Inorg. Chem. **1983**, *22*, 2163–2167

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Cyclic Polysiloxanes from the Hydrolysis of Dichlorosilane

DIETMAR SEYFERTH,* CHRISTIAN PRUD'HOMME,[1] and GARY H. WISEMAN

Received December 1, 1982

The hydrolysis of H_2SiCl_2 in dichloromethane solution, either with a stoichiometric amount of water at −30 to −20 °C or by slow, controlled addition of a slight excess of water at 0 °C, results in the formation of siloxanes of type $[H_2SiO]_n$. In the volatile fraction oligomers with n from 4 up to 23 were found. Those with n = 4–6 were isolated by GC and characterized (^1H and ^{29}Si NMR, IR, $n^{25}{}_D$, mass spectroscopy). A brief study was made of the hydrolysis of $MeSiHCl_2$ and Me_2SiCl_2 under comparable conditions.

Introduction

Studies dealing with the preparation and reactivity of dichlorosilane, H_2SiCl_2, were first reported by Stock and Somieski[2,3] in 1919. In the gas phase, it was claimed, dichlorosilane (bp 8.2 °C) reacts with a stoichiometric amount of water vapor to give gaseous, monomeric prosiloxane, $H_2Si{=}O$, which polymerizes, rapidly in the liquid phase and more slowly in the gas phase, to give liquid and solid polysiloxanes, $[H_2SiO]_n$.[3] The liquid, vacuum-distillable product became viscous and apparently gelled on brief standing at room temperature. The molecular weight of the freshly prepared liquid product (cryoscopy in benzene) indicated an *average* composition of $[H_2SiO]_6$. A solution of H_2SiCl_2 in benzene was hydrolyzed by brief contact with a large excess of water in another of Stock and Somieski's experiments. Analytical (Si, H) and molecular weight determinations on the benzene solution indicated that "n" in $[H_2SiO]_n$ was between 6 and 7 and that it increased slowly with time (between 7 and 8 after 1 h). Longer contact with the aqueous hydrolysis medium caused Si–H hydrolysis with evolution of hydrogen, and the final product was claimed to be a polymer, $[HSi(OH)O]_n$.[1] In 1919, dichlorosilane, prepared by the gas-phase reaction of monosilane with hydrogen chloride, was available in only millimole quantities, but with the growth of the silicone industry, dichlorosilane became available in large quantities. (The Linde Division of Union Carbide Corp. offers dichlorosilane in gas cylinders containing up to 250 lb, of material.) A Union Carbide patent[4] provided details of the large-scale (2.5-mol) hydrolysis of dichlorosilane in mixed ether/alkane solvent system at 0 °C to give a mixture of volatile (17% yield) and nonvolatile (15% yield) $[H_2SiO]_n$ in which, it was claimed, the cyclic tetramer, pentamer, and hexamer were the principal components. These were isolated by distillation and characterized (bp, $n^{25}{}_D$, molecular weight, % H). In marked contrast to these results, Fischer and Kriegsmann reported that their efforts to isolate cyclic oligomers, $[H_2SiO]_n$, by the hydrolysis of dichlorosilane or diiodosilane in hexane using $NiCl_2{\cdot}6H_2O$ as the water source resulted in failure.[5] The hydrolysis product present in the hexane solution (by IR) left a viscous residue when the solvent was removed. This oil became turbid on standing and finally solidified. These workers questioned the Bailey–York patent and claimed that the $[H_2SiO]_n$ oligomers were stable only in hexane solution in the presence of some anhydrous HCl. In another paper,[6] Fischer and Kriegsmann claimed that hydrolysis of H_2SiCl_2 in dilute Et_2O/CCl_4 medium at −10 °C gives a solution of $[H_2SiO]_n$ cyclics containing 70–80% of the tetramer. An IR spectrum of this species was published and assignments were made.

Table I. Composition of the c-$[H_2SiO]_n$ Mixture and Percent Yield of Individual Species Formed in the Hydrolysis of Dichlorosilane

"n" in $[H_2SiO]_n$	% by wt of $[H_2SiO]_n$ in mixture	% yield (based on H_2SiCl_2)
4	10.6	6.1
5	39.2	22.6
6	20.8	12.0
7	8.8	5.1
8	4.9	2.8
9	3.85	2.2
10	2.9	1.7
11	2.2	1.3
12	1.7	0.98
13	1.2	0.69
14	0.83	0.48
15	0.49	0.28
16	0.25	0.14
17	0.10	0.06

Dihalosilane hydrolysis also has been examined by Campbell-Ferguson,[7] who reported that the cyclic tetramer is the major volatile product (by gas-phase molecular weight measurements). The mass spectrum of the hydrolysis product showed evidence for the presence of $[H_2SiO]_4$, $[H_2SiO]_5$, and unspecified "species of still higher molecular weight". A gas-phase IR spectrum of the hydrolysis product was reported, and an NMR spectrum (in cyclohexane) showed the Si–H resonance at δ 4.71. In a later study,[8] $[H_2SiO]_4$ was isolated from the hydrolysis of H_2SiI_2 vapor with Cu_2O or hydrated PbO, and its structure was determined by gas-phase electron diffraction.

