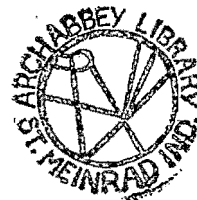


An Analysis of the Products of the Hydrolysis of
Diethyldichlorosilane as Influenced by Acids, Bases,
and Solvents, With Special Reference to Benzene as a Solvent

A Research Paper

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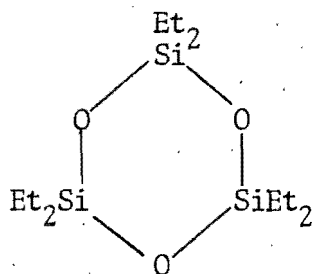
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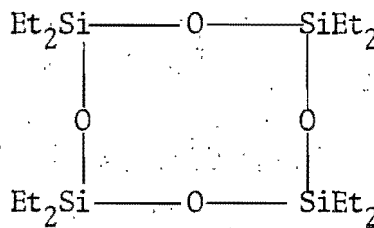
INTRODUCTION

The water hydrolysis of diethyldichlorosilane (Et_2SiCl_2) and the related compound, dimethyldichlorosilane (Me_2SiCl_2), is an exothermic reaction which yields linear and cyclic products containing silicon-oxygen linkages (1-21). At standard temperature and pressure diethyldichlorosilane is a clear liquid. The literature boiling point at these conditions is 129°C (1).

Hydrogen chloride is a by-product of the reaction. The cyclic products of primary concern in this study are hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane, which will be referred to as the ethyl trimer and ethyl tetramer respectively. The structures of the cyclic products are given below.



Ethyl Trimer



Ethyl Tetramer

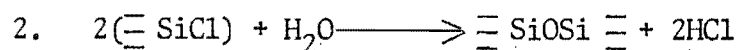
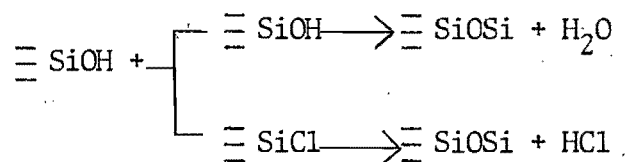
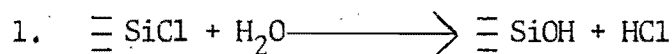
Various published (1-14) and unpublished (15-21) studies indicate that a great number of reaction variables affect the proportion of products resulting from the water hydrolysis of alkylhalosilanes. These variables include the presence of an acidic or basic medium; the amount of medium; the presence of a solvent; the nature and amount of solvent; the reaction temperature and pressure; the use of a catalyst; and the purity of the dihalide.

Most of the conditions influencing the proportions of the products of this hydrolysis favor the production of trimer and tetramer (1).

The existence of a linear dialkylsilanediol intermediate has been reported by several studies (1-4). Diethylsilanediol ($\text{Et}_2\text{Si}(\text{OH})_2$) crystallizes from ether as colorless, flat prismatic, monoclinic holo-hedral crystals (2). The solubility of the intermediate diol appears to affect the amount of cyclic volatile product formed (3). The mechanism for this diol will be discussed later, as well as its behavior using benzene, (C_6H_6), as a solvent.

Hydrolysis using pure water

For the hydrolysis of any chlorosilane, Shaffer and Flanigen (4) propose the following as possible reactions.



Applying this to a dialkyldichlorosilane, the possible products are $\text{R}_2\text{SiCl}(\text{OH})$, $\text{R}_2\text{Si}(\text{OH})_2$, $\text{Cl}(\text{R}_2\text{SiO})_x\text{R}_2\text{SiCl}$, $\text{Cl}(\text{R}_2\text{SiO})_x\text{R}_2\text{Si}(\text{OH})$, $(\text{OH})(\text{R}_2\text{SiO})_x\text{R}_2\text{Si}(\text{OH})$, and $(\text{R}_2\text{SiO})_x$.

Brewer and Haber (5) hydrolyzed Et_2SiCl_2 by adding it drop by drop to ice water to produce, on destructive distillation, cyclic $(\text{Et}_2\text{SiO})_n$, where $n = 3$ or 4 (obtaining the tetramer in greatest proportion). Hyde and DeLong (6) observed cyclic trimeric condensation products in the

hydrolysis of diethyldichlorosilanes. Nasser and Gertner (7) hydrolyzed fatty dichlorosilane derivatives which yielded cyclosiloxanes. Pathet (8) obtained low molecular weight poly(dimethylsiloxanes) by passing Me_2SiCl_2 and slight amounts of steam upward through a vertical column into a reactor maintained at 22-25°C. Andrianov and Sokolov (9) performed a thermometric tracing of the hydrolysis of R_2SiCl_2 (where R = Me, Et, Bu, Am). The complete hydrolysis with excess water takes place obtaining higher order siloxanes as well as the monomer, R_2SiO , which is capable of polymerization. They noted that insufficient water yields a halosilanol which condenses to siloxanes. This stepwise condensation to siloxanes with an insufficient amount of water yields a multiplicity of products. The results seem to indicate that a limited amount of water results in only a partial hydrolysis of dialkyldichlorosiloxanes. In reviewing the literature, Rochow (10) states that cyclic compounds such as $(\text{Et}_2\text{SiO})_n$ are typical products of the hydrolysis of Et_2SiCl_2 .

In research on methylpolysiloxanes, Patnode and Wilcock (11) added 4 liters of dimethyldichlorosilane slowly to 12 liters of water at 15-20°C with vigorous stirring. The oily product was fractionally distilled at atmospheric pressure and at 20mm., yielding cyclic compounds of the type $(\text{Me}_2\text{SiO})_n$, where n ranged from 3 to 110. The methyl tetramer was 42.0% of the product, by far the largest identified fraction.

In similar research, Ostlick (12) added 555 grams of diethyldichlorosilane to 130 grams of distilled water, using the methods of Patnode and Wilcock, and obtained from the hydrolysis a higher yield of ethyl trimer (15%) and a lower yield of ethyl tetramer (30%) than Patnode and Wilcock obtained from the methyl counterpart. Much of the starting

material, Et_2SiCl_2 , was recovered unchanged as well as a large amount of non-volatile material.

Acid-base catalysis

Patnode and Wilcock (11) in their earlier studies of dialkyldichlorosilanes concluded that acid or base in the hydrolysis media had an effect on the proportion of low molecular weight product formed. For example, in the case of dimethyldichlorosilane an acidic medium generally increased the proportion of the trimer, and an alkaline medium had the opposite effect. For example the hydrolysis of Me_2SiCl_2 in water yielded 57% methyl trimer, and hydrolysis using a 6N HCl solution gave 71% trimer. Conversely the hydrolysis with 6N NaOH solution gave a 37% methyl trimer. Hyde and DeLong (13) observed that the formation of a cyclic trimer from diphenylsilanediol is promoted by the presence of aqueous HCl, ammonia, or small amounts of aqueous alkali.

Ostdick (12) added diethyldichlorosilane with ether to 0.7M HCl solution and produced the ethyl trimer in unusually high proportion. The product was 80% ethyl trimer and 11% ethyl tetramer. On the other hand diethyldichlorosilane and concentrated HCl reacted at 0°C for 1 hour produced only 50% hydrolysis. In the above study George, Sommer and Whitmore (14) said the main products were "higher dialkyldichlorosilanes." Miller et al., (15-21) in a joint unpublished study show that precise effects of solvents and acidic or basic media are not clearly known or not easily predictable. However certain trends were observed and will be discussed further in the following chapter.

