

# Deactivation with silazanes in chromatography, mechanism of the reaction and practical consequences in capillary GC and RP-HPLC : a <sup>29</sup>Si CP-MAS NMR study

**Citation for published version (APA):**

Ven, van de, L. J. M., Rutten, G. A. F. M., Rijks, J. A., & Haan, de, J. W. (1986). Deactivation with silazanes in chromatography, mechanism of the reaction and practical consequences in capillary GC and RP-HPLC : a <sup>29</sup>Si CP-MAS NMR study. *HRC & CC, Journal of High Resolution Chromatography and Chromatography Communications*, 9(12), 741-746. <https://doi.org/10.1002/jhrc.1240091206>

**DOI:**

[10.1002/jhrc.1240091206](https://doi.org/10.1002/jhrc.1240091206)

**Document status and date:**

Published: 01/01/1986

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Deactivation with Silazanes in Chromatography, Mechanism of the Reaction and Practical Consequences in Capillary GC and RP-HPLC: A<sup>29</sup>Si CP-MAS NMR Study

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## Key Words:

Capillary GC  
RP-HPLC  
CP-MAS NMR  
Deactivation methods  
Hexamethyldisilazane

## Summary

The reaction of Cab-O-Sil, a highly dispersed vitreous quartz, with hexamethyldisilazane (HMDS) was studied in the temperature range 380–500°C, using <sup>29</sup>Si solid state NMR and other techniques. Such studies are of importance in view of deactivation procedures of fused silica at high temperatures in capillary GC.

The commonly accepted reaction equation:



predominates only below ca. 400°C. Above ca. 400°C the intermediate cleavage product Me<sub>3</sub>SiNH<sub>2</sub> reacts with surface silanol groups to form ≡SiOSiMe<sub>2</sub>NH<sub>2</sub> + CH<sub>4</sub>. At higher temperatures these groups may ultimately form (≡SiO)<sub>3</sub>SiNH<sub>2</sub> groups (analogously to the formation of bi- and tridentate linkages starting from ≡SiOSiMe<sub>3</sub> groups), but (≡SiO)<sub>3</sub>SiNH<sub>2</sub> groups are also directly formed at lower temperatures, simultaneously with the ≡SiOSiMe<sub>3</sub> groups, probably by reaction with siloxane bridges:



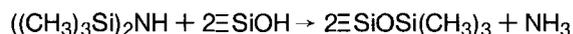
The reactions of the trimethylsilylamine part of HMDS with Cab-O-Sil were confirmed by an independent series of silylations using *N,N*-dimethyltrimethylsilylamine instead of HMDS. The presence of amino groups as ≡SiNH<sub>2</sub> was confirmed by FT-IR. This may be one of the reasons why very high temperature silylation with disilazanes does not provide a satisfactory deactivation of fused silica GC columns: the active ≡SiOH groups are “replaced” by active ≡SiNH<sub>2</sub> groups. However, such a material may be of interest in LC. Silylation with silazanes at ca. 350°C in humid atmosphere and/or after extensive hydroxylation (leaching) of the surface should yield sufficiently deactivated surfaces with a rather well defined surface structure.

## 1 Introduction

Some time ago we described a number of model processes for the deactivation of fused silica capillary columns for gas chromatography (GC) [1,2]. The previous studies comprised extensive use of CP-MAS NMR of <sup>29</sup>Si and, to a lesser

extent, of <sup>13</sup>C in order to follow the silylation reactions. Cab-O-Sil, a fumed silica, was used as a model compound mimicking properties of fused silica column surfaces. Also, a comparison was made between the model experiments and properties of similarly treated fused silica capillary columns for GC [2].

One of the deactivation methods studied in particular was silylation with hexamethyldisilazane (HMDS) at temperatures in the range of 350 to 510°C. It was shown that reactions of pretreated Cab-O-Sil, vacuum-dried overnight at 110°C or dried additionally over P<sub>2</sub>O<sub>5</sub> yield quite different silylation patterns. This underscored the important role of water in the formation of the different surface-linked moieties. We proposed a tentative reaction scheme that seemed to fit quite well with the “classic” reaction scheme, usually proposed for silylation with HMDS [3,4]:



The primary trimethyl-siloxysilanes at the surface, also referred to as “monodentate surface-linkages”, would then presumably react further with neighboring silanol groups at the surface with formation of dimethyl-disiloxysilanes (or “bidentate surface-linkages”) and evolution of methane. An alternative reaction occurs between two neighboring trimethyl-siloxysilanes with formation of two interconnected dimethyl-disiloxysilanes (sharing one siloxane bridge). For this latter reaction water is needed. In a similar way, cross-polymerization may eventually occur. Reaction of one trimethyl-siloxysilane with two neighboring surface silanols to form a tridentate surface-linkage seems improbable, considering steric constraints.