Dichlorosilane is now available commercially, and thus its chemistry, rather poorly developed thus far, can be studied much more conveniently. In view of the somewhat confused picture of the hydrolysis of dichlorosilane, we have begun our studies of the chemistry of dichlorosilane with a reinvestigation of this potentially important and interesting hydrolysis reaction.

Results and Discussion

In a typical experiment, a solution of about 0.5 mol of dichlorosilane in 350 mL of dry dichloromethane was prepared at −40 °C (under nitrogen), and 0.49 mol of distilled water was added slowly by syringe. At this temperature, ice formed in the reaction mixture. The hydrolysis was allowed to pro-

---

(1) Postdoctoral Associate, on leave from Rhône-Poulenc Recherches, Lyon.

(2) Stock, A.; Somieski, C. *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 695. For a report of "prosiloxane" from the hydrolysis of H_2SiBr_2, see also: Stock, A.; Somieski, C.; Winter, R. *Ibid.* **1917**, *50*, 1764.

(3) Stock, A.; Somieski, K. *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 1851.

(4) Bailey, D. L.; York, E. R. U.S. Patent 2 810 628, 1957; *Chem. Abstr.* **1958**, *52*, 1516. See also: French Brevet d'Invention (Gr14.-C1. 8) No. 1 147 792, 1956.

(5) Fischer, C.; Kriegsmann, H. *Z. Anorg. Allg. Chem.* **1969**, *367*, 233.

(6) Fischer, C.; Kriegsmann, H. *Z. Anorg. Allg. Chem.* **1969**, *367*, 219.

(7) Campbell-Ferguson, H. J. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2121.

(8) Glidewell, C.; Robiette, A. G.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1970**, 931. See also: Glidewell, C. *J. Chem. Soc. A* **1971**, 823.

0020-1669/83/1322-2163$01.50/0

Table II. Cyclic $[H_2SiO]_n$ Oligomers

compd	$n^{25}{}_D{}^a$	IR spectrum (in CCl_4)^b	proton NMR (270 MHz; in $CDCl_3$), δ^c
$[H_2SiO]_4$	1.3842	2200 s (ν(Si-H)) 1108 s (ν_{as}(Si-O-Si)) 984 m ($\delta(SiH_2)$) 938 vs ($\delta(SiH_2)$)	4.72 $J(^{29}Si-^1H) = 260.7$ Hz
$[H_2SiO]_5$	1.3907	1195 s (ν(Si-H)) 1110 s (ν_{as}(Si-O-Si)) 985 m ($\delta(SiH_2)$) 964 m ($\delta(SiH_2)$) 925 vs ($\delta(SiH_2)$)	4.71 $J(^{29}Si-^1H) = 258.8$ Hz
$[H_2SiO]_6$	1.3933	1195 s (ν(Si-H)) 1105 s (ν_{as}(Si-O-Si)) 987 m ($\delta(SiH_2)$) 958 m ($\delta(SiH_2)$) 915 vs ($\delta(SiH_2)$)	4.71 $J(^{29}Si-^1H) = 258.3$ Hz

^{a} Of a GC-collected sample. ^{b} Obtained with a Perkin-Elmer 283B grating infrared spectrophotometer. ^{c} Obtained with a Bruker WM-270 NMR spectrometer.

ceed, first at −30 to −20 °C and then during slow warming to room temperature. Strong HCl evolution was apparent when the temperature reached about −15 °C. Workup, as described in the Experimental Section, left a concentrated dichloromethane solution of hydrolysis products. Distillation of this solution at reduced pressure gave a solution of cyclic $[H_2SiO]_n$ oligomers in dichloromethane as the distillate and left a nonvolatile oil as residue. The composition of the distilled hydrolysis products was determined by GC and GC/CI mass spectroscopy. Table I gives the composition of this $[H_2SiO]_n$ mixture. The actual yield of $[H_2SiO]_4$ is higher since a substantial amount of this, the most volatile component, probably was lost during removal of the bulk of the large quantity of dichloromethane solvent that was used. Another hydrolysis procedure served equally well. In this, a dichloromethane solution of H_2SiCl_2 was cooled to 0 °C and a slight excess of water was added at a slow, constant rate by using a syringe pump. $[H_2SiO]_4$ cyclics up to $[H_2SiO]_{23}$ were detected (Table III). The yield of $[H_2SiO]_n$ cyclic siloxanes was variable, depending on reaction conditions. The highest yield was 56% in an experiment in which the yield of the nonvolatile oil was 27%.

The mixture of cyclic $[H_2SiO]_n$ oligomers showed a proton resonance in its NMR spectrum (CH_2Cl_2 solution) at δ 4.7. The cyclic tetramer, $[H_2SiO]_4$, pentamer, $[H_2SiO]_5$, and hexamer, $[H_2SiO]_6$, could be isolated by gas chromatography (GC) as pure species. Spectroscopic data and refractive indices are given in Table II. Solutions of these individual cyclic siloxanes in CCl_4 or $CDCl_3$ were stable at room temperature without significant change for a few days. However, when the individual cyclics were collected as pure compounds in flame-dried Pyrex capillary tubes, which then were sealed and kept at room temperature, rearrangement processes took place (see below).