Miller (15) produced ethyl trimer and ethyl tetramer in a hydrolysis of Et_2SiCl_2 using a 37% HCl solution and ether as a solvent. He repeated

the hydrolysis using a 24% HCl solution, to produce similar results of trimer and tetramer. Mulhern (20) in the same study performed the hydrolysis with a 37% HCl solution in pure water, the trimer was the larger portion of the product and no tetramer was produced. Grisley (16) used a 21% HCl solution along with ether as a solvent producing trimer and tetramer supporting Miller's claims. Employing a still lower percentage HCl solution (6.2%) in ether solvent he recorded a high percentage of trimer and also more tetramer. Anzlovar (19) repeated the hydrolysis using the 21% HCl solution without the use of an organic solvent and found the trimer in fair proportion, but no tetramer. Rush (21) then repeated the hydrolysis, but added alcohol as a solvent to the 21% HCl solution to yield a close ratio of trimer to tetramer.

Cyclic products are also derived from the hydrolysis of Et_2SiCl_2 in a basic medium. Ostdick (12) hydrolyzed Et_2SiCl_2 using a 5.6 M sodium hydroxide solution to produce 15% ethyl tetramer and 30% ethyl trimer. Wenske, Berwald, and Teischmann (22) hydrolyzed Me_2SiCl_2 with potassium hydroxide under a vacuum at 100-200°C to produce the methyl tetramer. The most extensive study containing a marked amount of data for basic media effect on the proportion of cyclic hydrolysis products, is currently unpublished. Miller (15), Grisley (16), Kirner (17), Verbish (18), Anzlovar (19), Mulhern (20), and Rush (21), have hydrolyzed diethyldichlorosilane in various organic solvents over a range of aqueous sodium hydroxide concentrations. The largest percentage of ethyl trimer (42.6%) was produced from the hydrolysis of Et_2SiCl_2 using diethyl ether as a solvent in a theoretically calculated concentration of sodium hydroxide that would (theoretically) neutralize the hydrogen chloride produced as a

by-product during the hydrolysis (17). The yield of the ethyl trimer in all concentrations but one (53.6% NaOH), exceeds the yield of ethyl tetramer, with or without solvent.

Solvent effects

Numerous reports have confirmed that the nature, type, and amount of solvent used in the hydrolysis has an effect on the proportion of products produced. Hexaethylcyclotrisiloxanes were prepared by Dobay (23-24) in the hydrolysis of Et_2SiCl_2 using methyl alcohol and water as solvents. A 81.0 gram yield of the trimer was obtained. He also prepared octaethylcyclotetrasiloxanes by a controlled hydrolysis of Et_2SiCl_2 added to a large amount of methyl alcohol and less water while stirring vigorously. The yield of tetramer was 101.5 grams. Sokolov and Akimova (25) prepared ethylchlorocyclosiloxanes by hydrolysis of EtSiHCl_2 in aqueous ethyl alcohol at 17°C . Sokolov, Andrianov, and Akimova (25) added MeSiHCl_2 to 200 grams of ethyl alcohol and water to produce a 96% mixture of cyclic siloxanes.

Employing the methods of Miller et al. (15-21) in the unpublished study, Rush (21) hydrolyzed Et_2SiCl_2 using ethyl alcohol as a solvent in both acidic and alkaline media. Using a 21% HCl solution and ethyl alcohol as a solvent Rush obtained 31.7% ethyl trimer and 20.6% ethyl tetramer. Next in a 56.6% NaOH solution using the same solvent he obtained 11.7% trimer and 15.1% tetramer.

McCusker and Greene (27) added diethylisopropoxychlorosilane dropwise to potassium hydroxide in isopropyl alcohol below 20°C to produce 25% trimer and 49% tetramer. Miller et al. (15-20), in their unpublished investigation of dialkyldichlorosilanes employed ether as a solvent in

the hydrolysis of Et_2SiCl_2 along with various concentrations of acids and bases as well as pure water. Several trends appeared as a result of the diverse combinations of acid-base concentrations in the solvents. The largest percentage of ethyl trimer (49.7%) was produced using the ether solvent and no added acid or base. The lowest percentage of trimer was found using ethyl alcohol as a solvent with a strong basic solution, that percentage being 11.7%. However the greatest percentage of ethyl tetramer (22.4%) was obtained in ether solvent with the 24% HCl solution. The lowest percentage yield (0%) was in ether solvent and a strong NaOH solution (and several cases where no solvent was present).

Karlin et al. (28), prepared organosiloxanes and ethylene chlorohydrin by hydrolyzing organochlorosiloxanes in the presence of ethylene oxide solvent. York and Bailey (29) hydrolyzed (H_2SiCl_2) in hydrocarbon-ether solution, a mixture of 70% C_5H_{12} and diethyl ether to produce cyclopoly siloxanes. Andrianov and Yakushkina (30) conducted the hydrolysis of Et_2SiCl_2 and PhSiCl_3 with water in the presence of diethyl ether, benzene, or acetone. The solvents were observed to affect the OH group context of the cyclic products in the order: diethyl ether > acetone > benzene. The highest molecular weight products were obtained when benzene was employed as a solvent.

Kurlova, Dmokhovshaya, Yuzhelevakis, Kagan, and Larionova (31) hydrolyzed silanediols and dialkyldichlorosilanes in amine and organic solvents to yield organocyclotrisiloxanes. Patnode and Wilcock (11) added 33 moles of methyl homolog to 66 moles of water at 15 to 20°C with vigorous stirring to produce only 0.5% methyl trimer; but 42.0% methyl tetramer. In similar research, employing the same general methods as Patnode and Wilcock, Ostdick (12) hydrolyzed Et_2SiCl_2 with an excess of

0.2 moles of water. He obtained 15% ethyl trimer and 30% ethyl tetramer as primary products of the reaction, as well as a large amount of the starting dialkyldichlorosilane and a higher-boiling product.

Anzlovar (19) using the same procedure as Miller (15), Grisley (16), Kirner (17), and Verbish (18), obtained 17.5% ethyl trimer and 7.5% ethyl tetramer as primary products from the pure water hydrolysis of Et_2SiCl_2 without any organic solvent. Continuing the part of this study without the use of organic solvent, Anzlovar (19) and Mulhern (20) in their hydrolyses of Et_2SiCl_2 using various acid-base concentrations, found that the yield of trimer fell in most cases, while producing a variety of changes in the yield of tetramer. It remained under 15% in all cases, and in two instances of high acidic medium no tetramer was found.

Mechanism: The Intermediate Diol

In Rochow's discussion (32) of Kipping's early publications on organosilicon compounds, an important intermediate, diphenylsilanediol, was reported. From the hydrolysis of diphenyldichlorosilane, Kipping observed the intermolecular condensation of the silanediol to cyclic and linear siloxanes. The hydrolysis of dialkyldichlorosilanes is a more vigorous reaction. Therefore the dialkylsilanediols were not isolated at first, but the existence of such an intermediate was assumed on the basis of the diphenylsilanediols.

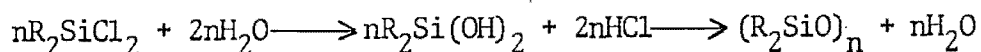
Andrianov and Sokolov (3) in 1952 employed thermometric tracing as a method of proving the existence of an intermediate silanol in the hydrolysis of dialkyldihalosilanes. Hydrolysis with insufficient water gives a halosilanol which condenses stepwise to siloxanes. With excess water

the complete hydrolysis takes place; however the stepwise hydrolysis is not observed but assumed on the basis that the hydrolysis produces a variety of products. Hyde and DeLong (6) in a study concluded that the condensation of an organosilanediol produces cyclic structures as well as linear ones. Thus the cyclic trimer and tetramer were among the first molecular types to be isolated from mixed condensation products of diphenylsilanediol.

