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Synthesis of silicon oxynitride from a polymeric precursor

Part II *The formation of trimethylcyclotrisilazane and tetramethylcyclotetrasilazane from the ammonolysis of dichloromethylsilane in diethyl ether*

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Proton nuclear magnetic resonance (^1H NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy and gas chromatography (GC) have been used to study the products of ammonolysis of dichloromethylsilane in diethyl ether at 0 °C. Results indicate that the major products are trimethylcyclotrisilazane and tetramethylcyclotetrasilazane. Hydrolysis of the cyclosilazanes has also been qualitatively investigated. A simple and useful method for the identification of cyclosilazanes has been developed using the ^1H NMR technique.

1. Introduction

Difficulties encountered in the production of high-purity material have been the major reason for the lack of interest in the exploitation of the excellent chemical, thermal and mechanical properties of silicon oxynitride (Si_2ON_2). However, recently reported preparative routes for Si_2ON_2 have provided purer samples of the oxynitride and this has generated a renewed interest in this material as an engineering ceramic (e. g. [1–3]). An important development is the synthesis of Si_2ON_2 from a precursor prepared from dichloromethylsilane (DMS) [4]. The precursor is obtained by the copolymerization of cyclopolymethylsiloxanes and cyclopolymethylsilazanes. As part of our work to develop the preparative route into a procedure suitable for larger-scale work and eventually the fabrication of artefacts from Si_2ON_2, we have reported in Part I [5] a method by which a high yield of the required cyclopolysiloxanes was obtained by hydrolysis of dichloromethylsilane (DMS) in a solution of hydrochloric acid. There remains the problem of understanding the chemical process by which the cyclopolysilazanes are formed, their analysis and the establishment of reaction conditions which give good yields. Our progress in these areas is reported in this paper.

Cyclotrisilazane and cyclotetrasilazane can be prepared by several methods, but usually by ammonolysis of a chlorinated silane and these have been reviewed extensively [6–13]. However, since organosilazane polymers have been found to be convertible to high-performance ceramics such as silicon nitride and silicon carbide [14–17], research into the preparation and chemistry of cyclosilazanes has intensified. In particular, the ammonolysis of DMS to prepare intermediate cyclomethylsilazanes has been the subject of several studies [18–21].

The reaction of ammonia with DMS in ether solution is reported to yield trimethylcyclotrisilazane and some linear polymers [22]. The suggested mechanism for the formation of the cyclic compounds during the ammonolysis of dichloroorganosilanes indicates that the cyclization step controls the rate of the reaction [8, 9]. Semenova *et al.* [23] isolated tetramethylcyclotetrasilazane (25% yield) from the ammonolysis of dichloromethylsilane in benzene solution at room temperature. Seyferth and Wiseman [19, 24] claimed that trimethylcyclotrisilazane, tetramethylcyclotetrasilazane and pentamethylcyclopentasilazane were obtained by passing NH_3 through DMS in diethyl ether. Three major peaks were seen in the gas chromatograph of their products, and by analysis of the ^1H NMR spectrum the composition of the mixture was given as 28 wt% $(CH_3SiHNH)_3$, 54 wt% $(CH_3SiHNH)_4$ and 17 wt% $(CH_3SiHNH)_5$.

Trimethylcylotrisilazane and tetramethylcyclotetrasilazane have been found to be difficult to separate and the analysis of the mixture has presented difficulties. Brewer and Haber [22] were able to distil only trimethylcyclotrisilazane ($(CH_3SiHNH)_3$) from the ammonolysis product. Attempts to distil other cyclics, e. g. tetramethylcyclotetrasilazane ($(CH_3SiHNH)_4$), resulted in the production of a cross-linked polymer. Zhinkin *et al.* [25] have reported that the cyclosilazanes, $(CH_3SiHNH)_{3\text{ or }4}$, were stable only up to about 200 °C. $(CH_3SiHNH)_{3\text{ or }4}$ react easily with acids, alcohol or water [7–9]. Zhinkin *et al.* [26] indicated that $(CH_3SiHNH)_4$ was easily hydrolysed at 65 °C to yield silanols and ammonia. Alcohols and organic acids either caused ring cleavage to form dialkoxy-trisilazanes or dialkoxy-disilazanes, or resulted in complete breakdown of the cyclic silazanes to give diorganyloxysilanes [9]. The reactivity of the Si–H bond in the cyclics was studied by Lebedev and Reikhsfel'd [27] and by Seyferth and co-workers [20, 28] who used cleavage of the Si–H bond in the cyclic compounds by reaction with a strong base, such as KH in THF solution, to form sheet-like polymers as preceramic precursors.

