

# Siloxanes from the hydrolysis of isopropyltrimethoxysilane

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Received 21 March 1994; in revised form 8 August 1994

## Abstract

The behavior of isopropyltrimethoxysilane (**1**) in the presence one equivalent of water and a dibutyltin dilaurate catalyst has been investigated. Under these conditions, partial hydrolysis of the methoxy groups of **1** occurred, followed by condensation reactions leading to the formation of low molecular-weight oligomers. Disiloxane **4**, trisiloxane **6** and cyclic siloxanes **7** and **8** have been isolated and fully characterized. Transient reaction intermediates silanol **3** and hydroxydisiloxane **5** have been characterized spectroscopically. The time evolution of these species was followed by gas chromatography and  $^{29}\text{Si}$  NMR. A reaction scheme for the hydrolytic condensation of **1** is proposed to accommodate these results.

*Keywords:* Silicon; Siloxanes; Hydrolysis; Nuclear magnetic resonance

## 1. Introduction

The condensation of alkoxy silanes to siloxanes under hydrolytic conditions is a reaction that has been widely exploited in polymer and surface adhesion applications [1]. Important commercial processes involve the cross-linking of polyethylene chains possessing randomly incorporated trialkoxy silane functions using this type of chemistry to give materials with the required rigidity [2]. The work reported in this contribution was undertaken in connection with a study of the complications of oxidation during the processing of such polymers, where it was necessary to know the background hydrolytic chemistry of the alkoxy silane moiety. To this end, a model hydrolysis study was performed on isopropyltrimethoxysilane (**1**), whose isopropyl group mimics the local hydrocarbon environment of the cross-linking unit in the polymer. This low molecular-weight silane does, however, give products with suitable properties for isolation, characterization, and analysis by the usual techniques of organic chemistry. Much of the published work on the hydrolysis of alkyl-trialkoxysilanes was carried out in the 1950s using the limited techniques (distillation, elemental analysis, infrared spectroscopy, etc.) available at the time [3]. The

subsequent application of more modern methods has generally involved the analysis of unfractionated reaction mixtures [4–7]. Furthermore, most previous studies have examined compounds with simple, unhindered primary alkyl groups. The present contribution applies modern methodology to an analysis of the chemistry of the more hindered secondary alkylsilane **1** in the presence of the relatively small amounts of water typical of the polymer cross-linking process. These features of the reaction slow down the hydrolysis and condensation steps [8] of siloxane formation, and permit a better understanding of the initial phases of this important process that is of relevance to the many other applications of this chemistry.

## 2. Results

The chemistry of isopropyltrimethoxysilane (**1**) has been examined with limited amounts of water in the presence of dibutyltin dilaurate (DBTDL), a typical catalyst for polymer cross-linking. Thus, the hydrolysis of **1** with one equivalent of water and 2% of DBTDL (little reaction occurred in the absence of DBTDL) was performed at 100°C under nitrogen in a small volume of THF for homogeneity, in a sealed tube. Periodic GC analysis permitted monitoring of the evolution of the reaction. After 0.5 h, a single important product had

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accumulated as ca. 20% of the volatile materials. This material, which has a slightly longer retention time than **1**, was subjected to GC-mass spectrometric analysis. Although no molecular ion was observed for the new compound, the only fragment peak of significant abundance was the base peak at  $m/z$  107. This corresponds to fragment-ion **2**, logically derived from silanol structure **3** by loss of the isopropyl group. This is the characteristic fragmentation mode of alkyltrialkoxysilanes, which generally show weak or non-existent molecular ions, and base peaks resulting from loss of the alkyl group [9]. On this basis, structure **3** is assigned to the first intermediate observed in the hydrolysis of **1**.

Although it was not possible to isolate **3** in pure form, this structural assignment was confirmed by several additional spectroscopic measurements on reaction mixtures enriched in this component.  $^{29}\text{Si}$  NMR spectroscopy has proven to be an extremely valuable tool for following the course of hydrolysis experiments on tetraalkoxysilanes [10–13] and alkyltrialkoxysilanes [4–7]. In these studies,  $^{29}\text{Si}$  signals deshielded slightly relative to those of the alkoxy silanes have been attributed to the silanol products derived from the successive replacement of alkoxy groups by hydroxy groups (1–2 ppm increment for each exchange), although the silanols were not isolated and further characterized.  $^{29}\text{Si}$  NMR analysis of a typical hydrolysis reaction of **1** showed, in addition to starting material at  $\delta$  –43.8, a resonance at  $\delta$  –42.1 attributable to structure **3**. In a similar experiment with two equivalents of water, silanol **3** represented as much as 40% of the volatile product. In this instance, careful concentration permitted  $^{13}\text{C}$ -NMR analysis of the mixture, which showed new signals for **3** at  $\delta$  10.7, 16.76, and 50.5, displaced slightly from those of the starting material at  $\delta$  10.3, 16.85 and 50.7. The  $^1\text{H}$  NMR spectrum of the mixture was not sufficiently resolved for detailed analysis of the alkyl region, but a new signal for the methoxy group of **3** at  $\delta$  3.57 was observed adjacent to the peak for **1** ( $\delta$  3.58).

Hydrolysis studies of tetraalkoxysilanes using an excess of water have been reported to involve more highly hydrolyzed silanes and, indeed, the  $^{29}\text{Si}$  NMR data has been interpreted in terms of the presence of all possible  $\text{Si}(\text{OH})_n(\text{OR})_{4-n}$  structures during the initial stages of reaction [10–13]. Alkyltrialkoxysilanes appear to behave similarly [4–7,14] and in the case of phenyltrimethoxysilane careful hydrolysis even provided crystalline phenylsilanetriol [15]. In the present study with much less water available, small quantities of components with slightly longer retention times than **3** were observed by GC, although there is no conclusive evidence that these include the corresponding silanediol and silanetriol. If such intermediates are formed, they either do not accumulate under the reaction conditions or are not stable to GC analysis.