Georgio, Sommer, and Whitmore (33) were the first to isolate diethylsilanediol by carefully controlling the conditions in the hydrolysis of Et_2SiCl_2 in dry ether solvent added to a 1.5N alkali solution, at a low temperature with a short reaction time. A 65% yield of the intermediate diol was produced. Other hydrolyses included Et_2SiCl_2 in ether solvent with a saturated aqueous NaCl solution at $0-5^\circ\text{C}$ to give a 40% $\text{Et}_2\text{Si}(\text{OH})_2$. Saratov, Reikhsfel'd, Zakomoldina, and Kremniorg (34), produced diethylsilanediol and hydrogen gas in the reaction of Et_3SiH with ethyl alcohol-sodium ethoxide in dioxane, methylcyanide and $\text{P}(\text{O})(\text{NMe}_2)_3$. Araki and Osuga (35) hydrolyzed Me_2SiCl_2 to yield $\text{Me}_2\text{Si}(\text{OH})_2$, the dimethylsilanediol. Hydrolysis of $\text{Et}_2\text{Si}(\text{OAc})_2$ produced the diethylsilanediol for Adrianov and Zhdonov (36).

Gueyne and Duffaut (37) started with Et_2SiCl_2 under hydrolysis and polycondensation and produced siloxane polysilanol, $\text{HOSiEt}_2(\text{OSiEt}_2)_n\text{OSiEt}_2\text{OH}$. Shostokovskiy, Kochkin, Kondrat'ev, and Rogov (38) obtained Et_2SiOH_2 by adding NaOH or KOH to the hydrolysis of Et_2SiCl in ether and dry ether along with 6 drops of phenolphthalein below 40°C .

The intermediate diol is vital to the proportion of products in the hydrolysis of dialkyldihalosilanes. The following simple reaction path has been proposed:



During the studies of the mechanism of HCl and HClO₄ catalysis in the condensation of Et₂Si(OH)₂ in dioxane, the effects of additional small amounts of methyl alcohol, isopropyl alcohol, and phenol as well as LiBr, Bu₄NI, and LiClO₄ were measured. In this study Lasocki and Michalska (39) discovered that at high concentrations of alcohols, the condensation was found to proceed smoothly according to the second order kinetics up to 15-20% conversion. Addition of salts had a pronounced effect on the rate of condensation catalyzed by HCl.

In a rate-acidity correlation in condensation of diethylsilanediol in dioxane, Lasocki and Michalska (39) found that the effect of water on the condensation of Et₂Si(OH)₂ depends on the acid used as a catalyst. The activation energies of the silanediol condensations were determined by several water concentrations. These activation energies were very low, increasing with H₂SO₄, and were much higher, almost constant, when HClO₄ was employed as a catalyst.

Andrianov and Sokolov (3) reported that generally the amount of cyclic product formed depends on the solubility of the intermediate R₂Si(OH)₂ in the medium, the better the solubility the higher the yield of cyclic products. They measured the solubility of Et₂Si(OH)₂ in grams per 100 ml. of solvent at 20°C. In water the solubility is 9.7-10.8 g/ml; in ethyl alcohol 67.3-67.5 g/ml; 50% ethyl alcohol 38.8 g/ml; 25% ethyl alcohol 13.5 g/ml; methyl alcohol 111.9 g/ml; butyl alcohol 33.8 g/ml; isoamyl alcohol 23.0 g/ml; diethyl ether 10.5 g/ml; acetone 29.7-30.4 g/ml; benzene 1.12 g/ml; petroleum ether 0.35 g/ml; insoluble in carbon tetrachloride, nitrobenzene, toluene, xylene, phenyl chloride.

$\text{Et}_2\text{Si}(\text{OH})$ does not condense even after 24 hrs. in N acetic acid or 12% Ammonium hydroxide, but is rapidly condensed in 0.1N hydrochloric acid or 0.1N sodium hydroxide. Nitric acid and sodium hydroxide are more effective than are hydrochloric or sulfuric acids; no condensation takes place in solutions of inorganic salts. Solubility of $\text{Et}_2\text{Si}(\text{OH})_2$ in water rises from 5% at 0° to 16% at 40° .

Rochow (40) in his discussion of Kipping's earlier works, states that, $[\text{R}_2\text{Si}(\text{OH})_2]$, these silanols condense intermolecularly to form polymeric organosiloxanes. The rate of their condensation is governed principally by the size of the alkyl group.

DISCUSSION

In this continuation of the local study concerning the water hydrolysis of diethyldichlorosilane (15-21), a somewhat thorough attempt will be made to summarize and analyze the data collected thus far. Hopefully, as a result of this further examination, a clearer view of the problem will be obtained by finding the conditions under which the trimer and tetramer may be obtained. In addition, there will be a discussion of the possible trends not yet mentioned by previous workers; as well as a summary of the trends and conclusions of Miller (15), Grisley (16), Kirner (17), Verbish (18), Anzlovar (19), Mulhern (20), and Rush (21).

Comparisons will be made to show conflicting trends as well as to support the existence of other trends. The mechanism and solubility of the diol intermediate will be treated in still another section of this chapter.

Product Trends for Hydrolysis Without Solvent

On examination of the data available in this study, there are five cases where the hydrolysis was performed without employing the use of an organic solvent (cf. Table I). Of the five runs, two were carried out in acidic medium, one, in pure water (however the overall hydrolysis was acidic because the hydrolysis produces HCl as a byproduct), and the final two were performed in a dilute then more concentrated basic medium.

Of these hydrolyses using no organic solvent, certain trends are apparent. In the acidic medium, no tetramer was produced. In the most basic medium, the percentage tetramer is very low. As the base concentration decreases, the amount of tetramer increases considerably, and the

TABLE I: Percent Yield of Each Fraction and Percent Loss, Based on the Total Theoretical Yield of Et_2SiO

Acid or Base Concentration	Solvent	% Trimer	% Tetramer	% Cyclic Volatile A Material	% Non- Volatile B Material	% Loss (100 - (A+B))	Data Source
37% HCl	ether	32.8	19.3	67.5	11.9	20.5	Miller
37% HCl	none	17.9	0	23.3	19.9	56.8	Mulhern
24% HCl	ether	39.6	22.4	73.4	11.0	15.6	Miller
21% HCl	ether	19.6	11.6	38.5	3.8	57.7	Grisley
21% HCl	none	19.6	0	37.6	19.4	43.0	Anzlovar
21% HCl	alcohol	31.7	20.6	68.3	2.2	29.5	Rush
6.2% HCl	ether	40.2	15.3	62.3	17.6	20.2	Grisley
pure water	ether	49.7	6.5	70.3	16.5	13.2	Miller
pure water	none	17.5	7.5	32.5	12.0	55.5	Anzlovar
14.2% NaOH	ether	32.5	5.8	46.2	1.9	51.9	Kirner
14.2% NaOH	none	16.1	14.5	37.8	18.6	43.6	Mulhern
28.3% NaOH	ether	42.6	2.5	74.0	1.5	24.5	Kirner
53.6% NaOH	ether	34.7	0	64.3	1.3	34.3	Verbish
53.6% NaOH	none	25.1	2.8	57.4	0.6	42.0	Anzlovar
53.6% NaOH	alcohol	11.7	15.1	50.2	4.0	45.8	Rush
62.0% NaOH	ether	24.2	0	54.7	2.3	43.0	Verbish

ratio of trimer to tetramer is within less than two percentage points apart favoring the trimer, where there had been from 17.9 to 22 percentage points between the two in favor of the trimer in other cases. To conclude it seems as though in more than half of the cases, the absence of organic solvent has a negative effect on the production of both the trimer and tetramer.