Several methods have been used to analyse the products of the ammonolysis of DMS. Infrared spectroscopy has been used [10], and gas chromatography (GC) and proton nuclear magnetic resonance (^{1}H NMR) were used by Seyferth and Wiseman [20]. The later work [20] indicates that in a ^{1}H NMR spectrum the resonances in the region $\delta = 4.3$ –4.9 p.p.m. are due to the Si–$\underline{H}$ protons while the resonances for the protons of N–$\underline{H}$ and Si–C$\underline{H}_3$ occur at about $\delta = 0.7$–1.1 and 0.2 p.p.m., respectively. However, more detailed assignments have not been made.

In the present work, combined data from GC, ^{1}H NMR and (FT-IR) spectroscopy allow a more precise assignment of the chemical shift to the protons of the cyclotrimer and cyclotetramer. This assignment makes possible the quantitative analysis of the cyclotrimers and cyclotetramers by ^{1}H NMR spectroscopy. Also, the qualitative study of the hydrolysis of these cyclic compounds provides evidence for a better understanding of the ammonolysis process.

2. Experimental procedure

2.1. Starting materials

DMS was obtained from Aldrich Chemical Co. (Poole, UK). The middle cut from the distillation of DMS over magnesium metal under dry nitrogen was used in all the experiments described below. Ammonia was obtained from BOC (London, UK). The ammonia was dried before use by passing it firstly through a column of coarse barium oxide powder and then through a column of sodium on glass wool.

2.2. Ammonolysis of DMS in a flask

A 500 cm^3 round-bottom flask, cooled in an ice-bath, was equipped with a magnetic stirrer and a solid-CO$_2$–acetone condenser. It was charged with 250 cm^3 of diethyl ether (freshly distilled from sodium benzophenone) and DMS (20–30 g) under dried N$_2$. A stream of dry NH$_3$ was passed into the stirred solution and a voluminous white precipitate appeared immediately so that no separate liquid phase was discernible. After 2 to 5 h (depending on the gas flow rate), when condensed ammonia was seen and a liquid phase was clearly present in the reaction mixture, the stream of ammonia was stopped and the reaction mixture was left to warm to room temperature. The liquid phase was transferred to another flask by filtration under N$_2$.

2.3. ^{1}H NMR spectroscopy

A sample of the ammonolysis reaction product was injected into a 5 mm diameter NMR tube under dry N$_2$. Subsequently, the tube was connected to a vacuum line to remove most of the ether solvent and CDCl$_3$ was added to make the appropriate solution for NMR. The NMR experiments were carried out on a Jeol FX200 spectrometer at 200 MHz for ^{1}H. A 6 to 10 s delay time was used between pulses to ensure the proton signals were completely relaxed before the next pulse. Usually, tetramethylsilane (TMS) was used as a reference, otherwise the resonance for the residual CHCl$_3$ at 7.25 p.p.m. was utilized.

2.4. Gas chromatography (GC)

A sample of the mixture of products of the ammonolysis reaction was analysed using a Shimadzu GC-14A gas chromatograph with a 1.5 m long glass column (internal diameter 3 mm) containing 5% SE30 on diatomite. The temperature was programmed to increase at 10 °C min^{-1} over the range 60–230 °C and the injection port and detector (FID) temperatures were set at 80 and 150 °C, respectively. The results were recorded and processed with a Shimadzu C-R5A Chromatopac.

2.5. Fourier transform infrared spectroscopy (FT-IR)

A sample of the products of the ammonolysis reaction was placed on a potassium bromide disc and investigated using a Nicolet 710 FT-IR spectrometer purged with dry air (1 p.p.m. CO$_2$ and H$_2$O). The sample was scanned with a resolution of 4 cm^{-1} to obtain a spectrum in the frequency range of 4000–400 cm^{-1}. The sample was then taken out of the spectrometer and exposed to air. Spectra were recorded at intervals in order to investigate the hydrolysis behaviour.

