The Oligomeric Silsesquioxanes, $(HSiO_{3/2})_n$

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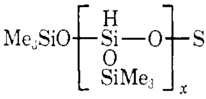
Received April 6, 1970

Abstract: An improved method has been devised for the preparation of $(HSiO_{3/2})_8$. The previously unknown higher homologs $(HSiO_{3/2})_{10-16}$ have also been prepared and characterized. They were isolated from a soluble, silanol-free resin obtained by a rather unusual hydrolysis and condensation procedure whereby water is generated *via* the sulfonation of an aromatic solvent such as benzene. Evidence for the existence of structural isomerism in the larger cage systems was obtained from nmr studies; *i.e.*, only the octamer and decamer exhibit simple single-line spectra.

Despite the attention accorded to prismatic silsesquioxane oligomers $[(RSiO_{3/2})_{8,10,12}]$ in recent years,[1] relatively little information is available concerning the oligomeric forms of the simplest member of the class, namely silsesquioxane (*i.e.*, $(HSiO_{3/2})_n$) itself. The only $HSiO_{3/2}$ oligomer to be reported is the octamer T_8 (where T represents the trifunctional silsesquioxy unit $HSiO_{3/2}$); Müller and coworkers obtained[2] this material fortuitously and in exceedingly small yield (about 0.2%) while studying the preparation of



$$Me_3SiO\left[\overset{H}{\underset{\overset{|}{\underset{SiMe_3}{O}}}{Si}}-O\right]_x SiMe_3$$

by the hydrolysis of $HSiCl_3$ with 80% H_2SO_4 in the presence of $Me_3SiOSiMe_3$. The structure which Müller, *et al.*, assigned on the basis of molecular weight and other analytical data was subsequently confirmed by single-crystal X-ray crystallography.[3] In the present paper we report an improved method affording T_8 in much increased yield (13%); we also describe the preparation of a soluble, fully condensed (*i.e.*, SiOH-free) $HSiO_{3/2}$ resin containing isolable quantities of the higher oligomers, T_{10-16}.

Discussion

Our initial efforts to improve Müller's synthesis were abandoned when we discovered that a soluble resinous product could be obtained by a "scarce-water" hydrolysis procedure involving the addition of a benzene solution of $HSiCl_3$ to a stirred mixture of benzene and SO_3-fortified sulfuric acid. The volatile components of this resin were isolated by preparative vpc and identified by mass and nmr spectroscopy as the oligomeric silsesquioxanes, T_{10-16}. This volatile fraction accounted for 15–35% of the total product, depending on experimental conditions. The composition of the volatile fraction was usually approximately 5–15% T_{10}, 40% T_{12}, 40% T_{14}, and 15–5% T_{16}. Although T_8 was generally present in only trace quantities, its content was found to be increased by shorter contact times. It was also observed that T_8 and, to a lesser extent, T_{10} were highly susceptible to rearrangement by H_2SO_4, thus accounting for their relatively low levels in our reaction products. Attempts to use sulfuric acid in combination with nonaromatic solvents such as hexane, $HCCl_3$, or CCl_4 produced only gels which were probably silyl sulfates, judging from their exothermal reaction to water upon work-up.

Because of the sensitivity of T_8 to H_2SO_4, a much less acidic medium was required for its efficient preparation. After some experimentation, it was found that acceptable yields (13%) of T_8 could be obtained from the dilute-solution hydrolysis of $HSi(OMe)_3$ with concentrated hydrochloric acid in a cyclohexane–acetic acid medium.

As might be expected, these oligomers all exhibit closely similar infrared spectral features (see Table I). All show absorption maxima arising from Si-H stretching (2260–2285 cm^{-1}), asymmetric stretching of polycyclic $SiO_{3/2}$ moieties (1140 cm^{-1}), Si-H rocking (870 cm^{-1}), and silsesquioxane skeletal deformations (one at about 565 and the other at about 400 cm^{-1}). In the case of T_8 the absorption at 565 is not nearly so intense, and an additional distinct maximum occurs at 465 cm^{-1}. The soluble nonvolatile amorphous $HSiO_{3/2}$ resin is similar except that it contains an additional relatively weak band at about 1075 cm^{-1} (asymmetric $SiO_{3/2}$ stretching), which is believed to arise from the occasional junctures of incompletely closed-cage moieties. The relative intensities of the bands at 1075 and 1140 cm^{-1} indicate that even the resinous portion of this material is made up of largely polycyclic components, which are presumably strung together in a more or less random bead-chain fashion. The spectrum of the resin also shows an additional band at 830 cm^{-1} also found in the T_{14} spectrum and presumably associated with Si-H rocking motion (our failure to observe this line in the T_{16} spectrum is probably a consequence of having used a more dilute CS_2 solution since we had only a trace of this oligomer in hand). The oligomers smaller than T_{14} have an additional Si-H rocking absorbtion at 910 cm^{-1} rather than at 830 cm^{-1}.