Supporting this is the fact that the amount of cyclic volatile material decreased to its lowest percentage in four out of the five runs without organic solvent. In the cases of the acidic solutions, the pure water, and the dilute sodium hydroxide concentration, the percentages of cyclic volatile material are low compared to the amount of cyclic product formed throughout the study (15-21). All four of these hydrolyses failed to produce more than 19.6% trimer. Two of the hydrolyses, in the acidic media, produced no tetramer and the remaining two increased in tetramer yield slightly. In the hydrolysis involving the strong basic conditions with no organic solvent, the percentage of cyclic volatile material exceeded the other four runs. Yet only half of this modest yield was ethyl trimer and a minimal amount was tetramer. In this case also, the trimer exceeded 19.6%. All of the percentages of trimer in the hydrolyses without organic solvent are lower than the average yield of trimer in this study, the average being 28.5%.

The Comparison of Product Trends for Hydrolyses Using Diethyl Ether as a Solvent.

Concerning the hydrolysis of diethyldichlorosilane using diethyl ether as a solvent several trends are evident as the medium changes from strong acid to dilute acid, pure water, dilute base, strong base. The

percentage of trimer varies with the concentration of the hydrochloric acid in diethyl ether. In general, as the acid concentration increases the percentage of trimer decreases. Conversely as the concentration decreases to dilute acid then to pure water, the percentage of trimer rises to 49.7%. This is the highest yield of trimer in the study. Following a similar pattern, the mild basic medium and ether solvent hydrolyses, produced practically the same percentages of trimer as did the dilute acid and ether hydrolysis. As the medium increases to stronger basic concentrations, the percentage of trimer decreases. In the case of the ethyl tetramer there is a general decline in the percentage from strong acid to strong base. The percentage tetramer declines steadily from 22.4% in strong acid to none in strong basic conditions. From these trends it appears that the hydrolysis not only depends on the presence of an organic solvent (as concluded in the previous section without solvents); but also the acid-base concentrations.

The Comparison of Product Trends for Hydrolyses Using Ethyl Alcohol as a Solvent

Thus far in the study, ethyl alcohol has only been used as a solvent in the two runs by Rush (21). Once ethyl alcohol was used in the hydrolysis of diethyldichlorosilane with a 21% hydrochloric acid medium, and in a second run with a strong sodium hydroxide medium. In both cases the ethyl tetramer was among the higher percentage yields in this study. Moreover in the strong sodium hydroxide medium and ethyl alcohol, the percentage of tetramer exceeded the percentage of trimer for the first time in the study. In fact this is also the lowest percentage yield of trimer (i.e. 11.7%) produced in the study. The trimer and tetramer

production in ethyl alcohol solvent seems to be affected by the acid-base concentrations when compared with all of the data. In the runs with acidic medium with no solvent, no tetramer was produced and under 20% trimer was obtained. Using the ethyl alcohol and same acidic conditions, the percentage of trimer increased considerably and the amount of tetramer produced was only 1.8 percentage points from being the highest yield of tetramer in the study.

In the 53.6% base medium using ether as a solvent 34.7% trimer was yielded and no tetramer was produced. Under these same basic conditions with ethyl alcohol as a solvent the trimer dropped to the lowest yield (as stated above), and the tetramer increased to a relatively high amount. Conversely, at the other end of the scale, the 21% acidic medium using ethyl alcohol solvent produced the same results as the 37% acidic medium and diethyl ether as a solvent.

Comparison of Diethyl Ether and Ethyl Alcohol to No Solvent

There are two obvious results that are apparent when comparing the hydrolyses using organic solvents and the hydrolyses not using the solvents. The production of cyclic volatile material drops well below the 50% mark in four out of the five runs not employing the solvent, whereas in the case of diethyl ether only two out of nine runs are below 50% and both ethyl alcohol runs are above the 50% mark (cf. Table I). Hence, the solvent definitely has a tremendous effect on the amount of distillable product. In addition, the percentage yield of the ethyl trimer decreases substantially without the employment of the organic solvent, diethyl ether in most cases. In one case the runs without solvent exceed the run using ethyl alcohol and strong base, in the production of trimer. In the

other hydrolysis using ethyl alcohol and acid medium, the production of trimer is greater than those hydrolyses employing no solvent.

At one extreme, tetramer is favored in the strong acidic concentrations and ether solvent, then declines to no tetramer in the strong base and ether solvent. At the other extreme, tetramer is favored in one hydrolysis without solvent in the basic concentrations, and no tetramer is produced in the strong acidic conditions without solvent. Ethyl alcohol and/or acid-base concentrations favor the tetramer yield.

All of these trends and conclusions have also been noted by Miller (15), Grisley (16), Kirner (17), Verbish (18), Anzlovar (19), Mulhern (20), and Rush (21). In addition Kirner (17), Miller (15) and Verbish (18) note that most of the reports discussed previously on the hydrolysis of dialkyldichlorosilanes using salts in the medium reported a minimum of cyclic products. In particular, sodium chloride was one of the salts used by the British Thomson-Houston Co., Ltd. (41) to yield a minimum of polymers boiling below 200°C in the presence of concentrated sulfuric acid and no solvent. On the contrary, Verbish (18) and this study show a high percentage of cyclic yield in the presence of sodium chloride, possibly due to the use of ether as a solvent.

Kirner (17) after analyzing the work of York (42), found that in his study the hydrolyses were performed using an alkaline medium, and the temperature of the reaction rose to 70°C (higher than the hydrochloric acid hydrolysis). This led him to believe that the ethyl tetramer was produced by the hydrolysis, but then was converted to ethyl trimer during the reaction. York found that a limited amount of alkaline, potassium compound, such as the hydroxide or carbonate and heat converts ethyl tetramer to ethyl trimer.

As concluded in a previous section, the acid-base concentrations have an effect on the proportion of the products. If this conclusion of previous workers is taken one step further, it seems that certain combinations of solvents and acid or solvents and base concentrations influences the percentage of trimer and tetramer produced. For example (cf. Table I), using ether as a solvent and sodium hydroxide; it appears that as the sodium hydroxide concentration increases, the production of tetramer ceases to occur. The highest yield of tetramer in the ether solvent is 5.8% with mild sodium hydroxide concentration. As the concentration increases to strong sodium hydroxide concentration, the percentage of tetramer drops to zero. Conversely the ether-acid hydrolyses have the opposite effects. Dilute acid (2%) and ether solvent produce low tetramer percentages, whereas when the medium changed to more acidic, the tetramer percentage reached its highest point and then dropped slightly as the medium went to strong acidic conditions.

According to the study performed on the solubility of the diethylsilanediol, Andrianov and Sokolov (3), concluded that the diol was more soluble in ethyl alcohol than in diethyl ether therefore making the production of cyclic volatile material higher in the case of ethyl alcohol. Hence, the percentage of products (i.e. trimer and tetramer) should increase with the greater solubility in the medium. The total amount of cyclic volatile material produced in the study is in support of Andrianov; but the products, ethyl trimer and ethyl tetramer produced in the presence of alcohol fall short of the percentages produced in diethyl ether. Diethyl ether produces the best results thus far, and ethyl alcohol in sodium hydroxide produces the lowest percentage trimer.