Without a doubt, the results cited in the Bailey–York patent[4] are correct: the cyclic tetramer, pentamer, and hexamer are the major products of H_2SiCl_2 hydrolysis under these conditions, and they may be isolated and characterized. The following refractive indexes are quoted in the patent ($n^{25}{}_D$): $[H_2SiO]_4$, 1.3827; $[H_2SiO]_5$, 1.3891; $[H_2SiO]_6$, 1.3910, and these are in reasonable agreement with the values in Table II.[9]

Proton NMR spectroscopy is of no utility in distinguishing between $[H_2SiO]_n$ cyclic species. The ^{29}Si NMR spectra show the silicon atoms in the smaller rings to be deshielded relative to the SiH_2O units in linear species, which show $\delta(Si)$ at ~−49. The shieldings are seen to increase in the order $[H_2SiO]_4$, $[H_2SiO]_5$, and $[H_2SiO]_6$. However, it is the infrared spectra that are the most useful in distinguishing between the lower $[H_2SiO]_n$ cyclics, in particular, the strong, sharp absorption bands due to the SiH_2 unit in the 1000–900-cm^{-1} region at 938, 925, and 915 cm^{-1} in the spectra of the tetramer, pentamer, and hexamer, respectively (Figure 1). From these data it is clear that the figure showing the IR spectrum of $[H_2SiO]_4$ in the Fischer–Kriegsmann paper[6] is, in actual fact, the IR spectrum of a mixture of $[H_2SiO]_4$, $[H_2SiO]_5$, and $[H_2SiO]_6$.

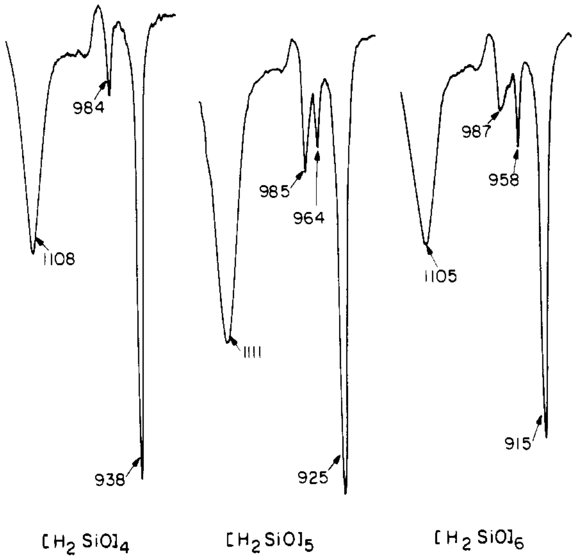


Figure 1. Infrared spectra of the $[H_2SiO]_4$, $[H_2SiO]_5$, and $[H_2SiO]_6$ cyclic oligomers in the 1200–900-cm^{-1} region.

Attempts to hydrolyze dichlorosilane using other procedures did not give volatile cyclic siloxanes. Treatment of an ethereal solution of dichlorosilane with an excess of water at 0–10 °C gave an insoluble white solid, very likely the same polymeric "prosiloxane" reported by Stock, Somieski, and Winter in 1917.[2] Obviously, under these conditions some Si–H bond hydrolysis and cross-linking occurred. Adding dichlorosilane at 0–10 °C to an aqueous solution containing a 1 M $NaH_2PO_4 \cdot H_2O$ and 1 M Na_2HPO_4 buffer mixture (pH 7) resulted in formation of a gel.

The rearrangement of the $[H_2SiO]_n$ cyclics is of some interest. As mentioned above, the pure cyclic $[H_2SiO]_n$ tetramer, pentamer, and hexamer underwent rearrangement on storage in sealed Pyrex capillary tubes at room temperature. Thus, after ~3 h at room temperature, a sample of originally pure $[H_2SiO]_4$ was composed of a mixture of $[H_2SiO]_n$ oligomers with n = 4–17. The amounts of cyclic siloxane present decreased with increasing "n", but the GC peaks for $[H_2SiO]_8$ and $[H_2SiO]_{12}$ stood out as being larger than expected for a smooth drop-off with increasing "n". This may be explained in terms of a ring-growth process of the type shown in eq 1 and 2. In similar manner, $[H_2SiO]_5$ rearranged to give a

$$2[H_2SiO]_4 \rightarrow [H_2SiO]_8 \qquad (1)$$

$$[H_2SiO]_8 + [H_2SiO]_4 \rightarrow [H_2SiO]_{12} \qquad (2)$$

mixture of $[H_2SiO]_n$, with n = 4–15. In similar manner, $[H_2SiO]_5$ rearranged to give a mixture of $[H_2SiO]_n$, with n = 4–15. The $[H_2SiO]_{10}$ GC peak, in this case, was unexpectedly large.

Although samples of $[H_2SiO]_4$, $[H_2SiO]_5$, and $[H_2SiO]_6$ were much more stable in dilute solution, rearrangement processes did take place. Thus, after a sealed sample of a 7% solution of pure $[H_2SiO]_4$ in C_6D_6, which had been used to

---

(9) Unfortunately, Fischer and Kriegsmann's contention that the claims of the Bailey–York patent cannot be reproduced has entered the review literature: "Gmelin Handbook of Inorganic Chemistry", 8th ed.; Springer-Verlag: Berlin, 1982; Suppl. Vol. B1, pp 247–249.

record the ^{29}Si NMR spectrum, was examined again 6 days later, the resonance due to this species had decreased greatly in intensity and strong resonances due to $[H_2SiO]_5$ (δ(Si) −48.38) and higher cyclic oligomers (δ(Si) −48.71) were observed. Similarly, a C_6D_6 solution of $[H_2SiO]_5$, after 6 days at room temperature, had undergone partial redistribution to form a small amount of $[H_2SiO]_4$ and larger amounts of higher cyclic oligomers.

