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Investigations by ^{29}Si cross-polarization magic angle spinning NMR spectroscopy of reaction pathways of silica gel polyfunctional modification

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SUMMARY

Di- and trifunctionally modified silica gels (C_{18}) were investigated by ^{29}Si cross-polarization magic angle spinning NMR spectroscopy and the relative amounts of surface species were determined by peak deconvolution. On the basis of structure assignment and change in species decomposition with different reaction conditions, it is possible to construct a scheme for reaction pathways in polyfunctional modifications. Thus, distinct species composition can be correlated with reactions occurring at the surface.

Synthesis with and without an argon atmosphere and the use of the stationary phases in high-performance liquid chromatography (HPLC) cause dramatic changes in species composition. Derivatization in a dry argon atmosphere results in the formation of monodentate species (D_1 , D_2) (difunctionally modified) or bidentate species (T_2) (trifunctionally modified), whereas without an argon atmosphere mainly condensed species ($\text{D}_4 + \text{D}'_4$ and $\text{T}_4 + \text{T}'_4$) are formed. Disregarding the reaction procedures, modification with dichlorosilanes preferentially forms monodentate species, and trifunctional modification favours the formation of bidentates. Condensation reactions seem to play a minor role during modification. However, they are most important in the ageing process of polyfunctional modified phases, both in the dry form and during their use in HPLC.

INTRODUCTION

The chemical modification of silica surfaces by organosilanes is of increasing interest in different fields of chemistry, especially in view of their use as stationary phases in reversed-phase (RP) chromatography¹. ^{29}Si solid-state NMR magic-angle spinning (MAS), ^1H high-power decoupling² and cross-polarization (CP)³ have been used to distinguish between the different chemical species on the surface^{4–7}.

It has been shown that, with the exception of monofunctional derivatization^{4–8}, reactions used to prepare chemically modified silica do not lead to single chemical species. Many assignments^{5,6} and descriptions of the qualitative changes in species composition after solvent or heat treatment have been reported previously^{5,7,9}. How-

ever, no complete assignment and quantitative analysis of the species compositions has been performed. The composition of the surface species is essential for a comparison of the changes that occur during different modification procedures and of the changes that occur during the ageing process of stationary phases and for correlation with chromatographic performance.

Therefore, we have determined the quantitative amounts of different surface species, obtained under different conditions, in order to establish systematic correlations between species composition and preferred pathways occurring in polyfunctional modifications. Hence it should be possible to correlate a given species composition with distinct reaction pathways. The changes in surface species composition during prolonged elution with the mobile phase acetonitrile and ageing in the presence of air was also investigated.

We prepared several stationary phases with di- and trichlorosilanes under controlled reaction conditions and investigated them by ^{29}Si -CP-MAS-NMR spectroscopy, estimating the relative amounts of surface species obtained.

EXPERIMENTAL

Surface modification

Silicas were modified according to Kinkel and Unger¹⁰. Briefly, 5 g of silica were activated at 473 K and at a reduced pressure of $<10^{-3}$ mbar. After 12 h, the material was cooled to room temperature. A solution of 0.15 mol of 2,6-lutidine and of 0.12 mol of the appropriate organosilane in 30 ml of dry dichloromethane was added to the activated silica gel. The reaction mixture was stirred and heated thoroughly, washed with dichloromethane, ethanol, 50% aqueous ethanol, and diethyl ether and dried at 340 K and $<10^{-3}$ mbar for 24 h. Some operations were performed in an argon atmosphere.

Silylation reagents and the analytical techniques have been described previously¹¹. Reactions of silica with octadecylsilanes were performed on Nucleosil with a particle size of 7 μm , an average pore size of 100 Å and a surface area of 350 m^2/g (Machery, Nagel & Co, Düren, F.R.G.).

Solvent experiment

The flow experiment were performed at a flow-rate of 1 ml/min using a Bruker LC 31 HPLC instrument (Karlsruhe, F.R.G.) with stainless-steel HPLC columns (125 \times 4 mm I.D.) and acetonitrile, (HPLC grade; Merck, Darmstadt, F.R.G.) as the mobile phase for 3–4 days. The columns were stored under acetonitrile for 2 weeks and then flushed again to prevent them from drying. The whole procedure was repeated several times up to 3 months. The samples were then taken from the columns, dried and investigated by ^{29}Si solid-state NMR spectroscopy.

NMR parameters

Solid-state ^{29}Si NMR spectra were obtained on a Bruker MSL 200 Fourier transform NMR spectrometer with samples of 200–300 mg in double-bearing rotors of ZrO_2 . MAS was routinely performed at 4-kHz spinning rates. The pulse sequence of the CP-MAS experiment used has been described in detail elsewhere¹². Typically, the proton 90° pulse length was 6 μs and the repetition time 2 s.