In the reaction of **1** with one equivalent of water, condensation to disiloxanes was the next process apparent by GC analysis. Thus, after ca. 1 h, two additional components were present in the reaction mixture. One of these, which builds up steadily over the course of the reaction, was isolated by distillation and identified as 1,3-diisopropyl-1,1,3,3-tetramethoxydisiloxane (**4**). The other component appears prior to **4**, but builds up to a maximum after several hours and then slowly disappears. The hydroxydisiloxane structure **5** is attributed to this material. Whereas the former type of disiloxane was reported in the early hydrolysis studies [3], hydroxydisiloxanes such as **5** have not been fully characterized, although they have been proposed as components of complex hydrolysis mixtures in certain  $^{29}\text{Si}$  NMR experiments [7].

The mass spectrum of **4** does not show a molecular ion, but the base peak at  $m/z$  239 corresponds to loss of an isopropyl radical from the molecular ion. The IR spectrum shows characteristic bands at 1194, 1092 and  $1065\text{ cm}^{-1}$ . A strong peak near  $1090\text{ cm}^{-1}$  is commonly present in the IR spectrum of compounds with a Si–O–C unit, whereas an  $1190\text{ cm}^{-1}$  band is typical for Si–O–CH<sub>3</sub> compounds [4,16]. The additional band at  $1065\text{ cm}^{-1}$  appears to be diagnostic of the Si–O–Si moiety [16]. The  $^{13}\text{C}$  NMR of **4** displays signals at  $\delta$  11.0, 16.9, and 50.5, with only the more shielded methine carbon of **4** showing an appreciable shift relative to **1** ( $\delta$  10.3). The  $^{29}\text{Si}$ -NMR signal for **4** is observed at  $\delta$  –51.5, shielded about 8 ppm relative to that of **1**. This increment is consistent with this structural perturbation (replacement of SiOR by SiOSi) in the tetraalkoxysilane-derived series [10–13].

The structure of hydroxydisiloxane **5** is based on  $^{29}\text{Si}$ -NMR and mass spectral data obtained on reaction mixtures because it was not possible to isolate it in pure form. GC-mass spectrometry allowed for the characterization of the appropriate component which showed its base peak at  $m/z$  225, consistent with the fragment that would be derived by loss of an isopropyl moiety from **5**. The  $^{29}\text{Si}$  spectrum of **5** was obtained in a supplementary experiment in which **1** was hydrolyzed by the addition of concentrated HCl in THF to a benzene-*d*<sub>6</sub> solution of **1** at room temperature. Under these conditions, hydrolysis first generated **3**, followed by hydroxydisiloxane **5**, and then disiloxane **4**. The course of this reaction was monitored by both GC and  $^{29}\text{Si}$  NMR. In addition to the  $^{29}\text{Si}$  resonances for **1**, **3** and **4**, new signals appeared at  $\delta$  –50.5 and  $\delta$  –51.6 which were assigned to **5**. Fig. 1 shows a representative  $^{29}\text{Si}$  NMR of this reaction at the stage where **3** and **5** have been formed, but **4** has not yet appeared. The more shielded peak is attributed to the dimethoxy-substituted Si, since it is shifted only slightly relative to the structurally similar Si of **4** ( $\delta$  –51.7). The other signal is assigned to the hydroxy-bearing Si; the 1 ppm shift

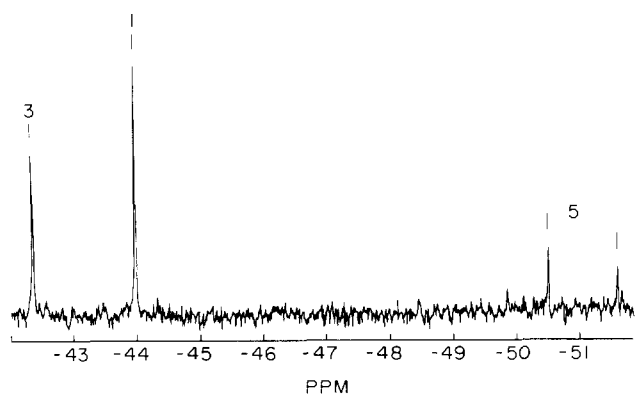


Fig. 1.  $^{29}\text{Si}$  NMR spectrum of an aqueous HCl hydrolysis of **1** in benzene- $d_6$  after 0.75 equiv. water was added. Signals for **1** (–43.9 ppm), **3** (–42.3 ppm) and **5** (–50.6 and –51.6 ppm) are observed.

here is consistent with the anticipated increment for exchange of a hydroxy for a methoxy group (vide supra). There is no clear-cut evidence for more highly hydrolyzed products under these modified conditions.

Higher condensation products were isolated from a large-scale reaction using one equivalent of water. A constant reaction profile was achieved after heating for several days as indicated by GC analysis. Vacuum transfer followed by spinning-band distillation and preparative GC provided for fractionation of this product, which also included substantial amounts of non-volatile materials. The  $^{29}\text{Si}$  NMR spectrum of the unfractionated volatile product shown in Fig. 2 illustrates the nature of the mixture. Disiloxane **4** accounted for ca. 40% of the volatile product, but **3** and **5** were no longer present in significant amounts. Three trimeric components were identified. One of these, representing about 10% of the volatile product, was obtained in

