on the water hydrolysis conducted in the presence of 53% NaOH concentration and ethyl alcohol, the percentage yield of ethyl trimer in the presence of 14.2% NaOH should be less than the same hydrolysis with ethyl ether or no solvent.

Tetramer. Based on the reports of Lasocki and Mickalska (38), the hydrolysis conducted in the presence of 37% HCl condensation and ethyl alcohol should yield a greater percentage of ethyl tetramer compared to the same hydrolysis with ethyl ether or no solvent. Based on the reports of Rush (34), the hydrolysis conducted in the presence of 14.2% NaOH and ethyl alcohol should yield a greater percentage of ethyl tetramer compared to the same hydrolysis with ethyl ether. However, it is questionable whether the hydrolysis in the presence of ethyl alcohol would yield a greater percentage of ethyl tetramer than the same hydrolysis without solvent.

Tetramer/Trimer Ratio. Dobay's (13,14) reports indicate that the hydrolysis of Et_2SiCl_2 in methyl alcohol and water yield maximum amounts of ethyl trimer when excess water compared to methyl alcohol is present in the hydrolysis. The best yield of ethyl tetramer is produced when insufficient water compared to methyl alcohol is present in the hydrolysis. Following Dobay (13,14) the ratio of tetramer to trimer may well be near 1.00 when the hydrolysis of Et_2SiCl_2 is conducted in the presence of 37% HCl concentration with ethyl alcohol as solvent. The ratio of tetramer to trimer may well be near 0.5 when the hydrolysis is conducted in the presence of 14.2% NaOH concentration with ethyl alcohol as solvent.

Mechanism. The silanol intermediates, diethylsilanediol or chlorosilanol, could be less soluble in the presence of sodium hydroxide with ethyl alcohol as solvent than in the same hydrolysis with ethyl ether or no solvent. On the other hand, the silanol intermediates could be more soluble in the presence of hydrochloric acid with ethyl alcohol as solvent than in the same hydrolysis with ethyl ether or no solvent. The two proposed hydrolyses should confirm the above conjectures.

Total Distillable Products. The conjectures in the discussion of the mechanism may indicate that when the hydrolysis is conducted in 37% HCl concentration with ethyl alcohol as solvent, the percentage yield of cyclic products may be greater than in the same hydrolysis with the presence of ethyl ether or no solvent. The percentage yield of cyclic products may be less when the hydrolysis is conducted in the presence of 14.2% NaOH with ethyl alcohol as solvent than in the same hydrolysis with the presence of ethyl ether or no solvent.

General Conclusion.

The percentage results briefly described in the present chapter are not conclusive. They are made available so that the actual results from the experimental hydrolysis may confirm or disprove them. This may lead to a clearer understanding as to the amounts of cyclic

structures produced by the hydrolysis of diethyldichloro-
silane.

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