The ring-opening polymerization of $[(CH_3)_2SiO]_n$ cyclics by the action of sulfuric acid is well-known.[10] When a drop of concentrated sulfuric acid was added to a mixture of $[H_2SiO]_n$ cyclics, a rapid increase in viscosity was observed. A colorless elastomer was obtained in less than 10 min at room temperature. This material, with its abundant Si–H functionality, should be of interest for further study.

It may be such ring-opening polymerization that makes mass spectroscopy an impractical tool for the routine analysis of $[H_2SiO]_n$ mixtures. It was noted that introduction of these compounds into the mass spectrometer ion source resulted in considerable fouling of the focusing plates, as evidenced by loss of sensitivity. Extended bakeout or complete ion source cleaning after each GC/MS run was found to be necessary when these samples were being analyzed. It is likely that polymerization occurs at the higher ion source temperature, perhaps on contact with the metal surfaces.

A comparison of the present results with those of the hydrolysis of CH_3SiHCl_2 and $(CH_3)_2SiCl_2$ is of interest. The hydrolysis of both of these chlorosilanes, especially of the latter, has been studied in great detail.[10] However, a comparison would be meaningful only when the hydrolysis procedure used is the same for all three dichlorosilanes.

As noted above, the hydrolysis of dichlorosilane could be effected readily by the slow, controlled addition of an excess of water to a solution of dichlorosilane in CH_2Cl_2 at ~0 °C. In contrast to the rapid hydrolysis of H_2SiCl_2 under these two-phase conditions, dimethyldichlorosilane reacted only very slowly at 0 °C and slowly even at room temperature. Complete hydrolysis was achieved during an 18-h reflux period. As might be expected, the reactivity of methyldichlorosilane toward water in this two-phase system was intermediate between that of H_2SiCl_2 and $(CH_3)_2SiCl_2$. A reaction at room temperature resulted in rapid and complete hydrolysis of CH_3SiHCl_2. Under these conditions, the hydrolysis of $(CH_3)_2SiCl_2$ and CH_3SiHCl_2 gave a good yield of cyclic siloxanes, mostly the cyclic tetramer, pentamer, and hexamer but also higher cyclic siloxanes: up to $[CH_3SiHO]_{22}$ in the case of CH_3SiHCl_2 and $[(CH_3)_2SiO]_{19}$ in the case of $(CH_3)_2SiCl_2$. Thus, the hydrolysis reactions of all three dichlorosilanes, H_2SiCl_2, CH_3SiHCl_2, and $(CH_3)_2SiCl_2$, are quite similar and differ only in rate. The observed rate difference very likely results from increasing steric effects as the H substituents of dichlorosilane are replaced by bulkier methyl groups. The hydrolysis products and their relative yields are listed in Table III. It will be noted that under these hydrolysis conditions the cyclic trimers, $[CH_3SiHO]_3$ and $[(CH_3)_2SiO]_3$, are formed in only very low relative yield. In the hydrolysis of H_2SiCl_2 we have obtained no evidence for the formation of $[H_2SiO]_3$. The possibility that this compound is volatile enough to have been lost completely when the dichloromethane solvent was removed prompted us to carry out a similar H_2SiCl_2 hydrolysis experiment in the higher boiling *sym*-tetrachloroethane. However, the cyclic trimer was not found among the volatile components of the reaction mixture that were distilled away from the solvent. It is noteworthy that the previous workers who have isolated $[H_2SiO]_n$ cyclic species also have not found $[H_2SiO]_3$ among the H_2SiCl_2 hydrolysis products. It may be that this compound is not formed at all. However, we consider it more likely that it is formed but that it is too reactive to permit isolation. In this connection, we note the limited stability with respect to cyclooligomerization of $[H_2SiO]_4$ that we mentioned above. If the cyclic tetramer is that reactive, the cyclic trimer may be expected to be even more reactive.

Table III. Composition of c-$[H_2SiO]_n$, c-$[CH_3SiHO]_n$, and c-$[(CH_3)_2SiO]_n$ Mixtures Formed in the Hydrolysis of H_2SiCl_2, CH_3SiHCl_2, and $(CH_3)_2SiCl_2$, Respectively

	%		
n	$[H_2SiO]_n$[a]	$[CH_3SiHO]_n$[b]	$[(CH_3)_2SiO]_n$[c]
3	none	trace	1.07
4	22.27	36.97	48.11
5	37.46	26.43	24.27
6	17.18	13.80	13.40
7	7.94	6.95	5.28
8	4.42	3.72	1.80
9	2.89	2.46	1.06
10	1.96	1.88	0.69
11	1.32	1.57	0.50
12	1.00	1.34	0.52
13	0.87	1.21	0.62
14	0.67	1.04	0.70
15	0.48	0.87	0.78
16	0.43	0.68	0.76
17	0.32	0.51	0.45
18	0.25	0.38	trace
19	0.19	0.22	trace
20	0.13	trace	
21	0.10	trace	
22	0.07	trace	
23	0.05		

[a] GC conditions: 6-ft SE-30; 60–250 °C program at 10 °C/min.
[b] GC conditions: 2-ft SE-30; 80–300 °C program at 10 °C/min.
[c] GC conditions: 2-ft SE-30; 80–300 °C program at 15 °C/min.