Perhaps the basic condition suppresses the solubility of the diol in the medium.

For the hydrolyses using diethyl ether solvent, the ratio of tetramer to trimer decreases from a maximum of 0.6 in strong acid media to 0.0 in a strong basic medium. The ratio using the 21% hydrochloric acid and ethyl alcohol is about the same as it is for the ether solvent at the same conditions; whereas in the case of the strong sodium hydroxide and ethyl alcohol, the ratio is 1.29 and for the strong base and diethyl ether the ratio is 0.0 (21). There are four instances in the study where the tetramer was not produced at all, and the percentage of trimer was particularly low in 3 of the four instances (cf. Table I). It appears in the cases of acid concentrations and no solvent that the lack of solvent had a pronounced effect not only on the percentage of tetramer and trimer; but also^{on} the percentage of cyclic volatile material which dropped to 23.3% and 37.6%, respectively. Apparently the solvent is necessary in the intermediate stages of the diol solubility, to produce more volatile material. In addition, the change of acid concentrations also seemed to have an effect on the percentage of cyclic volatile material. The more highly concentrated acidic medium produced less volatile material than the milder acidic medium.

Concerning the instances where the medium was one of strong base in diethyl ether the production of ethyl trimer rises considerably compared to the strong base and ethyl alcohol percentages. However, the tetramer is still non-existent. Apparently the strong basic conditions and ether solvent prevent the formation of tetramer. This is supported by the fact that strong basic conditions and ethyl alcohol produce high percentages

of tetramer (relative to the production of tetramer throughout the study). Yet these conditions that favor the tetramer also appear to affect the production of trimer. The strong base and no solvent conditions appear to have the opposite effect on the cyclic volatile material that the acid concentrations did. Both hydrolyses using the strong base produced over 50% cyclic volatile material. In addition to this dilemma, highly concentrated acidic media generally produce high percentages of tetramer and fair (relatively speaking) amounts of trimer. In conclusion it appears that in the case of the concentrated base medium the specific solvent used is the answer; whereas either of the two solvents in the high acid concentrations will work. If the tetramer is preferred, perhaps ethyl alcohol solvent and high acidic conditions will produce an even higher yield of tetramer than achieved thus far in this study.

Trends for Acid-Base Concentrations

As concluded previously, the acid-base concentrations have an effect on the proportion of trimer and tetramer produced. In general as the medium goes from 37% hydrochloric acid concentration to 21%, the percentage of trimer decreases. Then as the medium changes from 21% to dilute (2%) acid concentration the percentage trimer increases. In the mild basic medium the percentage trimer starts to increase to the theoretically neutral point, 28.3% NaOH. As the basic concentration increases, the trimer yield decreases. The tetramer yield increased with the acid increase and ether solvent. In general there is a decline in tetramer production in the basic media and ether solvent.

Strong acid concentration seems to give the highest percentage of tetramer, while concentrated base gives low percentages of tetramer with

one exception, (53.6% NaOH and ethyl alcohol). Dilute acid tends to favor the trimer in its highest yields, only to be matched by the theoretical neutral point.

Mechanism

Throughout the years of research in the water hydrolysis of diethyldichlorosilane and the related compound dimethyldichlorosilane, the presence of an intermediate silanediol was proposed and later actually isolated. Many researchers (1,3,6,11) believe that the solubility of this diol in the medium is a primary factor in the proportion of ethyl trimer and ethyl tetramer.

It has been suggested by Andrianov and Sokolov (3), that the amount of cyclic material produced in the hydrolysis of diethyldichlorosilane is dependent on the solubility of the silanediol in the medium. The comparison of Andrianov's data with the data from this unpublished study of Miller et al. (15-21) produces interesting results. The solubility of diethylsilanediol was measured by the amount of the diol in grams, that was found soluble in 100 ml of solvent at 20°C.

In the case of water, only 9.7 to 10.8 g of the diol was soluble. This indicates that the pure water hydrolysis of diethyldichlorosilane should have a low amount of cyclic product formed. Supporting this, Anzlovar (19) in a pure water hydrolysis of Et_2SiCl_2 obtained only 32.5% cyclic-volatile material. Of the 32.5% cyclic product formed only 17.5% was ethyl trimer and 7.5% ethyl tetramer. This hydrolysis produced the second lowest percentage of cyclic volatile material as well as one of the lowest percentages of trimer. On the other hand Andrianov and Sokolov (9) in their thermometric tracings of the hydrolysis of R_2SiCl_2

(where R = Me, Et, Bu, Am), stated that the complete hydrolysis with excess water yields higher order siloxanes.

It is surprising that only 10.5 grams of the intermediate diol was found soluble in diethyl ether (3). According to these results the amount of cyclic product should be low, as in the case of water. In this case, the unpublished study (15-20) does not support Andrianov (3). In all nine cases using diethyl ether as a solvent in this study, the percentage of cyclic volatile material exceeded 38% (cf. Table I). For seven of the nine runs the percentage of cyclic volatile material exceeded 50%, several of which reached 70% or better. Perhaps the presence of a variety of acid-base concentrations influence the solubility in the medium, as well as the solvent.

In the presence of 21% HCl, the ethyl alcohol run produced the highest percentage of cyclic volatile material, as expected from Andrianov's data. This percentage far exceeded the percentages obtained from the diethyl ether and water hydrolyses; as did the solubility of the diol in alcohol when compared to the solubility in water and ether. The solubility results of the diol in water and diethyl ether are almost identical. Furthermore, in the above comparison of data from this unpublished study (15-21), some of the results of the water and diethyl ether hydrolyses are almost identical in their percentages of cyclic volatile material produced. The ethyl alcohol and acid run exceeds the water and diethyl ether runs in production of trimer and tetramer as well as cyclic volatile material.

Using the same three solvents (i.e. ethyl alcohol, diethyl ether, and water), in a strong basic medium the data from the unpublished study

supports that of Andrianov (3). Comparing the 53.6% NaOH run with the 21% HCl, the amount of cyclic volatile material almost doubles in the cases of diethyl ether and water. Although this appears to contradict Andrianov, it might support his conclusion, particularly if the strong basic medium increases the solubility of the diol in the medium, causing the percentage of cyclic volatile material to increase.

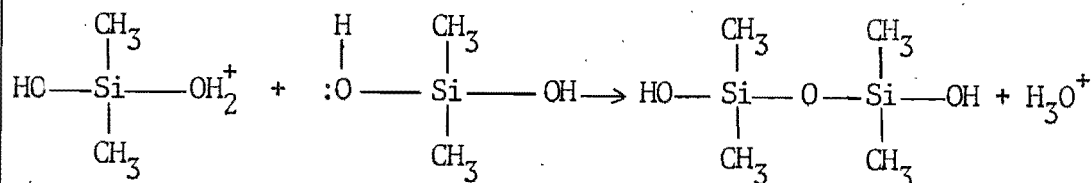
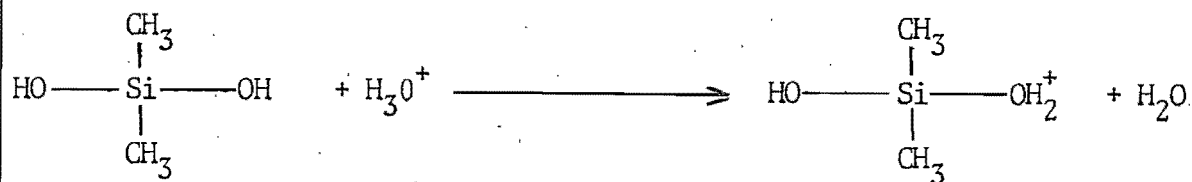
Although Andrianov does not take the acid-base concentrations into account, it would seem that the acidic nature of the hydrogens of the diol would make the diol very soluble in basic mediums. Thus the increasing solubility of the diol in the medium, due to the basic conditions, will cause an increase in the production of cyclic volatile material. This is supported in the unpublished study (15-21) while using strong sodium hydroxide conditions. Although Andrianov reports low solubility of the diol in water and diethyl ether (therefore low percentages of cyclic product), in the present study using water and ether in the presence of strong base the cyclic volatile product percentage almost doubles.