Contact-time variation experiments of di (D) and trifunctionally (T) modified phases revealed a common CP behaviour. The optimum contact time for maximum magnetization of all D-units was obtained at 5 ms, and the optimum of the T-units at 2.5 ms, independent of the silica gel used⁹, and these contact times were employed in the following measurements. All ²⁹Si spectra were externally referenced to liquid tetramethylsilane and the chemical shifts are given in parts per million.

Peak deconvolution

Calculated deconvolutions of the experimental spectra were based on Gaussian peak shapes. We used constant chemical shifts and a constant peak width for each surface species of the D- and T-units. The width ranged from 110 ± 5 Hz (T_1, T_1'), 120 ± 5 Hz (D_3), 140 ± 5 Hz (D_1, D_2) to 210 ± 5 Hz (T_2). The $T_3 + T_3', T_4 + T_4'$, and $D_4 + D_4'$ species, corresponding to various polymerized species, were calculated assuming variable peak width. Optimum results could be obtained by a simulation at

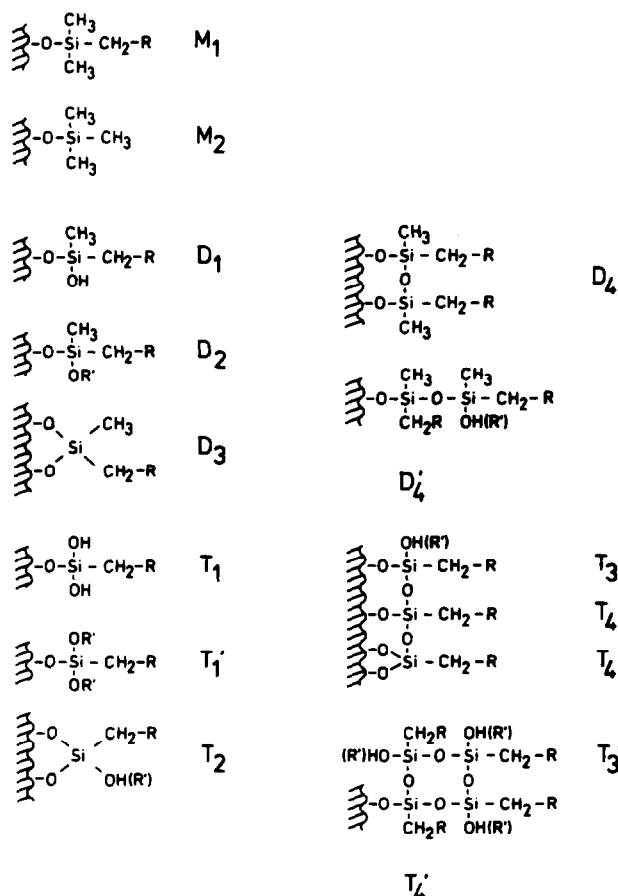


Fig. 1. Detectable surface species of a silica gel silylation with monochlorosilane (M), dichlorosilane (D) and trichlorosilane (T). R = *n*-alkyl, R' = CH₃. D₄, T₃ and T₄ are polymerized along the surface and D_{4'}, T_{3'}, and T_{4'} perpendicular to the surface.

constant chemical shift and constant peak width. The deviation of the intensities of experimental and simulated spectra was 3%.

RESULTS

The surface species (Fig. 1) are described by the D, T, Q notation, which refers to the number of oxygen (di-, tri- and tetraoxo) atoms bound to the silicon atom¹³. The assignments of the different Q-, D- and T-units, which have been described earlier⁴⁻⁶, are summarized in Table I.

The spectra of derivatized silica gels show the chemical shifts of the native silica gel, geminal silanediol groups Q₂ (-91 ppm), silanol groups Q₃ (-101 ppm) and siloxane groups Q₄ (-110 ppm), in addition to the signals of the silanes. After reaction with octadecylmethyldichlorosilane, we obtained signals of D₁ (-4 ppm), D₂ (-7 ppm), D₃ (-10 ppm) and of various D₄ + D'₄ species (-14 to -22 ppm) and after reaction with octadecyltrichlorosilane, resonances of T₁ (-46 ppm), T'₁ (-50 ppm), T₂ (-56 ppm), T₃ + T'₃ (-59 ppm) and T₄ + T'₄ species (-64 to -70 ppm).