Some of the earlier results, however, notably the appearance of as-yet unexplained <sup>29</sup>Si NMR signals after silylation of Cab-O-Sil with HMDS at temperatures between 460 and

500°C [1,2] and their possible relevance to the reaction scheme prompted us to carry out a number of additional investigations.

The results of silylation of carefully dried Cab-O-Sil with HMDS, hexamethyldisiloxane (HMDO), and *N,N*-dimethyltrimethylsilylamine (DMTMSA) at several temperatures are presented. The results will be interpreted in terms of a reaction scheme, complementing the "classic" picture and showing some new features.

## 2 Experimental

### 2.1 Materials

The Cab-O-Sil M5 (Cabot Corp., Tuscola, Ill. USA) was a gift from Heybroek & Co's Handels Maatschappij N.V. Amsterdam. The specific surface area of grade M5 is, according to the manufacturer,  $200 \pm 25 \text{ m}^2/\text{g}$ . The Cab-O-Sil was ignited at 720°C, rehydrated as described before [1], and kept in a vacuum desiccator over  $\text{P}_2\text{O}_5$  for at least a fortnight.

Hexamethyldisilazane was from Pierce Chemical Co., Rockford, Ill. USA (specially purified grade). *N,N*-Dimethyltrimethylsilylamine was obtained from Janssen Chimica, Beerse, Belgium. Solvents were all analytical grade from E. Merck, Darmstadt, FRG.

### 2.2 Preparation of the Reaction Ampoule

The amount of reagent added to the Cab-O-Sil samples was  $10.5 \mu\text{mol}/\text{m}^2$ . Taking a specific surface area of  $200 \text{ m}^2/\text{g}$  this is 340 mg (438  $\mu\text{l}$ ) HMDS, 340 mg (445  $\mu\text{l}$ ) HMDO or 246 mg (336  $\mu\text{l}$ ) DMTMSA per gram Cab-O-Sil.

About 0.3 g Cab-O-Sil was placed in a thick walled tube of vitreous quartz (length 20 cm, i.d. 1 cm, wall thickness 1 mm). A constriction was drawn in the middle of the tube and the tube was placed again in the vacuum desiccator over  $\text{P}_2\text{O}_5$  for some days. Then the tube was evacuated and filled with dry nitrogen. This process was repeated twice. The tube was cooled in dry ice, the reagent was added with a syringe, the tube evacuated and sealed at the constriction.

### 2.3 Reactions and Rinsing

The ampoules were wrapped in aluminum foil and heated at the required temperatures for 16 h. Then the ampoules were opened and the contents were washed twice by decantation with toluene and twice with methanol or hexane. The modified Cab-O-Sil sample was shortly dried at 70°C to remove excess of solvent and then overnight in a vacuum oven at 110°C.

### 2.4 NMR Measurements

The  $^{29}\text{Si}$  CP-MAS NMR spectra were obtained on a Bruker CXP-300 spectrometer at 59.63 MHz as described before [1].

## 2.5 Gas Chromatography – Mass Spectrometry

In some cases the gaseous reaction products in the ampoules were examined by GC-MS. An ampoule with a drawn-out end was used. After reaction the ampoule was connected to a glass container (100 ml) with a short piece of polyethylene tubing. The container was provided with two teflon stopcocks and a silicone rubber septum. The container (and the connection tube) were evacuated and the seal of the ampoule was broken by bending the tube. To ensure more complete transfer of the volatile reaction products to the container, the ampoule was heated for a little while to 100°C in an oil bath. Finally, the container was filled with nitrogen to atmospheric pressure.