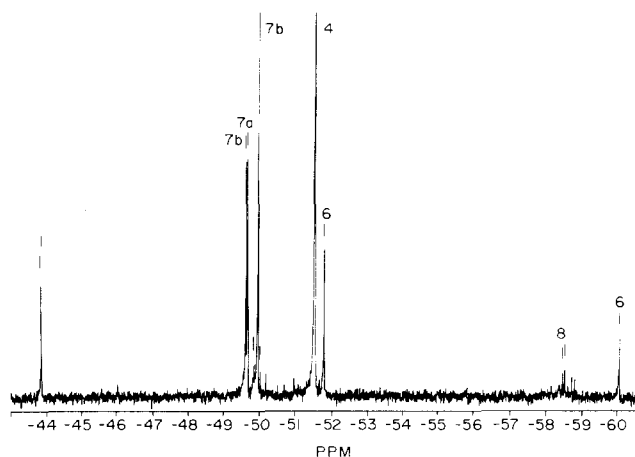
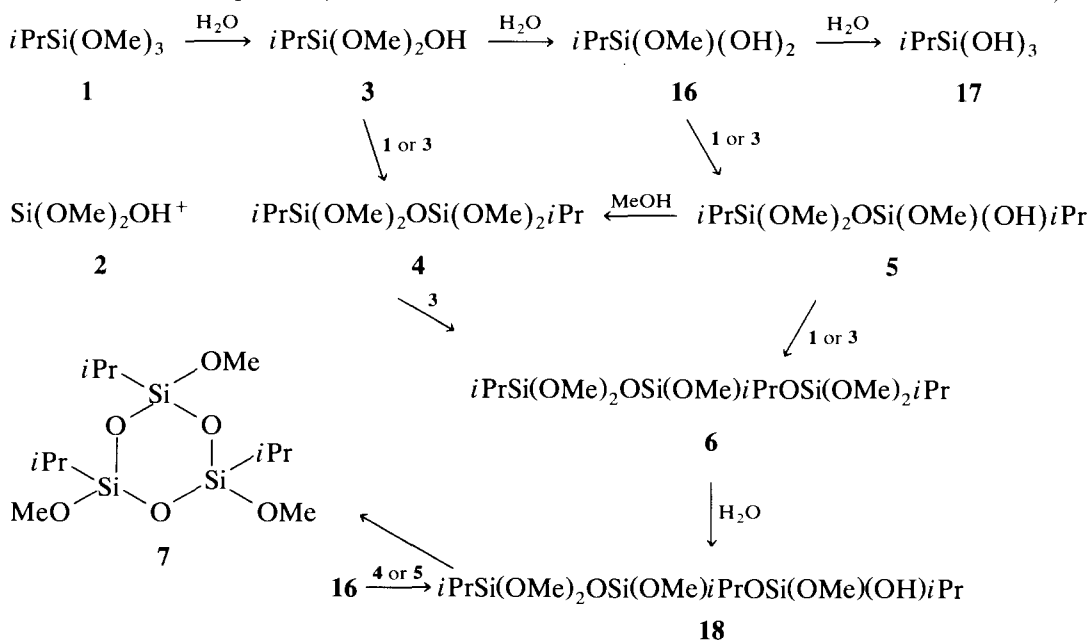


Fig. 2. Volatile products from the large-scale hydrolysis of **1** with 1 equiv. of water. Spectrum shows **1** (–43.8 ppm), **4** (–51.5 ppm), **6** (–51.8 and –60.0 ppm; 2:1 intensity ratio), **7a** (–49.65 ppm), **7b** (–49.61 and –49.94 ppm; 2:1 intensity ratio) and **8** (–58 to –59 ppm).

pure form. Its mass spectrum gave a base peak at  $m/z$  357 corresponding to the fragment ion expected from linear trisiloxane **6**. Similar trimers have been reported in other hydrolysis studies [3]. Structure **6** is supported by its  $^{29}\text{Si}$  NMR which shows peaks at  $\delta$  –57.8 and  $\delta$  –60.0 in a 2:1 ratio. The first resonance, which is only slightly displaced from that of **4**, is assigned to terminal Si, whereas the peak attributed to the central Si is shielded relative to **4** by an 8 ppm increment, similar to that for the replacement of an alkoxy by a siloxy substituent in the **1** to **4** comparison. The  $^{13}\text{C}$  NMR spectrum of **6** displays two signals of unequal intensity for each of the three types of carbon. The most significant variation is at the methine carbon, which is at  $\delta$



Scheme 1.

11.8 for the central isopropyl, deshielded slightly relative to the terminal one at  $\delta$  11.0, which is at the same place as the corresponding signal for **4**.

The other two trimeric species were obtained as an unresolved 2.5:1 mixture (ca. 30% of the volatile product). GC-mass spectrometric analysis showed that the two components had very similar spectra with base peaks at  $m/z$  311, suggesting that these materials are the two cyclic trimers of structure **7**, a common type of siloxane oligomer [3]. A chemical-ionization mass spectrum of the mixture gave an  $M + 1$  peak at  $m/z$  355 with an appropriate high-resolution mass for the composition of **7**. The  $^{29}\text{Si}$  NMR spectrum of the mixture displayed resonances at  $\delta$  -49.61, -49.65 and -49.9 in a 1:1.1:2 ratio. This indicates that the *cis, cis* isomer **7a**, which has a single type of silicon environment, is the minor component that gives rise to the intermediate  $^{29}\text{Si}$  NMR signal, whereas the more abundant *cis, trans* isomer **7b** is the source of the two remaining signals in a 2:1 ratio, as required by the symmetry of the molecule. Interestingly, these  $^{29}\text{Si}$  NMR resonances are deshielded about 10 ppm relative to the Si with a similar local environment in linear trimer **6**. Related cyclotrisiloxanes show similar shifts relative to the analogous linear siloxanes [17]. The  $^{13}\text{C}$  NMR spectrum of the mixture (Fig. 3) displays three resonances for both methine and methoxy carbons (one for **7a** and two for **7b**); however, there are a total of four signals for the methyl carbons. The *cis, cis* isomer **7a** should give a single methyl resonance, whereas the *cis, trans* compound **7b** possesses identical methyl groups on the unique isopropyl substituent, but has diastereotopic methyls on the two identical isopropyl groups. Thus, **7b** should give rise to three different methyl resonances. Finally, although the  $^1\text{H}$  NMR spectrum is not very useful in the isopropyl region owing to the overlapping of peaks, the mixture does show three distinct signals for methoxy groups at  $\delta$  3.57, 3.60 and 3.62 in a 1:2:1.1 ratio, fully consistent with the assignments.