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(1) (a) A. J. Barry, W. H. Daudt, J. J. Domicone, and J. W. Gilkey, *J. Amer. Chem. Soc.*, **77**, 4248 (1955); (b) M. M. Sprung and F. O. Guenther, *ibid.*, **77**, 3990 (1955); (c) J. F. Brown, Jr., L. H. Vogt, and P. I. Prescott, *ibid.*, **86**, 1120 (1964); (d) L. H. Vogt and J. F. Brown, Jr., *Inorg. Chem.*, **2**, 189 (1963); (e) K. Olsson, *Ark. Kemi*, **13**, 367 (1958); (f) K. Olsson and C. Gronwall, *ibid.*, **17**, 529 (1961); (g) K. Olsson and C. Gronwall, *ibid.*, **22**, 237 (1964); (h) K. Larsson, *ibid.*, **16**, 203 (1960); (i) K. Larsson, *ibid.*, **16**, 209 (1960); (j) E. Wiberg and W. Simmler, *Z. Anorg. Allg. Chem.*, **282**, 330 (1955).

(2) R. Müller, R. Kohne, and S. Sliwinski, *J. Prakt. Chem.*, **9**, 71 (1959).

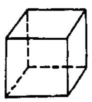
(3) K. Larsson, *Ark. Kemi*, **16**, 215 (1960).

Table I. Infrared and Nmr Spectral Data for $HSiO_{3/2}$ Oligomers

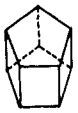
	Ir maxima, cm^{-1}						Nmr[c] (CCl_4)
T_8[a]	2285 (s)	1140 (vs)	910 (w) 870 (s)	570 (w) 540 (w)	465 (w)	400 (m)	5.79
T_{10}[a]	2270 (s)	1140 (vs)	910 (w) 870 (s)	560 (m)	440 (w)	400 (m)	5.73
T_{12}[a]	2260 (s)	1140 (vs)	910 (w) 870 (s)	565 (s)		400 (s)	5.67, 5.75 (3.2/1)
T_{14}[b]	2260 (s)	1140 (vs)	870 (vs) 830 (m)	570 (m)		400 (m)	5.61, 5.66
T_{16}	2260 (m)	1140 (vs)	870	570 (m)		400 (m)	5.65, 5.71
T_{resin}	2260 (s)	1140 (vs) 1075 (m)	870 (s) 830 (m)	565 (m)		400 (m)	Broad multiplet centered at ~5.64

[a] CCl_4 solutions (5–10%) were used for 3600–1300- and 600–250-cm^{-1} range; CS_2 solutions (~2%) were used for the 1300–600-cm^{-1} region. [b] KBr pellet was used rather than a solution. [c] Varian A-60 instrument; all values in τ units, employing Me_4Si reference.

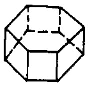
The nmr spectra of T_8 and T_{10} consist in each case of single lines. This was to be anticipated in view of the unique relatively strain-free structures (I and II) possible in these two cases. For T_{12} there are two possible unstrained geometrical isomers, III and IV. These alternatives were discussed previously by Vogt and Brown[1d] in their study of the oligomeric methylsilsesquioxanes; however, they found no evidence to substantiate the presence of more than one form. In the present case, the nmr spectrum of T_{12} does indeed show two singlets as should be the case if more than one structure is present. These singlets are present in a 3.2/1 ratio, while structure IV would afford a 2/1 ratio. This suggests that both III and IV are present and that the singlet for III overlaps one of the singlets produced by IV.



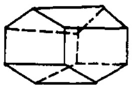
I(T_8)



II (T_{10})



III (T_{12})



IV (T_{12})

One additional possibility remains; examination of space-filling molecular models (Stuart–Briegleb models, using an SiOSi bond angle of 130°) suggests that two noninterconvertible conformations of III may exist. We are not at present able to dispose conclusively of this latter possibility. In any event, we are unwilling to draw any conclusions from the above-mentioned molecular models since with these same models, the presumably strained[1b] T_6 would appear to be readily formed, while T_{10} and T_{12} (form IV) both appear to be strained! In the T_{14-16} cases, the possibilities for isomeric complexity increase sharply, and this is evidenced by the nmr spectra of these materials. T_{14} shows two peaks; however, they are broad and may consist of more than one line. Similarly T_{16} shows two major peaks, both of which have numerous shoulders, suggesting a variety of isomers. The soluble resin (*i.e.*, total product containing the volatile oligomers) shows a broad envelope from which the individual singlets project. The nmr data (obtained on a Varian A-60 in CCl_4 solution) appear in Table I.