2.6. Distillation of ammonolysis products

The distillation was performed using a vacuum line. The solution of the products in diethyl ether was placed in a flask with a magnetic stirrer. The solvent, in this instance diethyl ether, was distilled to another flask cooled by solid CO$_2$. The first fraction of the products was distilled out at 65 °C at 0.4 mm Hg using a liquid N$_2$ trap. The second fraction was collected from 120 to 128 °C at 0.04 mm Hg using a liquid N$_2$ trap.

3. Results and discussion

3.1. Identification of cyclics

All ammonolysis experiments with DMS under the conditions described in Section 2.2 gave a similar mixture of products and showed two major peaks in the GC trace (Fig. 1). This indicates the presence of two compounds as main products. The same products were also obtained from the ammonolysis of DMS in tetrahydrofuran (THF) under conditions similar to those described in Section 2.2. Typically the peak at the lower retention time (5.8 min) was 24 wt% of the

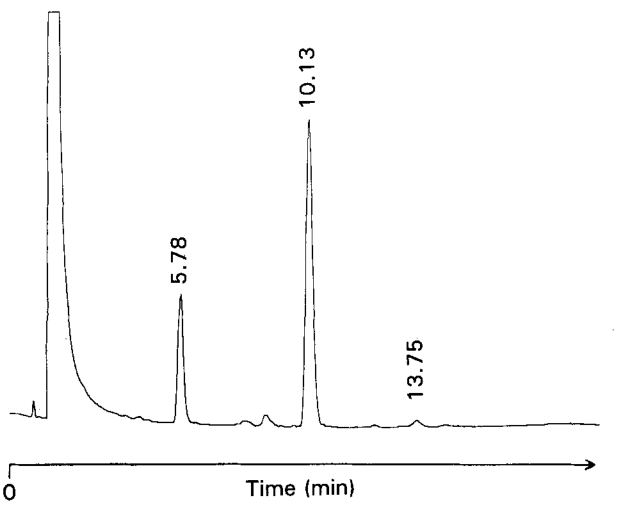


Figure 1 GC trace of the ammonolysis product mixture. Times corresponding to each peak are indicated. The peaks for trimethylcyclotrisilazane (peak 1 at 5.8 min) and tetramethylcyclotetrasilazane (peak 2 at 10.1 min) correspond to 24 and 71 wt%, respectively.

total product and the second peak (at 10.1 min.) was 71 wt% (it was assumed that the detector response factors for the cyclosilazanes were similar.). The product mixture gave a ^{1}H NMR spectrum (Fig. 2a) which had integral ratios for resonances in the region $\delta = 4.55$–4.85 p.p.m. (peaks 1 and 2 due to Si–$\underline{H}$) to those in the region $\delta = 0.40$–1.05 p.p.m. (broad peak 3 due to N–$\underline{H}$) and to those at $\delta = 0.20$ p.p.m. (peaks 4 due to Si–C$\underline{H}_3$ with only about 0.1 p.p.m. width) of about 1:1:3.2. This indicates that the major components of the mixture were cyclopolysilazanes: $[Si(H)(CH_3)N(H)]_n$.

The integral ratio of peak 1 to peak 2 in Fig. 2a is about 1:4 (it is possible that part of the trimethylcyclotrisilazane has been removed by the vacuum during preparation of the sample), which compares well with the peak area ratio for peaks 1 and 2 in the GC trace in Fig. 1. Therefore, it seems likely that the ^{1}H NMR resonances at $\delta = 4.62$ and 4.83 p.p.m. are due to the Si–$\underline{H}$ from tetramethylcyclotetrasilazane and trimethylcyclotrisilazane, respectively. The resonances for N–$\underline{H}$ from the two cyclics are not as clearly separated as those for Si–$\underline{H}$ at room temperature. However, at a lower temperature (e.g. -20 °C) the N–$\underline{H}$ resonances of these two cyclics are well separated (Fig. 2b). Comparison of integrals in the spectrum shows that peaks 3 and 5 (Fig. 2b) may be assigned to the N–$\underline{H}$ of tetramethylcyclotetrasilazane and trimethylcyclotrisilazane, respectively. The resonances at $\delta = 0.1$–0.2 p.p.m. (peak 4 in Fig. 2), which are in a narrow range, are assigned to the Si–C$\underline{H}_3$ from both types of cyclosilazane. These assignments are confirmed by the investigation of the ^{1}H spectra of the hydrolysed samples as described later.