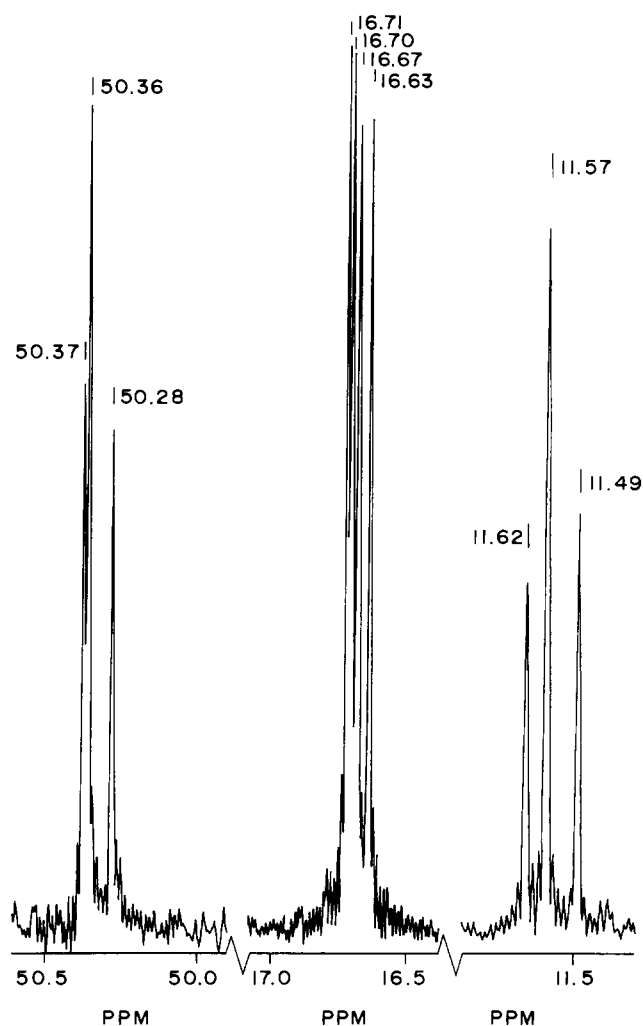
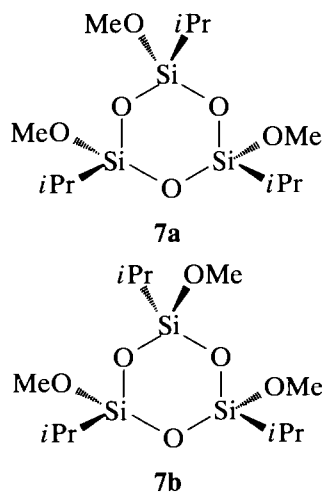
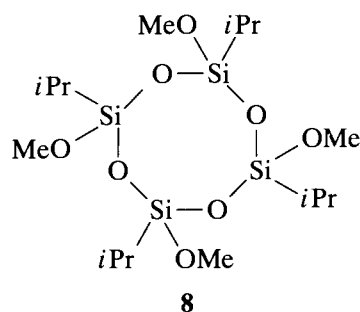


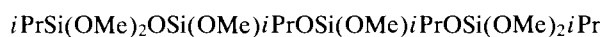
Fig. 3. The  $^{13}\text{C}$  NMR spectrum of a mixture of **7a** and **7b** showing the  $\text{OCH}_3$ ,  $\text{CH}_3$  and  $\text{CH}$  regions.



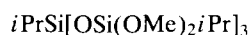
Finally, a less volatile fraction (ca. 8% of the total) was shown by GC analysis to be a 1:20:3:1 mixture of four closely spaced components. These are tentatively assigned as the four possible stereoisomers of cyclotetrasiloxane **8**. GC-mass spectrometry gave acceptable spectra for the two more abundant isomers, which showed very similar fragmentation patterns with a base peak at  $m/z$  429, appropriate for the loss of an isopropyl radical from the molecular ion of **8**. The  $^1\text{H}$  NMR spectrum was quite complicated, but integration demonstrated that there were equal numbers of

methoxy and isopropyl groups, as required for a cyclic structure. The IR spectrum of **8** displays characteristic Si–O bands at 1113, 1083, 1065, and 1027  $\text{cm}^{-1}$ . The  $^{29}\text{Si}$  NMR spectrum of the total volatile product from hydrolysis showed a series of weak peaks assigned to **8** at about  $-58$  ppm, shifted only slightly from the central Si of linear trimer **6** in accord with results on related cyclotetrasiloxanes [17].

Interestingly, significant amounts of a product with properties appropriate for linear tetramer **9** were not observed in any of these experiments. A further point of interest concerns the absence of branched tetrasiloxane **10**, which should be obvious by  $^{29}\text{Si}$  NMR, because the central silicon should be shielded significantly relative to the central silicon of **6** [17]. Signals in this region were not observed for any of the hydrolysis mixtures examined.



**9**

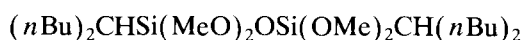


**10**

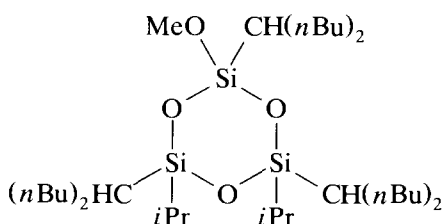
The detailed picture that has been developed for the hydrolysis of **1** can be applied in the examination of other alkyltrialkoxysilanes by  $^{29}\text{Si}$  NMR. Thus, hydrolysis of the higher molecular weight model **11** with one equivalent of water was performed for 48 h under the standard conditions used with **1**. Analysis of the reaction mixture by  $^{29}\text{Si}$  NMR showed five signals which can be attributable to starting material ( $\delta -43.6$ ), dimer **12** ( $\delta -51.5$ ) and cyclic trimers **13** ( $\delta -50.2$ ,  $-50.0$  and  $-49.9$ ) in the relative amounts 5:1.2:1. At this time in the reaction, there were no appreciable amounts of silanol species nor of linear trimer. Confirmatory evidence for the presence of dimer **12** is provided by the  $^{13}\text{C}$  spectrum which shows a new signal at  $\delta 22.9$  for the methine carbon, shifted 0.7 ppm downfield from the corresponding peak of **11**. This increment is identical to that found for the related isopropylsilanes (vide infra).