It is perhaps well to differentiate between the soluble resin produced by the H_2SO_4–benzene hydrolysis reported herein and other $HSiO_{3/2}$ resins. Most of the literature deals with various methods of preparing completely insoluble cross-linked polymeric gel.[4] The only other report of a soluble resin is that of Wiberg and Simmler,[5] who hydrolyzed $HSiCl_3$ in ether at −40°. The resulting clear hydrolysate solution was said to remain clear upon warming to room temperature; however, evaporation of the ether produced "mica-like crystals" (*sic*) which were completely insoluble and nonvolatile. It seems more likely that the ether solution contained a silanol-functional hydrolysate whose condensation was retarded by ether solvation. Upon evaporation of the ether, these silanols condensed, resulting in an intractable film of cross-linked polymeric $(HSiO_{3/2})_n$, pieces of which might easily have been mistaken for crystals. Contrastingly, in the present work, under the dehydrating influence of the concentrated H_2SO_4, silanol condensation is thoroughly completed prior to solvent removal, and under relatively high dilution conditions which favor intramolecular processes leading to a lower molecular weight resin of high polycyclic content. Because of the absence of silanol functionality, the solvent can be removed without fear of gelation. While solutions of our fully condensed silsesquioxanes in nonpolar solvents such as hexane, benzene, or $Me_3SiOSiMe_3$ are indefinitely stable, solutions in the more polar solvents such as acetone or ethyl acetate gel after several hours. Gelation of these silanol-free materials presumably involves redistribution of the relatively reactive siloxane bonds of these metastable silsesquioxanes to a more random state.

Experimental Section

Soluble $(HSiO_{3/2})_n$ by the Benzene–Sulfuric Acid Hydrolysis Method. A solution of $HSiCl_3$ (12.7 g, 0.094 mol) in 150 ml of benzene was slowly dripped over a 6-hr period into a rapidly stirred mixture of benzene (200 ml) and an acid phase made up from 80 g of concentrated H_2SO_4 and 60 g of fuming H_2SO_4 (15% SO_3). The temperature was at the ambient except during the first 15–30 min, when the temperature rose somewhat owing to the occurrence of benzene sulfonation. Upon completion of the $HSiCl_3$ addition, the layers were separated and the organic layer was washed free of acid. Emulsion formation, presumably aggravated by the sur-

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(4) See, for instance, G. H. Wagner and A. N. Pines, *Ind. Eng. Chem.*, **44**, 321 (1952).

(5) E. Wiberg and W. Simmler, *Z. Anorg. Allg. Chem.*, **283**, 401 (1956).

factant character of the benzenesulfonic acid by-product, was minimized by a preliminary extraction with 50% H_2SO_4 before washing neutral with water. After filtering to remove any insoluble material, the neutral benzene solution was then evacuated free of benzene to give 4.9 g (99% yield) of soluble $(HSiO_{3/2})_n$. A sample of the resin was examined by vpc, revealing the following volatile components (peak areas are compared): T_{10} (4%), T_{12} (43%), T_{14} (39%), T_{16} (14%). Several such preparations were subjected to sublimation and it was determined that the volatile T_x components ranged from 15 to 35% of the total resin. Preparative vpc afforded very small samples of the individual oligomers, T_{10-16}, which were then characterized by mass spectroscopy. Although no T_8 was detected by vpc, traces were detected in the T_{10} fraction by mass spectroscopy. As is customary for cage compounds, the most intense line in the mass spectrum of each of these oligomers corresponded to the loss of one peripheral group (one hydrogen in this case). In addition to the strong [P − 1] lines, there were in each case strong lines for the mass values [P], [P + 1], [P + 2], etc. These higher mass values arise, however, from loss of a single hydrogen from cages containing ^{29}Si and ^{30}Si isotopes; thus calculation[6] showed that in each instance not more than 2% of the nominal [P] line could be attributed to an actual parent molecular ion. As discussed elsewhere herein, structurally significant infrared and nmr data were also obtained (Table I).

$(HSiO_{3/2})_8$. A solution of trimethoxysilane (123 g, 1.01 mol) in 1.4 l. of cyclohexane was added over a 9-hr period to a vigorously stirred reaction flask containing 1125 cc of acetic acid (previously saturated with anhydrous HCl), 1500 cc of cyclohexane, and 40 cc of concentrated HCl. The reaction mixture was then washed with water until neutral and then evacuated free of solvent at an aspirator. The resulting solid material was placed in a small sublimation chamber, where it eventually afforded 7.1 g (13.3% yield) of volatile crystalline material shown by ir, nmr, vpc, and mass spectroscopy to be 97% T_8 containing 3% T_{10}. A pure sample of T_8 (1.95 g) was obtained by recrystallizing 2.7 g of this sublimate from 150 ml of cyclohexane. This material had the ir and nmr absorptions shown in Table I and the expected mass spectrum (P − 1 at 423).

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(6) R. J. Robinson, C. G. Warner, and R. S. Gohlke, *J. Chem. Educ.*, in press.