The resonances obtained between -64 and -70 ppm (trifunctionally modified) or between -14 and -21 ppm (difunctionally modified) are due to D₄ or T₄ units with different extents of cyclization, which influence the chemical shift. This has been also observed in ²⁹Si liquid high-resolution NMR. For instance, resonances of the cyclic species occur at $\delta = -20$ ppm for (Me₂SiO)₄, $\delta = -22.8$ ppm for (Me₂SiO)₅ and $\delta = -23$ ppm for (Me₂SiO)₆¹³ (where Me = methyl).

In order to construct the preferred reaction pathways, phases were prepared in the presence of moisture and in a dry argon atmosphere. The influence of the different

TABLE I
CHEMICAL SHIFTS OF THE SILANE SIGNALS

For assignments, see Fig. 1. D'₄, T'₃ and T'₄ are species polymerized perpendicular to the surface; D₄, T₃, and T₄ are polymerized along the surface. T₂ and T₃ were used to differentiate between a silicon having two (-O-Si-O-)_n units as neighbours (T₂) and a silicon having one (-O-Si-O-)_n unit and one (-O-Si-R-) unit as neighbours (T₃), because of different chemical shifts of the T₂ and T₃ groups due to the different chemical surroundings.

Structural type	δSi^a
Q ₂	-91
Q ₃	-101
Q ₄	-110
D ₁	-4
D ₂	-7.2
D ₃	-10
D ₄ + D' ₄	-14 to -21
T ₁	-46
T' ₁	-50
T ₂	-55.5 (R ≥ CH ₃)
T ₃ + T' ₃	-59 (R ≥ CH ₃)
T ₄ + T' ₄	-64 to -70

^a Chemical shifts in ppm with respect to liquid Me₄Si.

reaction procedures on the species composition of a difunctionally modified Nucleosil is shown in Fig. 2, and the different species composition of a trifunctionally modified Nucleosil is shown in Fig. 4. To obtain quantitative data, we performed a peak deconvolution by Gaussian peak shapes of the resonance patterns of the derivatized species. An example shows the deconvolution of the D units of Fig. 2 (Fig. 3).

Modification in an argon atmosphere leads to the preferred formation of monodentate D_1 and D_2 , whereas the amount of condensed species $D_4 + D'_4$ is 37% (Table II). Derivatization in the absence of an argon atmosphere reduces the monodentate D_1 , D_2 and the bidentate D_3 species, whereas condensation to $D_4 + D'_4$ increases to 49.6%. In addition to the already assigned signals (Fig. 1), we found a signal at +1.6 ppm, amounting to 3% (Table II) and 6.2% (Table III) of the total intensity. This resonance has also been obtained for other difunctionally modified phases.

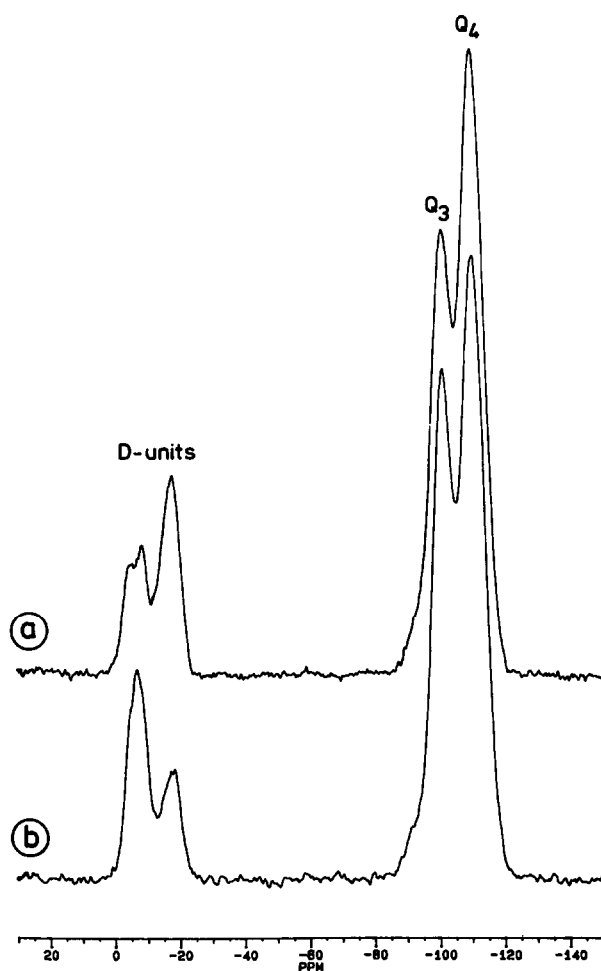


Fig. 2. ^{29}Si -CP-MAS-NMR spectrum of Nucleosil (batch 5051) silylated with octadecylmethyldichlorosilane. The contact time was 5 ms. (a) In the absence of argon; (b) in an argon atmosphere.