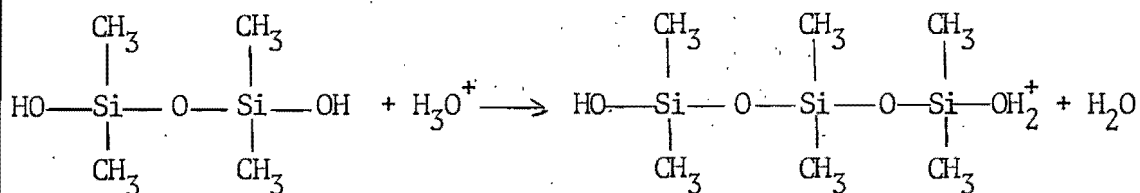
Using the results of Miller et. al. (15-20) from the hydrolyses of diethyldichlorosilane with water and diethyl ether in strong acidic conditions, one can see that Andrianov's conclusions are supported. According to Andrianov's solubility data, the diol is about equally soluble in diethyl ether and water, (about 10 g. per 100 ml for both solvents). Therefore they should produce approximately the same amount of cyclic volatile material under similar conditions. In strong acidic media the hydrolysis produces nearly the same amount of cyclic volatile material in ether and without solvent.

In the case of ethyl alcohol, in which the diol is very soluble, Rush (21) achieved 68.3% cyclic volatile material in the first hydrolysis using an acidic medium. This supports Andrianov's data about ethyl alcohol, however the second hydrolysis using a strong basic medium dropped in percentage of cyclic products. (Due to insufficient data at this time the conclusions can be merely conjectured on the data concerning ethyl alcohol and ether.) Although the diol is more soluble in ethyl alcohol than in diethyl ether and water, the ether produced higher percentages of cyclic product. Also the percentages of trimer in ether exceeded the percentage of trimer in almost all cases thus far. This leads one to the conclusion that in addition to solubility, the acid-base concentrations seem to effect the production of cyclic volatile material and trimer/tetramer formation.

Discussing the Mechanism

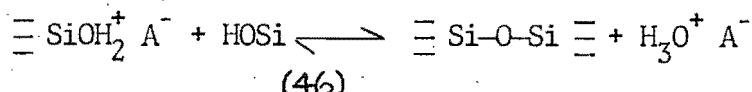
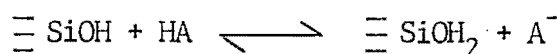
Several proposals have been made as to what actually takes place in the intermediate steps of the hydrolysis of Et_2SiCl_2 . Chrzczonowicz and Lasocki (43) proposed the migration of the hydronium ion for the condensation of the diol without mentioning the cyclization of the product.



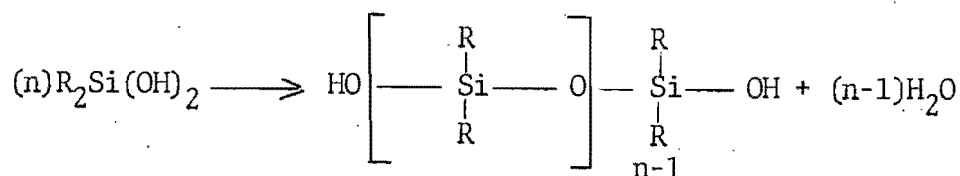
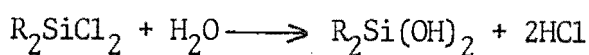


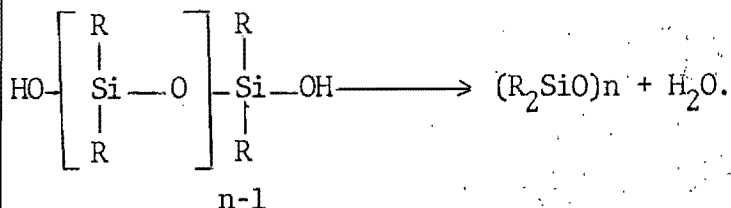
The hydrolysis and condensation above are not distinct, clear cut, step-wise reactions due to the fact that in their conductometric titrations Shaffer and Flanigen (44) indicated that an intermediate such as $\text{Cl}(\text{R}_2\text{SiO})_x\text{R}_2\text{SiCl}$ is formed. This chlorine-end-blocked siloxane is favored by lowering the reaction temperature and increasing the hydrochloric acid concentration.

Lasocki and Michalska (45) generalized the previous mechanism for the condensation of silanols by the following equation:

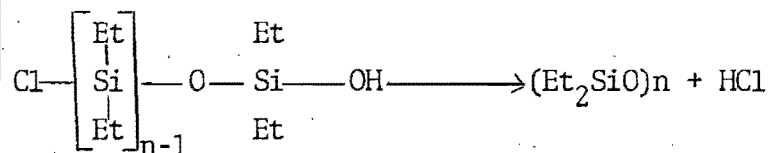
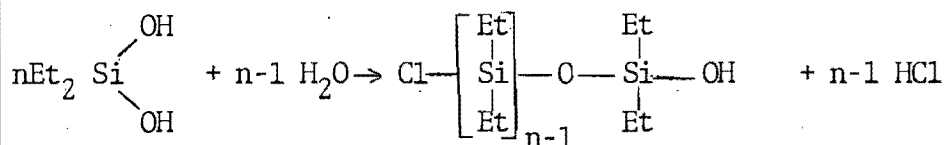
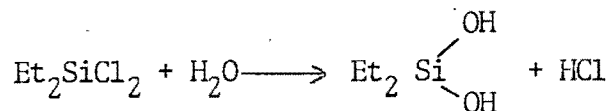


Andrianov and Izmailov[^] proposed that the hydrolysis of R_2SiCl_2 in dilute hydrochloric acid forms cyclic and linear products, while concentrated hydrochloric acid in the reaction leads to cyclic products exclusively. Their proposed reaction is as follows:





Anzlovar (17) proposed an alternative to these two mechanisms involving a chlorosilanol intermediate.



There are a number of problems that arise on examination of the mechanism of the intermediate diol which leads to the cyclic products, ethyl trimer and ethyl tetramer. For example the silanediol is reported to be very soluble in the sodium hydroxide medium (47), so it can be inferred that the amount of cyclic products depends on the solubility of the initially formed Et_2SiClOH (1) in the medium. When the chlorosilanol is soluble in the medium it may convert to the silanediol more quickly, and therefore the ring will close as soon as sterically possible. On the other hand, when there is no organic solvent present, there is a possibility of forming long-chain polymers before the final chlorine is lost to close the ring. This, however, is contrary to experimental evidence while using diethyl ether and a basic medium which favors the trimer. On

the other hand this is supported when ethyl alcohol and basic conditions are employed; because the tetramer is favored.