The FT-IR spectrum obtained for the ammonolysis products is shown in Fig. 3. The assignment of peaks is in general agreement with those previously published [10, 20] and the important features are described below. The Si–N–Si structure is characterized by bands at 3380 cm^{-1} from the N–H stretching, 1175 cm^{-1} from the N–H bending mode, 942 cm^{-1}

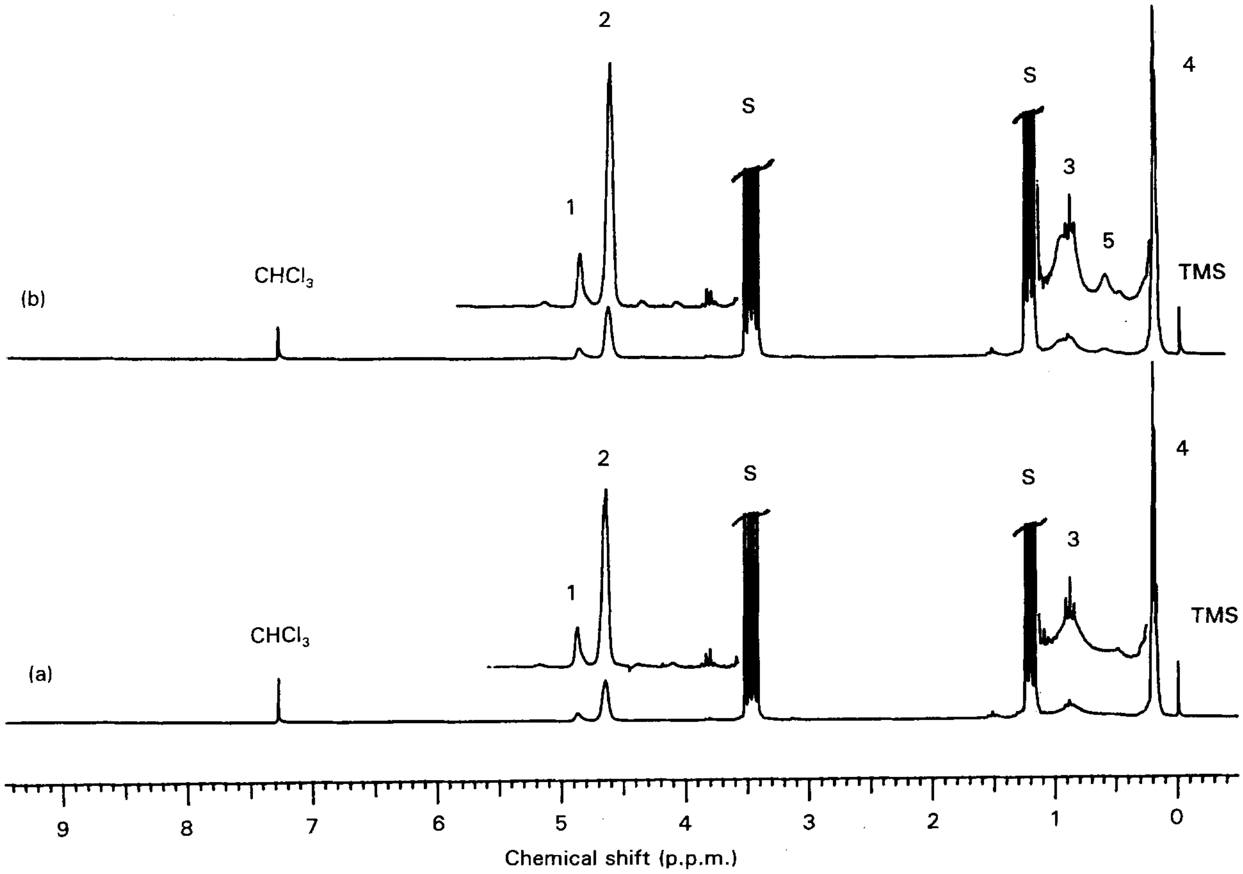


Figure 2 Proton NMR spectra of the ammonolysis product mixture in CDCl$_3$ at (a) room temperature and (b) -20 °C. TMS and CHCl$_3$ marked on the figures indicate the proton resonances for TMS and residual CHCl$_3$, respectively. S indicates peaks from diethyl ether protons. Peaks 1–5 indicated are defined in the text.

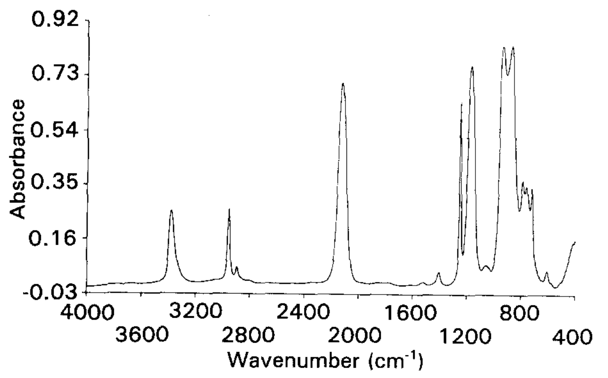


Figure 3 The FT-IR spectrum of the ammonolysis product mixture.

from the asymmetric Si–N–Si stretching and a weak band at 610 cm^{-1} from symmetrical Si–N–Si stretching. The band at 724 cm^{-1} is also believed to be due to the symmetrical Si–N–Si stretching mode.

3.2. Distillation of ammonolysis products

The first fraction (*ca.* 50 wt% of the total) has a similar proton spectrum to those shown in Fig. 2, but with a small additional peak at $\delta = 4.35$ p.p.m. and a similar FT-IR spectrum to that shown in Fig. 3. GC showed that the distillate had hydrolysed to some extent during the experiment and only 12 wt%, trimethylcyclotrisilazane and 69 wt% tetramethylcyclotetrasilazane are present. These results indicate that cyclic $(CH_3SiHNH)_{3\text{ and }4}$ can be distilled out from the reaction product. However, it was still difficult to determine the proportion of cyclics in the product mixture and the structures of the second fraction (*ca.* 20 wt%) and the residue (*ca.* 30 wt%). Both the second and third fractions are viscous liquids.