A Finnigan GC-MS system was used. Experimental conditions were: GC column: fused silica capillary 26 m, 0.32 mm i.d., stationary phase CP Sil 5CB, 5.1  $\mu\text{m}$ , a cross-linked 100% methyl silicone (Chrompack, Middelburg, The Netherlands); gas chromatograph: oven temperature 30°C, inlet pressure 0.4 bar gauge helium, splitter injection (split ratio 1:10); mass spectrometer: direct inlet, EI ionization (70 eV), scanned mass range 8–40, 40 scans per second. Under these conditions a separation of  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{HN}_3$  and  $\text{H}_2\text{O}$  was obtained.

About 40  $\mu\text{l}$  was taken from the glass container through the silicone rubber septum with a gastight syringe and injected on the GC/MS. The masses 14, 15, 16, 17, and 18 were continuously followed with the oscilloscope and the identity of the eluting GC peaks was established visually.

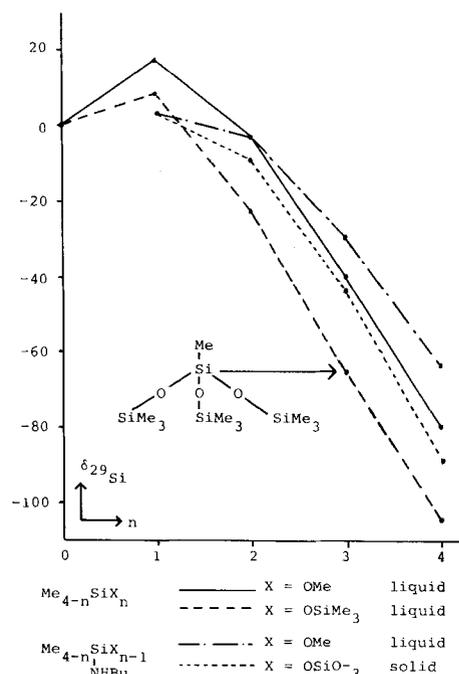


Figure 1

$^{29}\text{Si}$  NMR chemical shifts of some series of model silanes.

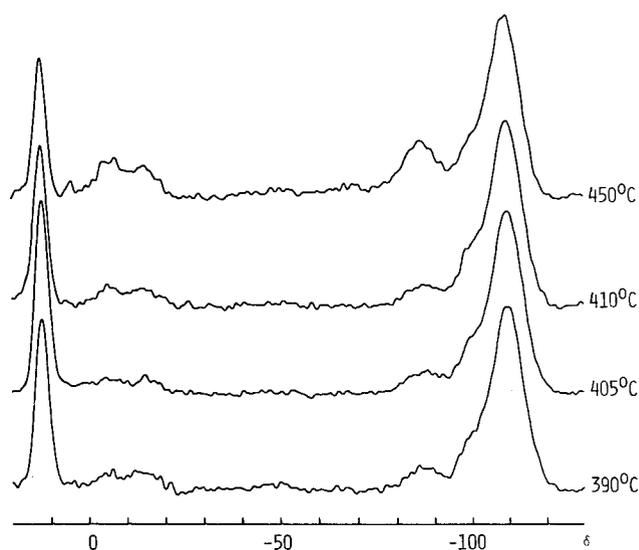
## Results and Discussion

Since some of the conclusions of this work rest primarily on  $^{29}\text{Si}$  NMR chemical shift assignments of silanes attached to the Cab-O-Sil surface, a brief outline of the assignment procedure seems in order.  $^{29}\text{Si}$  NMR chemical shifts for methylsiloxysilanes (general formula:  $(\text{CH}_3)_{4-n}\text{Si}(\text{OSi}\Xi)_n$ ) have been presented in the literature for liquid samples ( $n=0-4$ ) [5,6] as well as for their solid counterparts ( $n=1-4$ ) [7]. These assignments have been used in the present work without modifications. It turns out that for liquid and solid samples the  $^{29}\text{Si}$  NMR chemical shifts of methylsiloxysilanes, when plotted against the value of  $n$  yield a practically straight line for  $n=1-4$  with only a slight curvature between  $n=1$  and  $n=2$  (**Figure 1**). Replacement of a single methyl group by a siloxy moiety leads to a shielding of ca. 40 ppm. This means that differences between  $\alpha$  effects of methyl groups and of siloxy groups on the  $^{29}\text{Si}$  NMR chemical shift of the central silicon do not depend strongly on the numerical value of  $n$ .