In addition to the previous problem, more data must be known; such as activation energies, stability of the products, the ease with which the first and second chlorine are removed, and whether the condensation involves water elimination or hydrogen chloride elimination (17).

Rochow (40) concluded that dialkyldichlorosilanes condense intermolecularly to form polymeric organosiloxane. The rate of condensation is governed principally by the size of the alkyl group. According to Patnode and Wilcock (11) the diols tend to condense by dehydration with the passage of time. In addition they concluded that Si-O-Si linkages may be broken by sulfuric acid to produce shorter chains, leading to a rearrangement of the Me_2SiO units. Kipping (1) on the other hand concluded that the formation of the cyclic trimer from the diol is promoted by the presence of aqueous hydrochloric acid, ammonia, or small amounts of aqueous alkali.

Conclusions

Upon summarizing the pertinent data there are several general conclusions that can be drawn concerning the production of ethyl trimer, ethyl tetramer, and cyclic volatile material.

(1) It appears from local research (15-21), that ethyl trimer may be produced at a maximum amount under the following conditions: the hydrolysis of diethyldichlorosilane in ether and pure water with no added acid or base. However, according to the findings of Andrianov (3), the hydrolysis should employ methyl alcohol and a mild (2%) hydrochloric acid medium in order to get a maximum amount of trimer and tetramer. This is

supported because 111.9 grams of the diol is soluble in 100 ml. of methyl alcohol. Hence, the higher the solubility of the diol in the medium the higher the amount of cyclic volatile material produced, and the higher the amount of trimer and tetramer. The mild acidic conditions are required according to this unpublished study (15-21), where Miller (15) produced the highest yield of trimer.

(2) Also ethyl tetramer may be produced at a maximum amount under these conditions: the hydrolysis of diethyldichlorosilane in the presence of an organic solvent with a relatively large alkyl group and a 24 to 37% hydrochloric acid medium. This is supported by several studies. The ethyl tetramer is a higher molecular weight product than ethyl trimer. In order to produce a larger percentage of high molecular weight product, the alkyl group of the solvent must increase (48). In this study diethyl ether and acid produced the highest percentage of tetramer. Yet Bentkowska (48) shows that diethyl ether produces 94% lower molecular weight rings. He also showed that benzene produced the largest percentage of higher molecular weight rings, in comparison with diethyl ether and acetone. It is possible therefore that a maximum yield of ethyl tetramer could be obtained by using benzene and an acidic medium in the hydrolysis of diethyldichlorosilane.

(3) In addition to the above conclusions, one can project that a maximum amount of cyclic volatile material can be obtained by hydrolyzing diethyldichlorosilane in the presence of methyl alcohol at a theoretically neutral point. This can be supported by Andrianov's (3) solubility study. Generally the amount of cyclic product formed depends on the solubility of the diol in the medium. Since our study supports this

statement, methyl alcohol would be the logical solvent used due to the fact that it has the highest solubility results (i.e. 111.9 grams of diol in 100 ml of methyl alcohol). The reason for the theoretical neutral conditions follows from the data in this study. The highest amount of cyclic product was obtained in a theoretically neutral point with diethyl ether. Since methyl alcohol produces better solubility results than diethyl ether, the former would be the logical choice.

(4) A final statement could be made concerning the support that the data from this study (15-21), gives to Andrianov's conclusions regarding the solubility of the diol and its effects on the amount of cyclic volatile material, as well as trimer and tetramer production. The solubility results of water, diethyl ether, and ethyl alcohol to produce specific percentages of cyclic product were supported by this study in almost every case. The exception being that of ethyl alcohol in the strong basic medium, which fell short of its expected yield. Also the amount of trimer and tetramer distilled should be relatively related to the amount of cyclic product. This is supported by this study's data in many cases; however, varying concentrations of acids and bases does not allow a closer examination of this conclusion.

(5) Additional information has become evident as a result of this unpublished study (15-21) and Andrianov's (3) work. Andrianov made no mention of acids and bases in his solubility study concerning the production of cyclic volatile material. It has been noted in this thesis that while employing a strong alkali medium and the solvents, diethyl ether and water (reportedly the diol was not very soluble in them, hence a low yield of cyclic volatile product), that the amount of cyclic product reached an unexpected high percentage. One possible explanation is

that, due to the acidic nature of the hydrogens in the diol, it would appear to be very soluble in the basic mediums, hence the unexpected high yield of cyclic product.

PROJECTIONS

The Hydrolysis of Diethyldichlorosilane in the Presence of Benzene

The purpose of this section is to discuss the possible yield of ethyl trimer and ethyl tetramer using benzene as a solvent (in various concentrations of acid and base), by analyzing the information available concerning this solvent.

Andrianov and Yakushkina (30) conducted a water hydrolysis of diethyldichlorosilane and phenyltrichlorosilane in the presence of diethyl ether, benzene, and acetone. The solvents were observed to affect the OH group content of the products in the order: diethyl ether > acetone > benzene. The highest molecular weight products were obtained while using benzene solvent. Bentkowska (48) produced cyclosiloxanes by reaction of diethyldichlorosilane with mercury(I)oxide and copper(II)oxide, using benzene as a solvent. The yield of cyclics was improved in the presence of copper(I)oxide and a polar solvent such as ethyl ether instead of benzene. Kuznetsova, et al. (49) in a cohydrolysis of dimethyldichlorosilane and methylphenyltrichlorosilane in benzene yielded only 29-40% low molecular weight rings while in diethyl ether 94% low molecular weight rings were produced.

As stated earlier in this paper, Andrianov, et. al. (3) concluded that the solubility of the diol in the medium affects the amount of cyclic products formed. The higher the solubility, the higher the yield of cyclic product. It appears that the general trend of data leads to the conclusion that as the alkyl group of the solvent increases, the solubility of the diol decreases. There appears to be an inconsistency

or contradiction in Andrianov's statement about cyclic yield and the actual results. Only 1.12 g of the diol was soluble in 100 ml of benzene, yet in the same study Et_2SiCl_2 and aqueous benzene gave 79% cyclic volatile products.

In considering the results of Bentkowska (48) and Andrianov (3), there are several conclusions that may be drawn from the data. Bentkowska stated that in benzene solvent only 29-40% low molecular weight rings were produced. The higher molecular weight rings were favored. Also, Andrianov concluded in his solubility research, that the amount of cyclic volatile material in the hydrolysis of Et_2SiCl_2 , using benzene as a solvent, was high. Ethyl tetramer is a higher molecular weight product than ethyl trimer, therefore in this case the tetramer percentage should rise considerably and the trimer percentage should be suppressed or relatively low. Furthermore, the ratio of trimer to tetramer should be closer.

It can not be determined if benzene solvent produces the amount of trimer and tetramer desired. However, there may be another organic solvent which has been overlooked, that will produce more than satisfactory results. Once again, in Andrianov and Sokolov's (3) solubility test of the diol in solvents, methyl alcohol appears to be the best solvent. The solubility of the diol in methyl alcohol is higher than in any other solvent reported: 111.0 grams in 100 ml of methyl alcohol at 20°C. In addition, Dobay (24) prepared octaethylcyclotetrasiloxane (ethyl tetramer) by the controlled hydrolysis of diethyldichlorosilane in methyl alcohol and water. In another study, Dobay (25) employing similar methods, hydrolyzed diethyldichlorosilane dropwise to

methyl alcohol and water to produce hexaethylcyclotrisiloxane (ethyl trimer). Not enough information is available to calculate the percentage yield.