Table IV. $^{29}Si\{^1H\}$ NMR Spectra of Cyclic Siloxanes[a]

	δ(Si)		
n	$[H_2SiO]_n$	$[CH_3SiHO]_n$	$[(CH_3)_2SiO]_n$
4	−47.2	−32.1 −32.4 −32.7	−19.4
5	−48.9	−34.5 (several lines)	−21.7
6	−49.2 (+higher oligomers)	−34.8 (several lines) (+higher oligomers)	−22.0
7			−22.3
8			−22.6 (+higher oligomers)

[a] Spectra are recorded in C_6D_6 solution with ~0.03 M $Cr(acac)_3$ on a JEOL FX-90Q spectrometer operating at 17.76 MHz with a 1000-Hz window. Chemical shifts of $[CH_3SiHO]_n$ and $[(CH_3)_2SiO]_n$ are reported vs. internal Me_4Si. (An *internal* Me_4Si standard is preferred as we have noticed some small changes in chemical shift when an external standard is used (see also: Harris, R. K.; Kimber, B. J. *J. Organomet. Chem.* 1974, *70*, 43).) For the $[H_2SiO]_n$ ^{29}Si NMR spectra, an external Me_4Si standard was used.

The formation of very large rings when cyclic $[(CH_3)_2SiO]_n$ oligomers are formed is not unusual. Brown and Slusarczuk[11] have reported studies of the KOH-catalyzed equilibration of $[(CH_3)_2SiO]_4$ in which a combination of separation techniques was used to isolate milligram quantities of the oligomeric cyclic species up to $[(CH_3)_2SiO]_{25}$. Furthermore, gel permeation chromatography studies of an unfractionated equilibrium mixture from such a reaction demonstrated that a continuous mixture of macrocyclic species up to at least $[(CH_3)_2SiO]_{400}$ was present. Cyclics above $[(CH_3)_2SiO]_{12}$ were found to

---

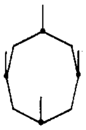
(10) Noll, W. "Chemistry and Technology of the Silicones"; Academic Press: New York, 1968; Chapters 5 and 6 and references cited therein.

(11) Brown, J. F., Jr.; Slusarczuk, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 931.

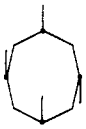
constitute ~2–3% of the total polymer in commercial dimethylsilicone oils. Such large ring dimethylsiloxanes have received detailed study by Semlyen and his co-workers.[12]

Also of interest was a comparison of the ^{29}Si NMR spectra of the cyclic $[H_2SiO]_n$, $[CH_3SiHO]_n$, and $[(CH_3)_2SiO]_n$ series. Our observed ^{29}Si shieldings are shown in Table IV. The same trend, the silicon atoms in the smaller rings deshielded relative to the silicon atoms in the corresponding linear polysiloxanes, with the shieldings increasing in the order cyclic tetramer, pentamer, and hexamer, was observed in each series. The effects of methyl-for-hydrogen substitution in the cyclic tetramer and pentamer and in higher cyclics are very similar, with the $\Delta\delta(^{29}Si)$ ~13.0 on going from $[H_2SiO]_n$ to $[CH_3SiHO]_n$ and $\Delta\delta(^{29}Si)$ ~14.5 on going from $[CH_3SiHO]_n$ to $[(CH_3)_2SiO]_n$. The decrease in shielding as a hydrogen substituent is replaced by a methyl group is in line with expectation.

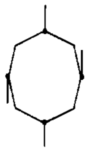
In the case of the $[CH_3SiHO]_n$ cyclic oligomers, geometric isomers are possible, e.g., the cis/trans isomers **1**, **2**, **3**, and **4** in the case of $[CH_3SiHO]_n$. Apparently, all isomers are



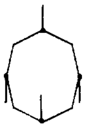
1



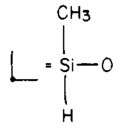
2



3



4



formed, so that several ^{29}Si resonances are seen for each cyclic oligomer, not just one as in the case of $[H_2SiO]_n$ and $[(CH_3)_2SiO]_n$.

In addition to these studies aimed at the synthesis of $[H_2SiO]_n$ cyclics, we also have investigated the synthesis and properties of linear siloxanes of type $Me_3SiO(SiH_2O)_nSiMe_3$. This work will be described in a later paper.

Experimental Section

General Comments. Dichlorosilane was purchased in gas cylinders containing 10 lb of material from the Linde Division of Union Carbide Corp. Since explosions could result if suck-back occurs, a regulator outlet equipped with a diffusion-resistant diaphragm seal valve and a check valve is essential in the setup for dispensing H_2SiCl_2.[13] The Linde Division literature states that dichlorosilane can inflame in air,[13] but it should be noted that it is known[14] that H_2SiCl_2/air mixtures can detonate.