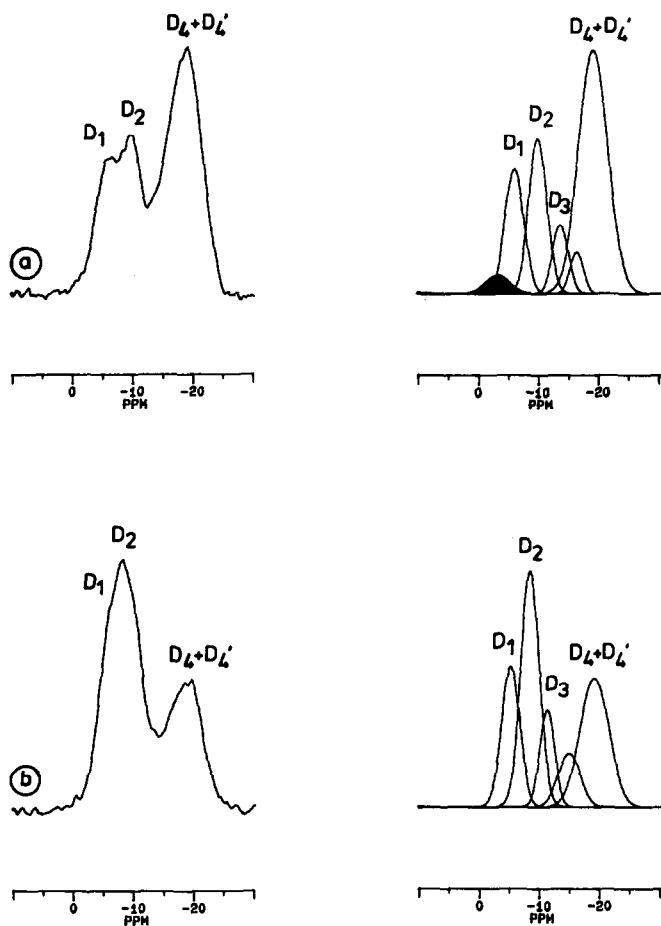


Fig. 3. Simulation of the D-units of the experimental spectrum in Fig. 2. (a) Experimental spectra and simulated species after silylation in air; (b) experimental spectra and simulated species after derivatization in an argon atmosphere. ■ = Unknown resonance.

It is interesting to note that in trifunctionally, in contrast to difunctionally, modified stationary phases, the amount of the monodentate species T_1 and T'_1 is relatively low. Their relative amounts, even for reactions in an argon atmosphere, do not exceed 10% (Table II). However, derivatization in an argon atmosphere yields mainly the bidentate species, T_2 (55.6%) and the cross-linked condensed species, $T_4 + T'_4$ (23.4%). Derivatization in the absence of an argon atmosphere leads to a reduced amount of T_2 (26.4%), whereas the amount of the condensed species, $T_4 + T'_4$, increased to 65.1% (Table II).

In order to characterize the preferred reactions of the surface after modification, especially in combination with solvent, we flushed polyfunctional modified samples in an HPLC apparatus with HPLC-grade acetonitrile for several days, stored the column in acetonitrile, and again flushed the columns every 2 weeks to prevent them from drying. We repeated this procedure for up to 3 months. The stationary phases