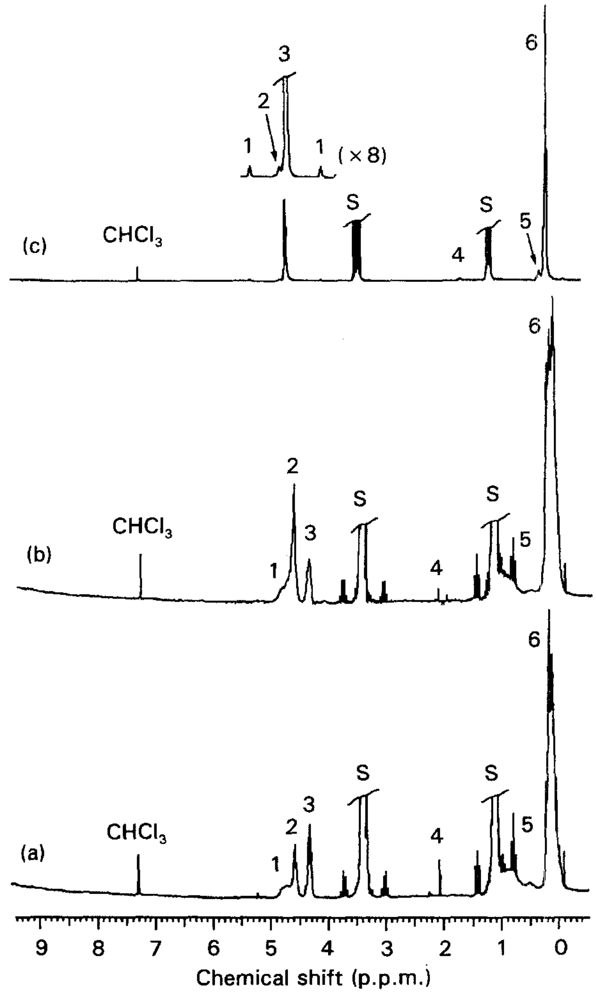


Figure 4 Proton NMR spectra of the cyclosilazanes during hydrolysis in $CDCl_3$ solution after (a) 5 days, (b) 14 days and (c) 22 days. $CHCl_3$ marked on the figures indicates the proton resonance for the residual $CHCl_3$. S indicates peaks from diethyl ether protons. Peaks 1–6 indicated are defined in the text.

3.3. Hydrolysis studies

Hydrolysis is not easily prevented during the analysis of the cyclosilazanes and this made the understanding of the analytical results more difficult. Of the three techniques (^{1}H NMR, FT-IR and GC) used in studies of the cyclosilazanes, ^{1}H NMR was found to be most useful. The sample used for the ^{1}H NMR study was the one from which the spectra in Fig. 2 were obtained. This sample was left in the NMR tube for some time to allow hydrolysis by ingress of moist air through a hole opened in the cap of the tube. The ^{1}H NMR spectra in Fig. 4 were recorded at different times (stated in the figure caption) to investigate the hydrolysis process.

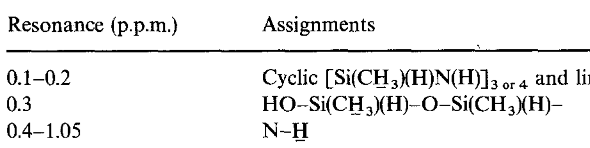
The ratio of the intensities of the Si–$\underline{H}$ resonances ($\delta = 4.3$–4.85 p.p.m.) to the N–$\underline{H}$ resonances ($\delta = 0.4$–1.05 p.p.m.) increased as hydrolysis proceeded (see Fig. 4a and b). Also, it is evident that the characteristic peaks for the cyclics at $\delta = 4.62$ and 4.83 p.p.m. (peaks 1 and 2 in Fig. 2) disappeared during hydrolysis but peaks appeared at $\delta = 4.65$ and 4.35 p.p.m. (peaks 2 and 3, respectively, in Fig. 4a and b). In addition, a broad peak (peak 1 in Fig. 4a and b) also appeared due to Si–$\underline{H}$ in the intermediate products after the rings were opened. After hydrolysis over 14 days, the intensity ratio of the two peaks at $\delta = 4.65$ and 4.35 p.p.m. was interchanged (Fig. 4b). Finally, after hydrolysis over 22 days, both peaks disappeared and a less well-defined peak (showing a less fine structure) appeared at $\delta = 4.70$ p.p.m. (Fig.4c). At this stage, N–$\underline{H}$ resonances (i.e. peak 5 of Fig 4a and b) could not be seen and the peaks centred at about $\delta = 0.2$ p.p.m. became much sharper with about 0.1 p.p.m. width. Comparison of Fig. 4c with the ^{1}H NMR spectrum for cyclopolysiloxane [5] indicates that the cyclopolysilazanes were hydrolysed to give cyclopolysiloxanes and linear polysiloxanes. GC results discussed later also provide additional evidence in support of this conclusion. The presence of linear polysiloxanes was confirmed by the appearance of two small peaks at $\delta = 4.80$ and $= 0.3$ p.p.m. (peaks 2 and 5 in Fig. 4c) with an intensity ratio of 1:3. These peaks were assigned to the Si–$\underline{H}$ and –C$\underline{H}_3$ at the end of the chains, i.e. HO–Si($\underline{H}$)(C$\underline{H}_3$)–O–. In addition to these important peaks, Fig. 4 also shows an extra peak 4 in each spectrum which is possibly due to $\underline{H}$O–Si (the variation of the chemical shift for this peak might be caused by the different pH values in the solution at different stages). In Fig. 4c, the two peaks denoted by 1 are the satellite peaks of H–Si coupling. It is also noticed the broad peaks from Si–C$\underline{H}_3$ (peak

6) appear in Fig. 4a and b (with 0.3 p.p.m. width). This is because the number of chemical species and the range of chemically different Si–C$\underline{H}_3$ groups increase as the hydrolysis proceeds. By contrast, after the hydrolysis has progressed over 22 days, the main resonances of the Si–C$\underline{H}_3$ (peak 6 in Fig. 4c) lie in a narrow range (with about 0.1 p.p.m width).