Hydrolysis of Dichlorosilane. Method 1. A 1-L three-necked, round-bottomed flask equipped with a magnetic stir-bar, a low-temperature pentane thermometer, a rubber septum, and a cold condenser (dry ice/isopropyl alcohol) was evacuated and flame-dried, and subsequently, argon was admitted. The evacuation–argon admission procedure was repeated two more times. Freshly distilled (from P_2O_5) dichloromethane (350 mL) then was added, and the flask was cooled to −40 °C (dry ice/isopropyl alcohol bath). Dichlorosilane (42.6 mL of liquid, 52.0 g, 0.515 mol) was condensed into a graduated cold trap and then was allowed to volatilize and bubble into the dichloromethane through Tygon tubing which led to a needle that was inserted through the rubber septum below the surface of the dichloromethane. Distilled water (8.82 g, 0.490 mol) then was added dropwise, with stirring, by syringe over a period of 20 min, to the dichlorosilane solution that was maintained at −40 to −30 °C. During the addition, ice formed in the reaction flask. After the addition had been completed, the ice was allowed to react slowly with the dichlorosilane at −30 to −20 °C. After 1 h, the cold bath was removed, and the reaction mixture was stirred for 45 min while the temperature rose from −20 °C to room temperature. Hydrogen chloride evolution became vigorous around −17 to −15 °C. A colorless, homogeneous solution resulted. This was washed with four 500-mL portions of distilled water (until the washings were neutral). The dichloromethane layer was separated and dried over anhydrous $MgSO_4$ for 40 h. The mixture was filtered through a 150-mL medium-porosity fritted funnel, and the filtrate was distilled (pot temperature to 55 °C) at atmospheric pressure in order to remove most of the solvent. A clear, colorless, mobile liquid residue (28.9 g) remained. The composition of this liquid was determined by using proton NMR spectroscopy. It contained 30% (by weight) of dichloromethane and 70% (by weight) of H_2SiO oligomers, which represents a yield of 85%, based on starting H_2SiCl_2.

A 5.5987-g aliquot of the liquid residue was trap-to-trap distilled (heat gun, 0.05 mmHg) into a receiver cooled to −78 °C. The yield of distillate was 4.2830 g and of residue was 1.2376 g. The distillate contained 38% by weight of CH_2Cl_2 (by ^{1}H NMR) and the *c*-$[H_2SiO]_n$ oligomers listed in Table I in the quantities given. These quantities were determined by GC assuming, as a first approximation, that all oligomers have the same response factor. Percent yields were calculated from these figures. (1) Nonvolatile $[SiH_2O]_n$ polymer: 27%. (2) *c*-$[H_2SiO]_n$ (*n*, % yield based on H_2SiCl_2): 4, 6.1; 5, 22.6; 6, 12.0; 7, 5.1; 8, 2.8; 9, 2.2; 10, 1.7; 11, 1.3; 12, 0.98; 13, 0.69; 14, 0.48; 15, 0.28; 16, 0.14; 17, 0.06. The yield of the rather volatile $[H_2SiO]_4$ actually must have been higher since it is likely that some portion of this compound was lost during the washing process and during the distillation of the dichloromethane. (The tetramer was detected by GC in the distilled CH_2Cl_2 but could not be determined quantatively.)

Method 2. A dry 500-mL three-necked Morton (creased) flask equipped with a cold condenser (dry ice/isopropyl alcohol), a mechanical stirrer, and a rubber septum was charged with 250 mL of dry dichloromethane and cooled to 0 °C. Dichlorosilane (44.1 mL, 53.8 g, 0.533 mol) was condensed into a graduated cold trap and then was allowed to volatilize into the dichloromethane in the usual manner. An Orion Research Inc. Model 341A syringe pump (connected to polyethylene tubing that, via the septum, protruded below the surface of the H_2SiCl_2 solution) was used to add a slight excess of distilled water (10.0 mL, 9.97 g, 0.554 mol at a constant rate of 5.9 mL/h. Upon completion of the addition, the solution was transferred (in air) into a separatory funnel and washed with five aliquots of water (until the washings were neutral). The organic layer was dried ($MgSO_4$) and stored in the refrigerator. GC analysis (6-ft column packed with 15% SE-30 on Chromosorb P; 60 → 250 °C; 10 °C/min; hold at 250 °C temperature program) using a Hewlett-Packard 5750 gas chromatograph and a Hewlett-Packard Model 3390A integrator was used first to determine the approximate percentages of the lower boiling oligomers, $[H_2SiO]_n$, n = 4–11. The dichloromethane then was removed by trap-to-trap distillation at 0.05 mmHg into a low-temperature trap, leaving a mobile liquid residue. The latter was analyzed by GC. The peak areas for the larger cyclics ($[H_2SiO]_n$, n = 12–23) were calculated relative to the nonvolatile $[H_2SiO]_{11}$ and then corrected back to the original reaction mixture to find the composition (Table III). Response factors were not measured, so all yields are uncorrected and are relative only to the sum of the measurable peak areas.