**11**

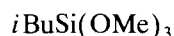


**12**

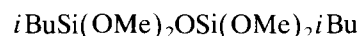


**13**

A limited study was also undertaken of the hydrolysis of the primary isobutyltrimethoxysilane (**14**) in the presence of one equivalent of water under the standard conditions. GC analysis after 35 h indicated starting material (60%), dimer **15** (20%) and peaks with retention times appropriate for linear and cyclic trisiloxanes (5% each). Disiloxane **15** was detected spectroscopically in the reaction mixture by  $^{29}\text{Si}$  NMR which showed a new signal at  $\delta -50.2$ , shielded the expected 8 ppm relative to that of **14**. In the  $^{13}\text{C}$  NMR the chemical shifts of disiloxane **15** are very similar to those of **14** with the exception of the methylene carbon which shows a 1.5 ppm deshielding that is similar to, but larger than, the corresponding perturbations of the secondary carbon attached to Si in the series discussed above. Thus, other alkyltrialkoxysilanes behave qualitatively like **1** and NMR spectroscopy is a good method for monitoring these transformations.



**14**



**15**

The preparation of **1** and **14** utilized the usual reaction of tetramethoxysilane with the corresponding Grignard reagent. This procedure was not effective for the preparation of the higher molecular weight analog **11**, but an in situ generation of the alkyllithium from the alkyl bromide, and lithium naphthalenide in the presence of tetramethoxysilane successfully yielded **11**.

### 3. Discussion

The chemistry of alkyltrialkoxysilanes is intermediate in complexity between that of the dialkyldialkoxysilanes [18], which generally give readily characterized silanols and oligomeric products, and tetraalkoxysilanes, which lead to complex, highly branched materials because of the increased possibilities for siloxane bond formation [10–13]. The use in the present study of the relatively hindered isopropyl derivative **1** with a limited amount of water permits better resolution of the various hydrolysis and condensation processes as a function of reaction time, and also limits the extent of oligomerization. This provides a more detailed accounting of the initial phases of this chemistry than has been available to date. In particular, the various stable oligomers generated under these conditions have been unambiguously characterized spectroscopically and key unstable silanols **3** and **5** have been documented in reasonable detail. This provides a comprehensive demonstration of these types of silanol species, and pinpoints their involvement in the acid-catalyzed condensation reactions of alkyltrialkoxysilanes.

The first step in the reaction of **1** under the conditions employed in this study is its DBTDL-catalyzed hydrolysis to silanol **3**, which rapidly builds up to

substantial concentrations before depletion by further reactions. The published work on the hydrolysis of trialkoxysilanes in dilute aqueous solutions shows that these materials can be hydrolyzed completely to the silanetriols prior to condensation, but under other circumstances hydrolysis and disiloxane formation are often competitive [4–8]. Kinetic studies have indicated that each successive hydrolysis step of an alkyltrialkoxysilane is faster than the previous one [6]. From this point of view, it is interesting that neither silanediol **16** nor the corresponding triol **17** has been unequivocally demonstrated to be present in significant amounts under the reaction conditions used in the present work. Nonetheless, we believe that **16** is likely to be an important intermediate that is consumed by condensation processes as rapidly as it is generated (*vide infra*). The intervention of silanetriol, **17**, however, is not required to explain any of the characterized products in this study and, indeed, the absence of branched siloxane **10** speaks against significant involvement of silanetriol **17**. This is feasible if other reactions of silanediol **16** are more rapid than its hydrolysis. Finally, it should be recalled that all of these hydrolysis steps are reversible processes, so that any of the silanol intermediates can react with methanol to revert to an alkoxysilane bond and water [8].

Condensations to give the Si–O–Si unit can, in principle, occur between two Si–OH moieties with the elimination of water, or by the loss of methanol from Si–OH and Si–OCH<sub>3</sub> residues [8]. It has been suggested that the former process is more facile. However, the greater availability of Si–OMe groups allows the latter conversion to become important, particularly during the later stages of the reaction when Si–OH functions are depleted.

The fact that hydroxydisiloxane **5** is the first dimeric species to be formed implicates silanediol **16** as a key intermediate. Thus, in order for hydroxydisiloxane **5** to appear prior to disiloxane **4**, the hydroxyl group of **5** must already be present in its precursor, as would be the case in the reaction of silanediol **16** with silanol **3** to yield siloxane **5** and regenerate water or, alternatively, the combination of **16** with **1** to give methanol and **5**. The condensation reactions of silanediol **16** are anticipated to be faster than those of silanol **4** because of steric hindrance [6]. This could account for the non-accumulation of **16** in the reaction mixture. The formation of disiloxane **4** presumably becomes more competitive as water is consumed and the condensation of silanol **3**, either with itself or with **1**, becomes more important. Furthermore, hydroxydisiloxane **5** can react with liberated methanol to generate disiloxane **4** and water. Since disiloxanes are less reactive towards hydrolysis than **1** [6], disiloxane **4** should accumulate as the reaction proceeds. Hydroxysiloxane **5** will, however, eventually disappear by further condensation reactions.