The  $^{29}\text{Si}$  NMR chemical shift of 1,3-di(isopropylamino)-1,1,3,3-tetramethyldisiloxane is reported at  $-16$  ppm in the liquid [5]. The so-called "solid state effect" [7] will usually result in a downfield shift, the magnitude of which may vary. Using the originally proposed value of ca.  $+10$  ppm, one arrives at a  $^{29}\text{Si}$  NMR chemical shift of ca.  $-6$  ppm for solid  $N,N$ -dimethylaminodimethylsiloxysilane, neglecting the different substitution patterns on the nitrogen atoms. Assuming that, to a first approximation, the stepwise replacement of methyl groups in this silane by siloxy groups will influence the  $^{29}\text{Si}$  NMR chemical shifts in the same way as indicated above for the methylsiloxysilanes series, one would arrive at  $^{29}\text{Si}$  NMR chemical shifts of ca.  $-46$  ppm for a  $N,N$ -dimethylaminomethylsiloxysilane and of ca.  $-86$  ppm for a  $N,N$ -dimethylaminotrisiloxysilane (**see Figure 1**). Very similar values would be expected for the amino analogues.

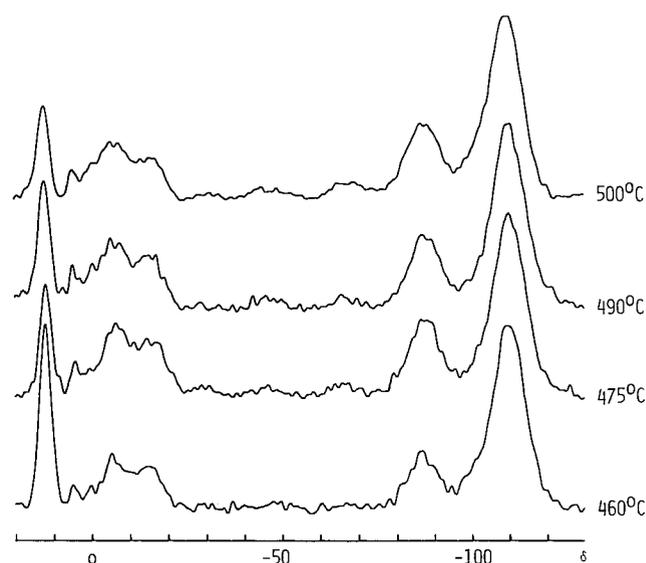
Actually, we observed  $^{29}\text{Si}$  NMR signals near  $-8$  ppm,  $-43$  ppm, and  $-88$  ppm after high-temperature silylation ( $485^\circ\text{C}$ – $510^\circ\text{C}$ ) of Cab-O-Sil with hexamethyldisilazane (HMDS) or with the model compound  $N,N$ -dimethyltrimethylsilylamine (DMTMSA). We, therefore, assign these signals to aminodimethylsiloxysilane, to aminomethylsiloxysilane and to aminotrisiloxysilane, respectively or to the appropriate  $N,N$ -dimethylamino analogues.

For two samples, obtained by HMDS silylation, showing relatively large  $^{29}\text{Si}$  NMR signals near  $-88$  ppm and no discernable signals near  $-101$  ppm (silanol groups), FT-IR spectra were taken. These spectra point unequivocally to the presence of amino groups: absorptions near  $3500\text{ cm}^{-1}$ ,  $3400\text{ cm}^{-1}$  and  $1550\text{ cm}^{-1}$  are assigned to the asymmetrical  $\text{NH}_2$  stretching, the symmetrical  $\text{NH}_2$  stretching and the  $\text{NH}_2$  deformation modes, respectively [8]. No absorptions characteristic of  $\text{SiOH}$  ( $3740\text{ cm}^{-1}$ ) were registered for these samples but evidence of extensive methylation ( $2970\text{ cm}^{-1}$



**Figure 2**

High temperature silylation of Cab-O-Sil with HMDS.



**Figure 3**

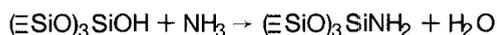
Very high temperature silylation of Cab-O-Sil with HMDS.

and  $2910\text{ cm}^{-1}$ ) was present. Finally, it should be recalled that also clear  $^{29}\text{Si}$  NMR signals near  $-88$  ppm were found after silylation of Cab-O-Sil with 1,3-diphenyl-1,1,3,3-tetramethyldisilazane and with 1,3-dimethyl-1,1,3,3-tetraphenyldisilazane at temperatures near  $425^\circ\text{C}$  and  $400^\circ\text{C}$ , respectively. This is in line with the relatively easy loss of phenyl groups from substituted disilazanes with formation of benzene [2].