Isolation of Samples of $[H_2SiO]_n$ (n = 4–6). Preparative GC was carried out with a Hewlett-Packard F & M Model 720 gas chromatograph with a 6 ft × $^1/_4$ in. column packed with 15%. General Electric Co. silicone rubber gum SE-30 on Chromosorb P that had been acid-washed and treated with dimethyldichlorosilane. A temperature program of 30–250 °C was used with a temperature increase of 7.5 °C/min. Because they had been found to be much more stable in dilute solution, these H_2SiO oligomers were collected directly in vials containing the solvent to be used for the spectroscopic measurement ($CDCl_3$, CCl_4, or C_6D_6). Neat samples were collected in flame-dried capillary tubes. These were used immediately after

---

(12) (a) Semlyen, J. A. S.; Wright, P. V. *Polymer* **1969**, *10*, 543. (b) Wright, P. V. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 51. (c) Dodgson, K.; Semlyen, J. A. S. *Polymer* **1977**, *18*, 1265. (d) Dodgson, K.; Sympson, D.; Semlyen, J. A. S. *Ibid.* **1978**, *19*, 1285. (e) Semlyen, J. A. S.; Wright, P. V. In "Chromatography of Synthetic Polymers and Biopolymers"; Epton, R., Ed.; Horwood: Chichester, England, 1977; Vol. 1. (f) Semlyen, J. A. S. *Pure Appl. Chem.* **1981**, *53*, 1797. (g) Edwards, C. J. C.; Stepto, R. F. T.; Semlyen, J. A. S. *Polymer* **1982**, *23*, 865, 869. (h) Edwards, C. J. C.; Bantle, S.; Burchard, W.; Stepto, R. F. T.; Semlyen, J. A. S. *Ibid.* **1982**, *23*, 873.

(13) Material Safety Data Sheet, Union Carbide Silane A-199 (Linde Div., Union Carbide Corp.); Linde Specialty Gases Safety Precautions and Emergency Procedures, F-12-237.

(14) Sharp, K. G.; Arvidson, A.; Elvey, T. C. *J. Electrochem. Soc.* **1982**, *129*, 2346.

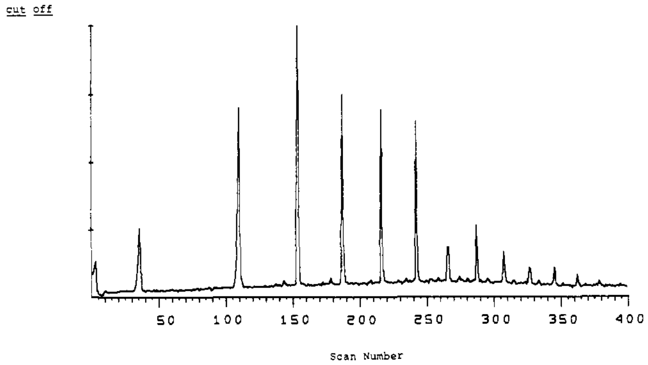


Figure 2. GC/MS study of H_2SiCl_2 cyclic hydrolysis products (total ionization plot shows $[H_2SiO]_7$ through $[H_2SiO]_{20}$).

Table V. GC/CI MS Experiment

$[H_2SiO]_n$: n	$nH_2SiO + NH_4^+$ calcd[a]	$nH_2SiO + NH_4^+$ found (max)	$[H_2SiO]_n$: n	$nH_2SiO + NH_4^+$ calcd[a]	$nH_2SiO + NH_4^+$ found (max)
7	339.95	340	14	661.86	662
8	385.93	386	15	707.85	708
9	431.92	432	16	753.83	754
10	477.91	478	17	799.82	800
11	523.90	524	18	845.81	846
12	569.88	570	19	891.80	892
13	615.87	616	20	937.79	938

[a] Maximum includes all ^{28}Si (27.976 929).

collection in the refractive index measurements.

The 12-eV electron-impact mass spectra of these three cyclic oligomers were measured (GC/MS). $[H_2SiO]_4$: m/z 183 ($M^+ - H$), 137 ($M^+ - H - H_2SiO$), 92 ($M^+ - 2H_2SiO$), 46 (H_2SiO^+), 45 ($HSiO^+$). $[H_2SiO]_5$: m/z 229 ($M^+ - H$), 199 ($M^+ - H - SiH_2$), 197 ($M^+ - 3H - SiH_2$), 137 ($M^+ - H - 2H_2SiO$), 108 ($H_4Si_2O_3^+$). $[H_2SiO]_6$: m/z 277 (M^+), 243 ($M^+ - 4H - SiH_2$), 195, 197, 198 ($M^+ - SiH_2 - SiH_2O - nH$; n = 2, 3, 5).

GC/CI-MS Study of the $[H_2SiO]_n$ Cyclics. This experiment was carried out in the laboratory of Dr. V. Reinhold, Department of Biochemistry, Harvard Medical School, with a Varian 3700 gas chromatograph (30-m capillary column; program: 40 °C (5 min) → 240 °C at 10 °C/min), a Finnigan MAT 312 mass spectrometer (CI (NH_3); 150 °C source temperature; (6–8) × 10^{-5} torr source pressure; 3-kV accelerating voltage; 250-V ionization voltage; 1 × 10^6 SEM gain, with a resolution $m/\Delta m$ = 1000), and a Finnigan SS-200 data system.

Figure 2 shows the GC/MS total ionization trace. The first peak is $[H_2SiO]_7$; $[H_2SiO]_{20}$ was the last one detected. The lower cyclics were not observed under these particular conditions. Table V shows the observed and calculated masses [$M + NH_4^+$].