Logical routes to linear trisiloxane **6** involve the further condensation of hydroxydisiloxane **5**, either with silanol **3** or with trialkoxysilane **1**. Another possible source of trisiloxane **6** is the combination of disiloxane **4** with silanol **3**. The pathway to cyclotrisiloxanes **7** is not as clearly defined by the available information. The unobserved hydroxytrisiloxane **18** would surely be a viable source of **7** by rapid cyclization with the elimination of methanol. The intramolecular nature of this condensation would probably greatly facilitate this reaction pathway, which could account for the non-accumulation of **18**. The hydrolysis of trisiloxane **6** is one potential source of hydroxytrisiloxane **18**; the reverse reaction of methanol with **18** would, of course, provide another route to acyclic trisiloxane **6**, if **18** were available by another pathway. The condensations of silanediol **16** with either disiloxane **4** or hydroxydisiloxane **5** are such alternate processes for the generation of hydroxytrisiloxane **18**. Finally, the production of tetrameric cyclotetrasiloxanes **8** is even more obscure, particularly because linear tetramer **9** does not accumulate during the hydrolysis reaction. However, it should be noted that cyclic trimers **7** were more prevalent than linear trimer **6**, a fact that is consistent with the idea that the generation of cyclic siloxanes from their acyclic analogs occurs rapidly under the reaction conditions. Other possibilities can be envisaged for the formation of oligomeric siloxanes, especially those involving dihydroxysiloxane intermediates of differing chain lengths, but evidence for the existence of such species under the reaction conditions is needed to justify consideration of these hypothetical processes.

In conclusion, a good delineation has been obtained for the early sequence of events which occur during the formation of small siloxanes from the treatment of **1** with relatively small amounts of water in the presence of a catalyst. Under these conditions, hydrolysis and condensation are competitive, so that partially hydrolyzed silanes are the key intermediates in the oligomerization process. This is probably a good model for the cross-linking process that takes place in the hydrophobic environment inside bulk polyethylene. A much different situation obtains in the more complicated and extensive condensations of alkyltrialkoxysilanes that occur in solution in an excess of water, where more complete hydrolysis is key to the formation of polymeric siloxanes. The differences in chemistry in these extreme domains need to be taken into account in developing a better understanding of the chemical basis of siloxane technology.

#### 4. Experimental details

Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AM-500 instrument at 500

MHz for  $^1\text{H}$  NMR and 125.7 MHz for  $^{13}\text{C}$  NMR on samples in  $\text{CDCl}_3$  unless otherwise specified. The AM-500 spectrometer was equipped with a 10 mm probe for  $^{29}\text{Si}$  NMR; spectra were recorded at 99.9 MHz on samples in  $\text{C}_6\text{D}_6$  using the DEPT [19] or inverse-gated decoupling techniques. All  $^{29}\text{Si}$  chemical shifts are reported in parts per million relative to tetramethylsilane as an external reference. Infrared (IR) spectra were recorded on liquid films (unless otherwise specified) with a Mattson Galaxy 4020 FTIR instrument or a Perkin-Elmer Model 298 grating spectrometer. Analytical gas chromatography (GC) was performed on a Hewlett Packard HP-5890 equipped with an HP-3396A integrator and a  $50\text{ m} \times 0.2\text{ mm} \times 0.33\text{ }\mu\text{m}$  HP-5 capillary column. Preparative GC was performed on a Varian 2700 utilizing a  $4.3\text{ m} \times 6.35\text{ mm}$  column packed with 5% OV-101 on Chromosorb-W. Mass spectrometry (MS) was conducted on a Kratos MS-80 instrument; GC-MS experiments utilized a Carlo Erba chromatograph fitted with a  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$  DB-5 capillary column. Tetramethoxysilane and dibutyltin dilaurate (DBTDL) were purchased from Aldrich and used as received.

#### 4.1. Isopropyltrimethoxysilane (1) [20]

A solution of isopropylmagnesium bromide prepared from 8.6 g (0.36 mol) of Mg and 40 g (0.32 mol) of isopropyl bromide in 320 ml of ether, was added to 44 g (0.29 mol) of tetramethoxysilane with stirring at  $0^\circ\text{C}$ . The slurry was stirred for 1 h at room temperature. Dry pentane (100 mL) was added; the mixture was cooled to  $0^\circ\text{C}$  and rapidly filtered through a glass frit. The solvents were removed and the residue was distilled to yield 27 g (56%) of **1**: bp  $70\text{--}72^\circ$  (95 torr).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  3.57 (s, 9), 1.28 (d, 6,  $J = 7$  Hz), 1.14 (m, 1).  $^{13}\text{C}$  NMR  $\delta$  50.7, 16.8, 10.3 (CH).  $^{29}\text{Si}$  NMR  $\delta$   $-43.8$ . IR 1467, 1193, 1092, 1004, 888, 802,  $744\text{ cm}^{-1}$ . GC-MS (EI)  $m/z$  (rel. intensity) 164 (1), 121 (100), 105 (6), 91 (33).

#### 4.2. Isobutyltrimethoxysilane (14) [21]

In a similar procedure, the Grignard reagent prepared from 20 g (0.15 mol) of isobutyl bromide and 3.9 g (0.16 mol) of Mg in 150 ml of ether was added to 20 g (0.13 mol) of tetramethoxysilane. Distillation afforded 10.5 g (45%) of **14**: bp  $85\text{--}87^\circ$  (65 torr).  $^1\text{H}$  NMR  $\delta$  3.56 (s, 9), 1.86 (nonet, 1,  $J = 7$  Hz), 0.96 (d, 6,  $J = 7$  Hz), 0.62 (d, 2,  $J = 7$  Hz).  $^{13}\text{C}$  NMR  $\delta$  50.3, 25.7, 23.7, 19.4.  $^{29}\text{Si}$  NMR  $\delta$   $-42.4$ . IR 1366, 1227, 1193, 1089,  $1038, 836\text{ cm}^{-1}$ .