Comparison of the  $^{29}\text{Si}$  CP-MAS NMR spectra of Cab-O-Sil, silylated with HMDS at temperatures between  $400$  and  $500^\circ\text{C}$  (**Figures 2 and 3**) shows that at higher temperatures, increasing amounts of disiloxysilanes and trisiloxysilanes (cross-polymerization products) are formed instead of

monosiloxysilanes. This can be concluded from the gradual disappearance of the signal near +12 ppm and the concomitant appearance of signals near -19 ppm and -62 ppm. The signal at -88 ppm of aminotrisiloxysilane is found after silylation at lower temperatures than the signals near -19 ppm and -62 ppm.

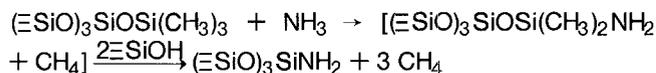
Transformations of monosiloxysilanes ("monodentate surface linkages") to disiloxysilanes ("bidentate surface linkages") can occur by reactions with neighboring silanol groups. It is improbable, in view of steric factors, that the observed trisiloxysilanes exhibit tridentate linkages to the surface. Most likely, these are mainly cross-linked groups (see above), the formation of which requires the presence of water [1]. As all Cab-O-Sil samples discussed here were thoroughly dried, one must consider either an alternative formation of the surface links or some source of water. One conceivable possibility for the latter would be reaction of  $\text{NH}_3$ , formed by the reaction of HMDS with Cab-O-Sil, with surface silanols:



This scheme was abandoned because of the following observations:

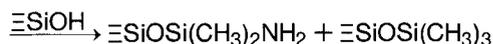
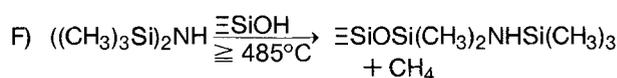
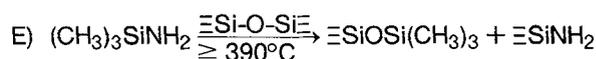
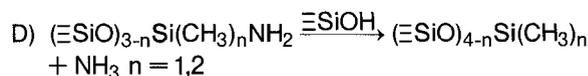
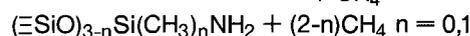
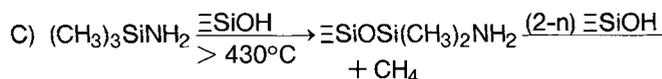
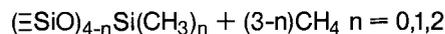
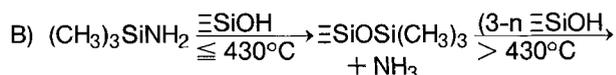
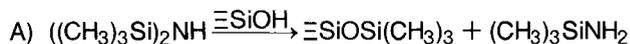
- I. Silylation of Cab-O-Sil with tetramethylsilane (TMS) and with hexamethyldisiloxane (HMDO) also yielded bi- and tri-dentate surface linkages apart from monodentate surface linkages, much in the same way as during silylation with HMDS.
- II. Subjection of Cab-O-Sil to  $\text{NH}_3$  under the silylation reaction conditions did not lead to any observable amounts of aminotrisiloxysilanes at the surface (i.e. no  $^{29}\text{Si}$  NMR signals near -88 ppm).

Thus, no alternative source of water (see above) seems available. Another way leading ultimately to aminotrisiloxysilane could be reaction of  $\text{NH}_3$  with already existing trimethylsiloxysilanes, with the loss of  $\text{CH}_4$ :