Hydrolysis of Methyldichlorosilane. A dry 500-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a water-cooled condenser, and two rubber septa was charged with 31.0 mL of CH_3SiHCl_2 (34.3 g, 0.298 mol, distilled from magnesium) and 250 mL of dichloromethane. Distilled water (6.0 mL, 5.98 g, 0.332 mol) was added (as in the case of H_2SiCl_2) by using the syringe pump at a constant rate of 5.9 mL/h to the CH_3SiHCl_2 solution at room temperature. Most of the water was consumed very quickly. The reaction mixture was stirred at room temperature overnight. The organic layer was washed with water, dried ($MgSO_4$), and concentrated with use of a 2-ft Vigreaux column. GC analysis of the residue (2-ft SE-30 column; temperature program 80 → 300 °C at 10 °C/min) showed the composition of c-$[CH_3SiHO]_n$ oligomers as listed in Table III. The remaining dichloromethane then was removed by trap-to-trap distillation (room temperature, 0.03 mmHg), and the clear oil that remained, a mixture of c-$[CH_3SiHO]_n$ oligomers (12.80 g, 0.213 mol, 71%), was characterized by ^{29}Si (Table IV) and ^1H NMR and IR spectroscopy and analysis. Anal. Calcd for CH_4OSi: C, 19.98; H, 6.70. Found: C, 20.25; H, 6.65. NMR (250 MHz, $CDCl_3$): δ 0.188 (s, slightly broadened), 4.696 (s). IR (thin film, cm^{-1}): 2965 (s), 2905 (w), 2162 (vs), 1407 (m), 1259 (s), 1135–1030 (vs, br), 920 (sh), 900–850 (vs, br), 830 (sh), 770 (vs), and 720 (sh).

Hydrolysis of Dimethyldichlorosilane. The same reaction vessel that had been used in the CH_3SiHCl_2 experiment was used. Distilled water (6.0 mL, 0.332 mol) was added at 0 °C to a stirred solution of 38.3 g (0.297 mol) of dimethyldichlorosilane (distilled from magnesium) in 250 mL of dichloromethane by using the syringe pump (5.9 mL/h). The reaction proceeded very slowly at 0 °C and also at room temperature, as evidenced by the separate water layer on top of the organic layer. Therefore, the reaction mixture was heated at reflux for 18 h. The workup procedure of the experiment above was used. Most of the dichloromethane was removed by distillation and was shown by GC to be free of lower boiling c-$[(CH_3)_2SiO]_n$ oligomers. GC analysis of the distillation residue (2-ft 15% SE-30; temperature program: 80–300 °C at 15 °C/min) showed the presence of a mixture of c-$[(CH_3)_2SiO]_n$ oligomers (Table III). Removal of all of the dichloromethane by trap-to-trap distillation left 19.88 g (0.268 mol, 90%) of a colorless oil, c-$[(CH_3)_2SiO]_n$. Anal. Calcd for C_2H_6OSi: C, 32.39; H, 8.16. Found: C, 32.82; H, 8.13. IR (thin film, cm^{-1}): 2963 (s), 2908 (w), 1410 (w), 1260 (vs), 1120–1020 (vs, br), 860 (sh), 805 (vs), 695 (m), and 655 (w). ^1H NMR (250 MHz, $CDCl_3$): δ 0.074 (D_4), 0.058 (D_5), 0.044 (D_6 and higher cyclics).

Acknowledgment. The authors are grateful to the Air Force Office of Scientific Research (NC)-AFSC and to the Rhône-Poulenc Co. for generous support of this work. We are indebted to Dr. Catherine E. Costello (MIT Mass Spectrometry Facility, supported by the NIH Division of Research Resources, Grant No. RR00317; K. Biemann, principal investigator), to Dr. Vernon Reinhold (Harvard Medical School), and to Dr. H. G. Langer (Wayland Research Laboratory, Dow Chemical Co.) for GC/mass spectra.

Registry No. $[H_2SiO]_4$, 293-51-6; $[H_2SiO]_5$, 294-40-6; $[H_2SiO]_6$, 295-01-2; $[CH_3SiHO]_4$, 2370-88-9; $[CH_3SiHO]_5$, 6166-86-5; $[CH_3SiHO]_6$, 6166-87-6; $[(CH_3)_2SiO]_4$, 556-67-2; $[(CH_3)_2SiO]_5$, 541-02-6; $[(CH_3)_2SiO]_6$, 540-97-6; $[(CH_3)_2SiO]_7$, 107-50-6; $[(CH_3)_2SiO]_8$, 556-68-3; $[H_2SiO]_9$, 296-43-5; $[H_2SiO]_{10}$, 4408-92-8; $[H_2SiO]_{11}$, 5300-39-0; $[H_2SiO]_{12}$, 4342-88-5; $[H_2SiO]_{13}$, 4342-89-6; $[H_2SiO]_{14}$, 85956-53-2; $[H_2SiO]_{15}$, 25399-13-7; $[H_2SiO]_{16}$, 85956-54-3; $[H_2SiO]_{17}$, 85956-55-4; $[H_2SiO]_{18}$, 25531-27-5; $[H_2SiO]_{19}$, 85956-56-5; $[H_2SiO]_{20}$, 85956-57-6; dichlorosilane, 4109-96-0; methyldichlorosilane, 75-54-7; dimethyldichlorosilane, 75-78-5.