#### 4.3. 5-(Trimethoxysilyl)nonane (11)

To 6.8 g of lithium dispersion (25 wt.%, 0.25 mol of Li), previously washed with pentane under argon was

added 40 ml of THF and 0.95 g (6 mmol) of biphenyl. After stirring for 30 min at room temperature, the solution became deep purple. It was cooled to  $-78^\circ\text{C}$  and 28 g (0.18 mol) of tetramethoxysilane in 100 ml of THF was added rapidly, followed by 10 g (61 mmol) of 5-chlorononane [22] over 30 min. After stirring for 4 h at  $-78^\circ\text{C}$ , the mixture was allowed to warm to room temperature and stirred for an additional hour. Approximately 10 ml of methanol was carefully added at  $0^\circ\text{C}$ . The solvents were removed under high vacuum and the solid residue was washed with pentane. The pentane extract was filtered, concentrated and the residual oil was distilled to afford 4.1 g (27%) of **11**: bp  $80\text{--}82^\circ$  (1.3 torr).  $^1\text{H}$  NMR  $\delta$  3.56 (s, 9), 1.51–1.43 (m, 2), 1.38–1.21 (m, 10), 0.87 (t, 6,  $J = 7$  Hz), 0.80 (m, 1).  $^{13}\text{C}$  NMR  $\delta$  50.6, 31.0, 28.6, 23.0, 22.2, 14.0.  $^{29}\text{Si}$  NMR  $\delta$   $-43.6$ . IR 1191, 1092, 805,  $758\text{ cm}^{-1}$ . MS (EI)  $m/z$  (rel. intensity) 248 (1), 217 (41), 126 (10), 123 (32), 121 (100), 91 (68). Exact mass 248.182, calc. for  $\text{C}_{12}\text{H}_{28}\text{O}_3\text{Si}$  248.1808.

#### 4.4. Hydrolysis of 1

In a typical experiment, a solution of 500 mg (3 mmol) of isopropyltrimethoxysilane (**1**), 10 mg of DBTDL and water (one or two equivalents) in 1 ml of THF was introduced into a 20 ml glass tube equipped with a high-vacuum Kontes valve. The apparatus was purged with nitrogen, closed, and heated at  $100^\circ\text{C}$ . Aliquots were removed periodically and diluted in pentane for GC analysis, which disclosed the time evolution of the reaction mixture. These results are presented in the Results section.

The effect of DBTDL was determined by a pair of experiments with and without this catalyst in the presence of one equivalent of water. After 1 h, 20% of isopropyltrimethoxysilanol (**3**) was formed in the presence of DBTDL; whereas less than 1% was observed without DBTDL after 24 h.

In a similar experiment, **1** was heated in the presence of 108  $\mu\text{L}$  (two equivalent) of water for 30 min. The mixture was analyzed by GC; **1**, **3** and 1-hydroxy-1,3-diisopropyl-1,3,3-trimethoxydisiloxane (**5**) were present in a 15:2:1 ratio. GC-MS performed on a sample diluted with  $\text{CH}_2\text{Cl}_2$  gave the following fragmentation patterns: **3**  $m/z$  (rel. intensity) 107 (100), 77 (41); **5**  $m/z$  (rel. intensity) 225 (100), 195 (15), 167 (23), 137 (15), 107 (12).

Direct observation of a reaction mixture by  $^{29}\text{Si}$  NMR after 30 min (dilution with 1.5 ml of  $\text{C}_6\text{D}_6$ ) showed **1** ( $\delta$   $-43.8$ ) and **3** ( $\delta$   $-42.1$ ) in a 4:1 ratio. GC analysis of the mixture confirmed the relative proportions.

Under comparable conditions, 250 mg (1.5 mmol) of **1** was heated with 55  $\mu\text{L}$  (3 mmol) of water, 5 mg of DBTDL and 500  $\mu\text{L}$  of THF. After 30 min, the mix-

ture was concentrated; GC showed **1** and **3** in equal proportions.  $^{13}\text{C}$  NMR of the mixture showed new signals for **3** at  $\delta$  50.5, 16.7, 10.3. The alkyl region of the  $^1\text{H}$ -NMR spectrum was not resolved, but a new methoxy signal was apparent at  $\delta$  3.57.

#### 4.5. Isolation of oligomers **4**, **6**, **7a**, **7b** and **8**

A solution of 6.7 g (41 mmol) of **1**, 0.74 ml (41 mmol) of water and 135 mg (2%) of DBTDL in 15 ml of THF was refluxed for 72 h. The solvent was removed and the resulting oil was vacuum-transferred at 0.2 torr leaving considerable pot residue. GC analysis showed the following oligomers (percentage of volatile material): dimer **4** (41%), linear trimer **6** (10%), cyclic trimers **7a** and **7b** (9% and 23%) and cyclic tetramer **8** (four isomers, 8%). Distillation through a spinning-band column afforded pure 1,3-diisopropyl-1,1,3,3-tetramethoxydisiloxane (**4**). Further fractionation of the pot residue by preparative GC gave the other materials in acceptable purity for spectral analysis. The  $^{29}\text{Si}$  NMR data for compounds **6** and **8** are deduced from the spectrum of the vacuum-transferred mixture.

Dimer **4** showed: bp  $57^\circ\text{C}$  (0.5 torr).  $^1\text{H}$  NMR  $\delta$  3.58 (s, 12), 1.05 (d, 12,  $J = 7$  Hz), 0.99 (m, 2).  $^{13}\text{C}$  NMR  $\delta$  50.5, 16.9, 11.0 (CH).  $^{29}\text{Si}$  NMR  $\delta$  -51.5. IR 1194, 1092, 1065, 1004, 888, 809  $\text{cm}^{-1}$ . MS (EI)  $m/z$  (rel. intensity) 239 (100), 209 (24), 181 (17), 151 (5), 121 (3). Anal. Calc. for  $\text{C}_{10}\text{H}_{26}\text{O}_5\text{Si}_2$ : C, 42.52; H, 9.28. Found: C, 42.20; H, 9.15%.

For 1,3,5-triisopropyl-1,1,3,5,5-pentamethoxytrisiloxane (**6**),  $^1\text{H}$  NMR integration and  $^{13}\text{C}$  NMR peak intensities were used for assignment to the central (C) and the terminal (T) silicon units:  $^1\text{H}$  NMR  $\delta$  3.58 (s, 3, C), 3.57 (s, 12, T), 1.07 (d, 6,  $J = 7$  Hz, C), 1.04 (d, 12,  $J = 7$  Hz, T), 0.97 (m, 3).  $^{13}\text{C}$  NMR  $\delta$  50.5 (C), 50.2 (T), 16.91 (C), 16.87 (T), 11.8 (C), 11.0 (T).  $^{29}\text{Si}$  NMR  $\delta$  -51.8 (T), -60.0 (C). IR 1193, 1093, 1056, 1027, 1002, 888  $\text{cm}^{-1}$ . GC-MS (EI)  $m/z$  (rel. intensity) 357 (100), 242 (5), 181 (10), 128 (15), 105 (10). Anal. Calc. for  $\text{C}_{14}\text{H}_{36}\text{O}_7\text{Si}_3$ : C, 41.97; H, 9.06. Found: C, 41.83; H, 9.14%.