In any case, perhaps methyl alcohol should be the next solvent used in the hydrolysis of Et_2SiCl_2 . There seems to be a trend in the solvents as to the production of cyclic volatile material and trimer/tetramer, with regard to the alkyl groups. Methyl > ethyl > diethyl > isopropyl > t-butyl > Amyl. It may be that with the collection of sufficient data on these organic solvents in the various concentrations of acids and bases, the conditions of optimum ethyl trimer and tetramer formation may be found.

REFERENCES

- (1) Rochow, E.G., An Introduction to the Chemistry of the Silicones, (New York: John Wiley and Sons, Inc., 1951), p. 185.
- (2) Kakudo, M., and Watase, T., J. Chem. Phys., 21, 167-8 (1953).
- (3) Andrianov, K.A., and Sokolov, N.N., Doklady Akad. Nauk., S.S.S.R., 101, 81-4 (1955); C.A., 50, 2418f.
- (4) Shaffer, L.H., and Flanigen, E.M., Phys. Chem., 61, 1591 (1957).
- (5) Brewer, S.D., and Haber, C.P., J. Am. Chem. Soc., 70, 3888-91 (1948).
- (6) Hyde, J.F., and DeLong, R.C., J. Am. Chem. Soc., 63, 1194-6 (1941).
- (7) Nasser, S., and Gertner, D., J. Am. Oil. Chem. Soc. (52) 1, pp. 18-21 (1975).
- (8) Pathet, R., Ger. Pat., 1,937,736, (July 24, 1968); C.A., 72, 67537k.
- (9) Andrianov, D.A., and Sokolov, N.N., Doklady Akad. Naak. S.S.S.R., 82, 909-12 (1952); C.A., 47, 4280g (1953).
- (10) Rochow, E.G., op. cit., 1, p. 80.
- (11) Patnode, W.I., and Wilcock, D.F., J. Am. Chem. Soc., 68, 358 (1946).
- (12) Ostdick, T., Doctoral Dissertation, University of Notre Dame, (1958).
- (13) Hyde, J.F., and DeLong, R.C., Op. Cit. 6.
- (14) George, P.D., Sommer, L.H., and Whitmore, R.C., J. Am. Chem. Soc., 75, 1585 (1953).
- (15) Miller, K., Bachelor of Science Thesis, Saint Meinrad College, (1970).
- (16) Grisley, T., Bachelor of Science Thesis, Saint Meinrad College, (1972).
- (17) Kirner, J., Bachelor of Science Thesis, Saint Meinrad College, (1972).
- (18) Verbish, W., Bachelor of Science Thesis, Saint Meinrad College, (1972).

- (19) Anzlovar, J., Bachelor of Science Thesis, Saint Meinrad College, (1973).
- (20) Mulhern, T., Bachelor of Science Thesis, Saint Meinrad College, (1975).
- (21) Rush, R., Bachelor of Science Thesis, Saint Meinrad College, (1976).
- (22) Wenske, R., Benwald, S., Teischmann, H., Brit. Pat., 1,198,197, (August 21, 1968), C.A., 73, 78846g.
- (23) Dobay, D., Union Carbide and Carbon Corp., U.S. Pat. 2,769,830, (Nov. 6, 1956); C.A., 51, P7403e.
- (24) Ibid., U.S. Pat. 2,769,829 (Nov. 6, 1956); C.A. 51, P7403d.
- (25) Sokolov, N.N., and Akimova, S., Zhur. Obshchei Khim, 26, 2276-9 (1956), C.A., 51, 5096b.
- (26) Sokolov, N.N., Andrianov, K.A., and Akimova, S.M., Zhur. Obshchei Khim., 26, 933-6 (1956); C.A., 50, 14782c.
- (27) McCusker, P.A., and Greene, C.E., J. Am. Chem. Soc., 70, 2807-8 (1948).
- (28) Karlin, A.V., Troitskii, A.P., Lobkov, V.D., Duseleva, S.F., Tenyaeva, I.M., U.S.S.R. Pat. 388,001, C.A., 80, 27847V.
- (29) York, E., and Bailey, D.J., Union Carbide Corp., C.A. 52, 1516b.
- (30) Andrianov, K.A., and Yakushkina, S.E., Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk, 1960, 457 (1960); C.A., 54, 22437c.
- (31) Kurlova, T.V., Dmokhovshaya, E.B., Yuzhelevakis, Y.A., Kagan, E.G., Larionova, O.N., U.S.S.R. Pat. 296,771 (Mar. 2, 1971).
- (32) Rochow, E.G., Op. Cit., i, p. 68.
- (33) Giorgio, P.D., Sommer, H., and Whitmore, F.C., J. Am. Chem. Soc., 68, 344 (1946).
- (34) Saratov, I.E., Reikhsfel'd, V.O., Zakomoldina, T.A., Kremniorg, M., Zh. Khim., 8, B1204 (1972); C.A., 81, 90906z.
- (35) Araki, T., and Osuga, K., Repts. Gov't. Chem. Ind. Research Inst. Tokyo, 45, 101-7 (1950); C.A., 46, 1799h (1952).
- (36) Andrianov, K.A., Zhdonov, A., Izvest. Akad. Nauk S.S.S.R. Otdel, Khim Nauk S.S.S.R., 1076-9 (1958).

- (37) Gueyne, J., and Duffaut, N., Fr. Demande 2,230,376 (Dec. Appl. 73 18,953 (May 24, 1973); C.A., 83, 28367n.
- (38) Shostokovskiy, M., Kochkin, D., Kondrat'ev, K., and Rogov, V., Zhur Obshchey Khim, 26, 3344-53 (1956), C.A., 51, 9514e.
- (39) Lasocki, Z. and Michalska, Z., Bull. Acad. Pol.; Ser. Sci. Chim., 14(11-12), 825-8 (1966), C.A., 67, 32717p.
- (40) Rochow, E.G., Op. Cit., p. 53.
- (41) The British Thomson-Houston Company, Ltd., Brit. Pat. 594,485 (Nov. 2, 1947); C.A., 42, 3206a (1948).
- (42) York, E.R., Brit. Pat. 774,040 (May 1, 1957); C.A., 51, 15619 (1957).
- (43) Chrzczonowicz, S., and Lasocki, Z., Bull. Acad. Polon. Sci. Ser. sci. chem., 9, 589 (1961).
- (44) Shaffer, L.H., and Flanigen, E.M., J. Phys. Chem., 61, (1957).
- (45) Lasocki, Z., and Michalska, A., International Symposium on Organosilicon Chemistry, Ed. V. Chalovsky, F. Mates, and J. Hetflejš, (Prague: Scientific Communication, (1965), p. 34.
- (46) Andrianov, K. A., and Izmailov, B.A., Kremniorg. Seodin. Tr. Sovesh., 1967 (3), 54 (1967); C.A., 70, 47532 (1968).
- (47) Lasocki, Z. and Chrzczonowicz, S., Bull. Acad. Polon. Sci. Ser. sci. chem., 13, 261 (1965).
- (48) Bentkowska, H., Roczniki. Chem., (10), 1101 (1963); C.A., 60, 6931 (1964).
- (49) Kuznetzova, A.G., Andrianov, K.A., and Zhinkin, D., Plasticheskie Massey, 1960, #10, 16 (1960); C.A., 55, 16457i (1960).