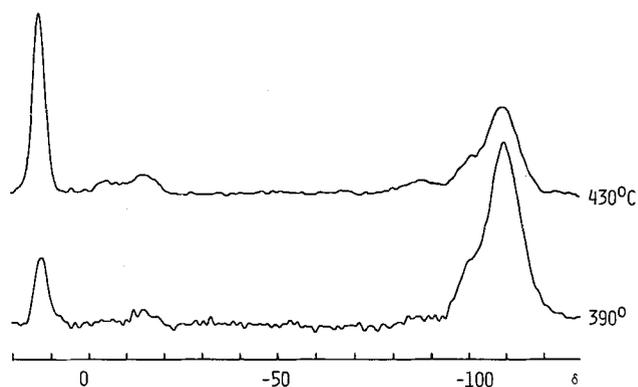


This possibility was dismissed since subjection of silylated Cab-O-Sil (mainly with trimethylsiloxysilanes) to  $\text{NH}_3$  under the silylation conditions yields exclusively dimethyldisiloxysilanes and methyltrisiloxysilanes (cross-polymerization) without any amino groups. Therefore, we propose that HMDS under the silylation conditions dissociates into two parts which react as indicated in the scheme below. The dissociation may take place either after initial reaction with a surface silanol (scheme F) or prior to the surface reactions as implied in schemes A-E. Very recently, silica-catalyzed gas phase disproportionation of disilazanes was proposed by Welsch and Frank [9]. Our results indicate, that attachment of HMDS to the surface prior to the dissociation(s) does also contribute (*vide infra*).

#### Reaction schemes



The  $\equiv\text{SiOH}$  symbol in the scheme indicates a silanol, bonded to three siloxy moieties. Our experiments have been carried out at certain temperature intervals, see e.g. **Figures 2-5**. Therefore, the temperature limits, indicated in the scheme should be considered as approximations. GC/MS analysis of the volatile reaction products of Cab-O-Sil and HMDS at  $500^\circ\text{C}$  proved the presence of  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $(\text{CH}_3)_3\text{SiNH}_2$  and of considerable amounts of hexamethyldisiloxane and of trimethylsilanol. Below ca.  $390^\circ\text{C}$  both  $(\text{CH}_3)_3\text{Si}$  groups formed from HMDS react with surface silanol groups according to the "classic" reaction schemes A and B. At slightly higher temperatures, however, the trimethylsilylamine reacts differently according to scheme E. This point will be discussed later. After silylation with HMDS at  $390^\circ\text{C}$ , still mainly trimethylsiloxysilane is found. However, small amounts of dimethylsiloxysilanes are observed and



**Figure 4**  
High temperature silylation of Cab-O-Sil with DMTMSA.

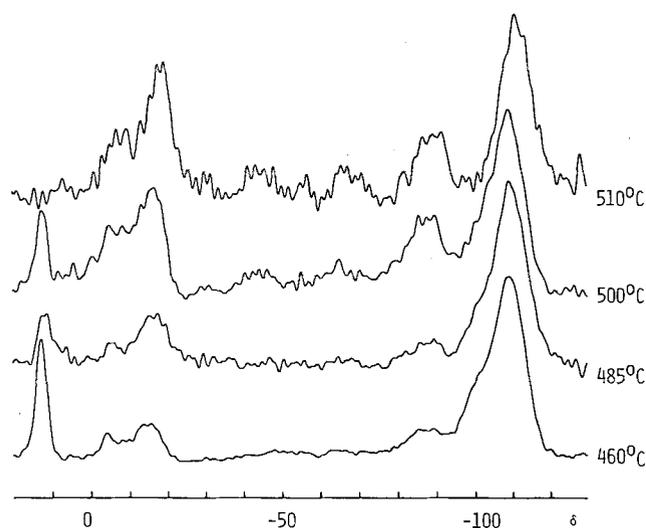


Figure 5

**Very high temperature silylation of Cab-O-Sil with DMTMSA.**

the  $^{29}\text{Si}$  NMR signal at  $-88$  ppm signifies the onset of formation of aminotrisiloxysilanes. After silylation at  $410^\circ\text{C}$ , amino (dimethyl)disiloxysilane is discerned in the NMR spectra. The silanol conversion is still incomplete: in the  $^{29}\text{Si}$  NMR spectrum an absorption is still found near  $-101$  ppm (Figure 2).

In principle, dimethyldisiloxysilanes may be formed from amino(dimethyl)siloxysilane moieties by reaction with neighbouring silanols, with concomitant evolution of  $\text{NH}_3$  (see scheme D). A similar route is feasible for amino (methyl)disiloxysilanes, leading to methyl(trisiloxy)silanes. In view of the rapid appearance (*i.e.* at relatively low temperatures) of significant amounts of aminotrisiloxysilanes, compared with the methylated bi- and tridentate surface-linked moieties (*vide infra*), we assume that these reactions do not contribute significantly to our results.