The hydrolysis of a cyclosilazane therefore appears to proceed in the following sequence. Firstly the cyclopolysilazanes are attacked by H_2O to become linear polymers such as HO–Si(CH_3)(H)–N(H)–[Si(CH_3)(H)–N(H)–]$_{n=1 \text{ or } 2}$–Si(C$\underline{H}_3$)(H)–NH_2. The linear polymers then undergo further hydrolysis with release of ammonia as water attacks the =Si(H)–NH_2 end groups and Si–N–Si bonds in the chains. The peaks at $\delta = 4.35$ p.p.m. were assigned to the resonances for Si–$\underline{H}$ from the units H_2N–Si(CH_3)($\underline{H}$)–N(H)– and HO–Si(CH_3)($\underline{H}$)–N(H)–. The procedure continues and silanols are formed. The newly formed silanols undergo condensation to form linear polysiloxanes and then possibly cyclopolysiloxanes. The resonances at $\delta = 4.65$ p.p.m. in Fig. 4a and b were assigned to the Si–$\underline{H}$ from the unit –Si(CH_3)(H)–O–. Table I summarizes the assignments for the proton NMR spectra of the cyclosilazanes and their hydrolysed products.

The hydrolysis of the cyclosilazane products was also studied qualitatively by GC and FT-IR. Fig. 5 is the GC trace of a sample in a dilute solution that has undergone incomplete hydrolysis (after being in contact with air in a specimen tube for 5 days). Comparison of Fig. 5 with the GC trace of a mixture of cyclosiloxanes obtained by the method described elsewhere [5] shows that the peaks at 3.5, 5.7 and 7.5 min are from pentamethylcyclopentasiloxane, hexamethylcyclohexasiloxane and heptamethylcycloheptasiloxane, respectively.

It was also noted that if water was mixed with a solution of the cyclics in diethyl ether (or in THF), a white precipitate appeared because of a cross-linking reaction which occurred in the presence of ammonia [29] as in scheme 1:



$$-\mathrm{Si}-\mathrm{H} + \mathrm{OH}^- \longrightarrow -\mathrm{Si}(\mathrm{H})(\mathrm{O})(\mathrm{OH}) \longrightarrow -\mathrm{Si}-\mathrm{O}-\mathrm{Si}-$$

cross-linked products

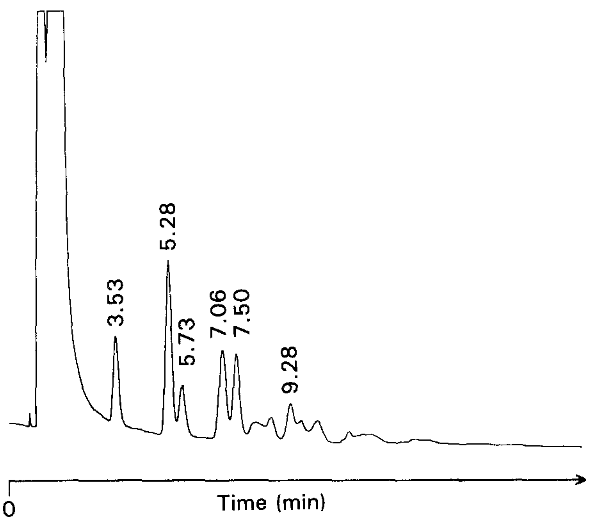


Figure 5 GC trace of the products after partial hydrolysis (over 5 days). Times corresponding to each peak are indicated.