For 1,3,5-triisopropyl-1,3,5-trimethoxycyclotrisiloxane (**7**) (unseparated mixture of isomers **7a** and **7b** in a 1:2.5 ratio), integration of the  $^1\text{H}$  NMR spectrum allowed assignments of the methoxy protons.  $^1\text{H}$  NMR  $\delta$  3.62 (**7a**), 3.60 (**7b**), 3.57 (**7b**) (total of 9), 1.09–1.05 (m, 18), 1.00 (m, 3).  $^{13}\text{C}$  NMR  $\delta$  50.37, 50.35, 50.28, 16.71, 16.70, 16.67, 16.63, 11.62, 11.57, 11.49.  $^{29}\text{Si}$  NMR (assigned by integration)  $\delta$  -49.65 (**7b**), -49.61 (**7a**), -49.94 (**7b**). IR 1106, 1023, 890, 804  $\text{cm}^{-1}$ . MS (CI)  $m/z$  (rel. intensity) 355 (6), 311 (100), 283 (15), 269 (7), 225 (6), 195 (4). Exact mass ( $M + 1$ ) 355.141, Calc. for  $\text{C}_{12}\text{H}_{31}\text{O}_6\text{Si}_3$  355.1428.

Cyclotetrasiloxane **8** is a mixture of four isomers in a 1:20:3:1 ratio by GC:  $^1\text{H}$  NMR  $\delta$  3.61–3.55 (series of

singlets, 12), 1.08–1.04 (m, 24), 1.01–0.92 (m, 4).  $^{29}\text{Si}$  NMR  $\delta$  -58.4 to -58.8 (series of weak peaks). IR ( $\text{CHCl}_3$ ) 1113, 1085, 1065  $\text{cm}^{-1}$ . GC-MS (EI)  $m/z$  (rel. intensity) (major isomer): 429 (100), 399 (3), 285 (4), 255 (4), 225 (3); (intermediate isomer): 429 (100), 399 (4), 357 (4), 315 (5), 285 (6), 255 (7), 225 (3).

#### 4.6. Hydrolysis of **1** in the presence of HCl

A solution of 110  $\mu\text{L}$  of conc. HCl in 500  $\mu\text{L}$  of THF was added in 10  $\mu\text{L}$  portions to 700 mg (4.2 mmol) of **1** in 2 ml of  $\text{C}_6\text{D}_6$ . In this solvent, the  $^{29}\text{Si}$  NMR chemical shift of **1** was displaced slightly to  $\delta$  -43.9. A  $^{29}\text{Si}$  NMR spectrum was taken after each addition (5 min intervals). Evolution of the signals showed successive appearance and growth of **3** (after 10 min), **5** (after 15 min) and **4** (after 20 min). GC monitoring of a similar experiment confirmed this evolution. A  $^{29}\text{Si}$  NMR spectrum of the reaction mixture after 25 min showed resonances for silanol **3** ( $\delta$  -42.3), hydroxydimer **5** ( $\delta$  -50.5 and -51.6), and dimer **4** ( $\delta$  -51.7).

#### 4.7. Hydrolysis of **11**

A mixture of 400 mg (1.6 mmol) of **11**, 29  $\mu\text{l}$  (1.6 mmol) of water and 10 mg of DBTDL in 1 ml of THF was heated at  $100^\circ\text{C}$  in a sealed tube under nitrogen for 48 h. The solvent was removed and spectroscopic analyses were performed on the 5:1.2:1 mixture (integration of the  $^{29}\text{Si}$  NMR spectrum) of **11**, **12** and **13**: IR 1190, 1112, 1092, 1063, 1021, 803  $\text{cm}^{-1}$ . 1,1,3,3-Tetramethoxy-1,3-bis(5-nonyl)disiloxane (**12**) showed:  $^{13}\text{C}$  NMR  $\delta$  50.3, 31.04, 28.59, 23.1, 22.9, 14.0.  $^{29}\text{Si}$  NMR  $\delta$  -51.5. Cyclic trimer **13** was characterized only by its  $^{29}\text{Si}$  NMR:  $\delta$  -49.9, -50.0, -50.2.

#### 4.8. Hydrolysis of **14**

In a heavy-wall glass tube were introduced 0.6 g (3.4 mmol) of **14**, 61  $\mu\text{l}$  (3.4 mmol) of water and 12 mg of DBTDL in 2 ml of  $\text{C}_6\text{D}_6$  and 500  $\mu\text{L}$  of THF. The tube was sealed under nitrogen and heated at  $100^\circ\text{C}$  for 33 h. GC analysis of the reaction mixture showed presence of dimer **15** (20%) and a trimeric species (5%).  $^{29}\text{Si}$  NMR displayed resonances for **14** and dimer **15** only. 1,3-Diisobutyl-1,1,3,3-tetramethoxydisiloxane **15** showed:  $^1\text{H}$  NMR  $\delta$  3.55 (s, 6), 1.87 (nonet, 1,  $J = 7$  Hz), 0.97 (d, 6,  $J = 7$  Hz), 0.64 (d, 2,  $J = 7$  Hz).  $^{13}\text{C}$  NMR  $\delta$  50.1, 25.8, 23.8, 20.9.  $^{29}\text{Si}$  NMR  $\delta$  -50.7. IR 1195, 1090, 815, 765  $\text{cm}^{-1}$ .

#### Acknowledgments

This work was supported by a grant from the Union Carbide Corporation. CMF was a participant in the



French VSNA program during the course of this work. The help of T.A. Ayers with the preparation of **11** is appreciated.

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