We prefer to explain the rather easy formation of aminotrisiloxysilane mainly by scheme E. Evidently, the pretreatment of the silica surface produced a dehydroxylation with formation of relatively exposed siloxane bridges. Trimethylsilylamine attacks these siloxane moieties with formation of aminotrisiloxysilanes and of trimethylsiloxysilanes which, as at lower temperatures, are also formed via the route described in scheme A.

In the case of HMDS silylation between  $480$  and ca.  $510^\circ\text{C}$  (Fig. 3), the monodentate methylated surface-linked moieties prevail over the methylated di- and tridentate surface-linked moieties, although this effect is largest at the lower temperatures. For the formation of siloxysilanes, containing amino- and methyl groups, a different behavior is evident. Already after silylation with HMDS at ca.  $390^\circ\text{C}$ , the aminotrisiloxysilane or tridentate form prevails within this subset of surface-linked moieties (scheme E, see above). Silylation at  $430^\circ\text{C}$  suffices to produce discernable amounts of amino (dimethyl)siloxysilane: the first step in scheme C. Only after

silylation at ca.  $500^\circ\text{C}$  the amino(disiloxy)methylsilane is observed in significant concentrations. This means that loss of a methyl group from an amino(methyl)siloxysilane (scheme C) requires more energy than loss of an amino group (scheme D). In order to substantiate our conclusions as depicted in the schemes B-E, the silylation of Cab-O-Sil with *N,N*-dimethyltrimethylsilylamine (DMTMSA) was also investigated. This compound qualifies, in our opinion, as a suitable model compound for the trimethylsilylamine part of HMDS. The results of the silylations with DMTMSA are illustrated by the  $^{29}\text{Si}$  CP-MAS NMR spectra of the reaction products, see Figures 4 and 5.

The agreement between silylation of Cab-O-Sil with HMDS and with DMTMSA is gratifying. We ascribe the differences in product distribution after silylation at a given temperature to the influence of the methyl substitution at the N atom of DMTMSA.

In the  $^{29}\text{Si}$  NMR spectra of Cab-O-Sils, silylated at higher temperatures with HMDS or with DMTMSA, signals are found between  $0$  and ca.  $+5$  ppm. One possible interpretation is that the HMDS or DMTMSA bind to the surface with concomitant formation of  $\text{CH}_4$ , *i.e.* according to scheme F. Such an explanation is in line with suggestions regarding silylation mechanisms made recently by Weisich [9].

It has been reported that very high temperature silylation ( $\geq 400^\circ\text{C}$ ) with disilazanes does not provide a satisfactory deactivation [9]. The present study reveals at least one of the possible reasons. Amino groups "replace" the originally active silanol sites to a considerable extent. However, the presence of amino groups may be of interest in liquid chromatography. Silylation with DMTMSA yields a grayish to black material already at lower temperatures, probably due to disproportionation. Therefore, DMTMSA is not a suitable silylation reagent for deactivation purposes. Perhaps, disilazane silylation at lower temperatures but longer reaction times will yield less amino groups for a given silanol conversion. Experiments to that effect are currently underway.

It may be concluded that under the reaction conditions usually applied in the deactivation of fused silica GC columns (*i.e.* a well dried column,  $400^\circ\text{C}$ , excess of reagent) HMDS will react mainly in the "classical way", yielding few amino groups at the surface, but mainly trimethylsiloxysilanes. Some important reaction conditions in this respect: type of silica, hydration situation of the surface (presence of water practically precludes the formation of surface-amino's below  $400^\circ\text{C}$ ! [1]), excess of reagent, *etc.* should be investigated to support our conclusions. Also, silylation of silicagel (Lichrosorb SI 60) under the conditions discussed here (15 h at  $440$ - $500^\circ\text{C}$ ) yields, in principle, a bonded phase material for HPLC [10]. Preliminary experiments indicate, that the selectivities of such phases *fore.g.* homologous *n*-alkyl-benzenes are rather high. This is probably due to the high degree of hydrophobicity: the percentage of carbon is higher than for most comparable, commercial RP-type

phases. At present, we are investigating the potential for practical use of such high-temperature silylations with disilazanes for HPLC. One important aspect will be the stability of such phases under a range of practical conditions, as performed earlier in these laboratories [11]. Moreover, the impact of the change in physical properties of the silica substrate, brought about by the conditions of the relatively high temperature will be studied.

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MS received: June 23, 1986  
Accepted by PS: August 1, 1986