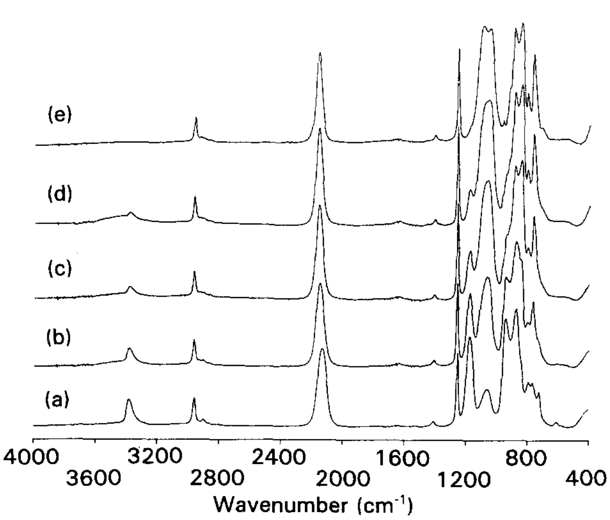


Figure 6 FT-IR spectra of the hydrolysed products after exposure to moist air after (a) 28 min, (b) 40 min, (c) 80 min, (d) 240 min and (e) 24 h.

Fig. 6 shows the effects of hydrolysis on the FT-IR spectra of the cyclics. The intensity of the peak at 942 cm^{-1}, associated with the Si–N–Si asymmetric vibration, reduced as hydrolysis proceeded and the same observation was made for the peaks at 3380 and

TABLE I Proton NMR assignments of the cyclosilazanes and their hydrolysed products

Resonance (p.p.m.)	Assignments
0.1–0.2	Cyclic [Si(C$\underline{H}_3$)(H)N(H)]$_{3 \text{ or } 4}$ and linear polysilazanes, –[Si(C$\underline{H}_3$)(H)N(H)]$_{n>3}$–
0.3	HO–Si(C$\underline{H}_3$)(H)–O–Si(CH_3)(H)–
0.4–1.05	N–$\underline{H}$
0.8–1.0	Cyclic [Si(CH_3)(H)N($\underline{H}$)]$_4$ at – 20 °C
0.5–0.6	Cyclic [Si(CH_3)(H)N($\underline{H}$)]$_3$ at – 20 °C
4.35	Low molecular weight linear H_2N–Si(CH_3)($\underline{H}$)–N(H)– and HO–Si(CH_3)($\underline{H}$)–N(H)–
4.62	Cyclic [Si(CH_3)($\underline{H}$)N(H)]$_4$ and high molecular weight linear polysilazanes
4.65	Low molecular weight linear polymer of HO–Si(CH_3)(H)–O–Si(CH_3)($\underline{H}$)–
4.70	Cyclic [Si(CH_3)($\underline{H}$)–O–]$_n$ and high molecular weight polymer of HO–Si(CH_3)(H)–O–[Si(CH_3)($\underline{H}$)–O–]$_n$–Si(CH_3)(H)–OH
4.80	HO–Si(CH_3)($\underline{H}$)–O–Si(CH_3)(H)–
4.83	Cyclic [Si(CH_3)($\underline{H}$)N(H)]$_3$

1175 cm^{-1} due to N–H stretching and N–H bending, respectively. In contrast, the peak at about 1070 cm^{-1} for the structure –Si–O–Si– and end groups, such as Si–O–Si–OH, increased in intensity. Finally, after hydrolysis over 24 h (Fig. 6e) the peaks at 3380, 1175 and 942 cm^{-1} completely disappeared and a spectrum similar to that obtained from polysiloxanes [30] appeared. It was also noticeable that as hydrolysis proceeded, the band at 2125 cm^{-1}, due to the Si–H stretching vibration, shifted to a higher wave number and finally reached 2166 cm^{-1} when the sample was hydrolysed over 24 h (Fig. 6e). Similarly the band at 1254 cm^{-1} due to the methyl group also shifted slightly to 1261 cm^{-1}.

4. Conclusions

The ammonolysis of dichloromethylsilane in diethyl ether at 0 °C produces trimethylcyclotrisilazane (24 wt%) and tetramethylcyclotetrasilazane (71 wt%). These constituents of the product mixture can be distilled under vacuum. Assignments for ^{1}H NMR spectra of these two compounds have been made. It is also shown that the cyclopolysilazanes in dilute solution are easily hydrolysed to produce silonals, polysiloxanes and even cyclopolysiloxanes.

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