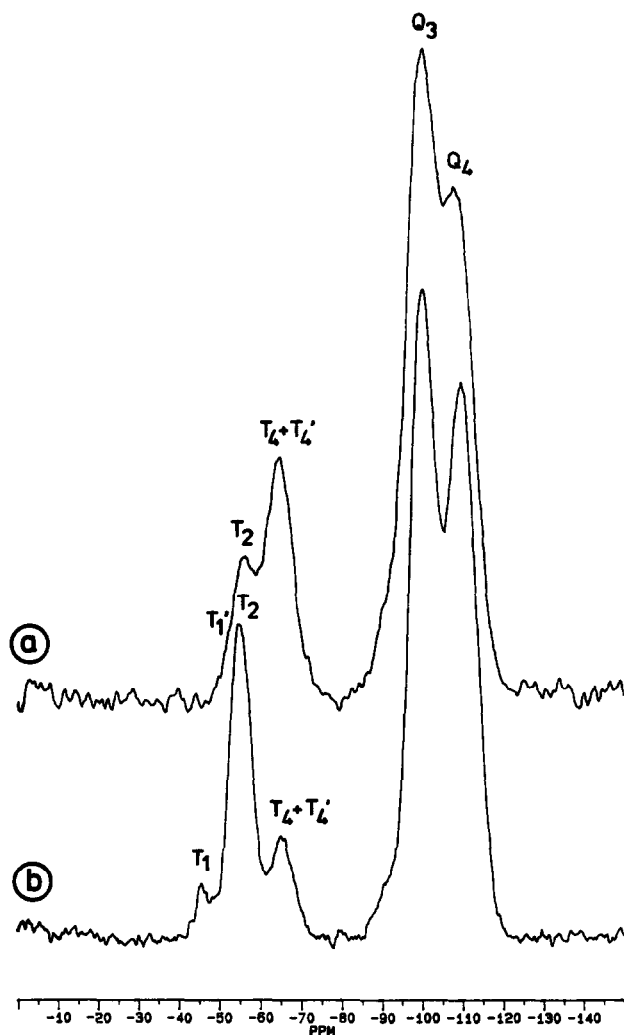


Fig. 4. ^{29}Si -CP-MAS-NMR spectrum of Nucleosil (Batch 5051), silylated with octadecyltrichlorosilane. The contact time was 2.5 ms. (a) In the absence of argon; (b) in an argon atmosphere.

were then taken from the columns, dried and investigated by ^{29}Si solid-state NMR spectroscopy. The experiments reveal a change in the variety of species. The monodentate species D_1 , D_2 , T_1 and T'_1 are reduced with a significant increase in the concentration of the condensed species D_3 , $\text{D}_4 + \text{D}'_4$, $\text{T}_3 + \text{T}'_3$ and $\text{T}_4 + \text{T}'_4$. Fig. 5 shows an example of a difunctionally modified phase. As shown in Table III, there is a 50% decrease in the amount of the monomeric species (unknown, D_1 and D_2), whereas the condensed species $\text{D}_4 + \text{D}'_4$ increase by 50%. Condensation, although slower, is also observed during ageing of dry stationary phases. The accelerated condensation in the presence of solvent is due to increased mobility and reaction ratio in the solvated form.

TABLE II

RELATIVE AMOUNTS OF MOLECULAR STRUCTURES OBTAINED AFTER TWO DIFFERENT MODIFICATION CONDITIONS OF NUCLEOSIL (BATCH 5051) WITH DICHLOROSILANE OR TRICHLOROSILANE

Modifier	Structural type	δ^a	Relative amount (%) ^b	
			No Ar	In dry Ar atmosphere
Dichlorosilane	Unknown	+ 1.6	3	—
	D ₁	-4.2	16.2	19.2
	D ₂	-7.2	19.7	32.9
	D ₃	-10.5	7.5	10.8
	D ₄ + D' ₄	-14 to -20	49.6	37
Trichlorosilane	T ₁	-46.5	—	5.7
	T' ₁	-50.0	2.9	3
	T ₂	-55.5	26.4	55.6
	T ₃ + T' ₃	-59.0	5.4	12.2
	T ₄ + T' ₄	-64 to -75	65.1	23.4

^a Chemical shifts in ppm with respect to liquid Me₄Si.

^b Error, $\pm 3\%$.

DISCUSSION

On the basis of the changes in surface species composition under various reaction conditions, it is possible to construct a scheme for the consecutive pathways in polyfunctional modifications of HPLC RP materials.

In difunctional derivatization with dichlorosilane (Fig. 6A), the first step is the formation of the monodentate I. This has also been observed by Sindorf and Maciel⁵. The intermediate is hydrolysed during washing at the end of the synthesis to the monodentates D₁ and D₂ (Fig. 6B). The amount of D₂ is therefore an indirect indication of the amount of monodentate I at the end of the reaction, as the D₂ species can only be formed from I in the washing step with ethanol. A large amount of D₂ can

TABLE III

RELATIVE AMOUNTS OF MOLECULAR STRUCTURES OF A DIFUNCTIONALLY MODIFIED NUCLEOSIL (BATCH 4111) AND AFTER FLUSHING THIS STATIONARY PHASE WITH ACETONITRILE AS SOLVENT

Structural type	δ^a	Relative amount ^b	
		Original	After solvation
Unknown	+ 1.6	6.2	—
D ₁	- 4.2	19.0	15.2
D ₂	- 7.2	35.1	17
D ₃	-10.5	12.8	12.8
D ₄ + D' ₄	-14 to -20	27.1	54.7

^a Chemical shifts in ppm with respect to liquid Me₄Si.

^b Error, $\pm 3\%$.

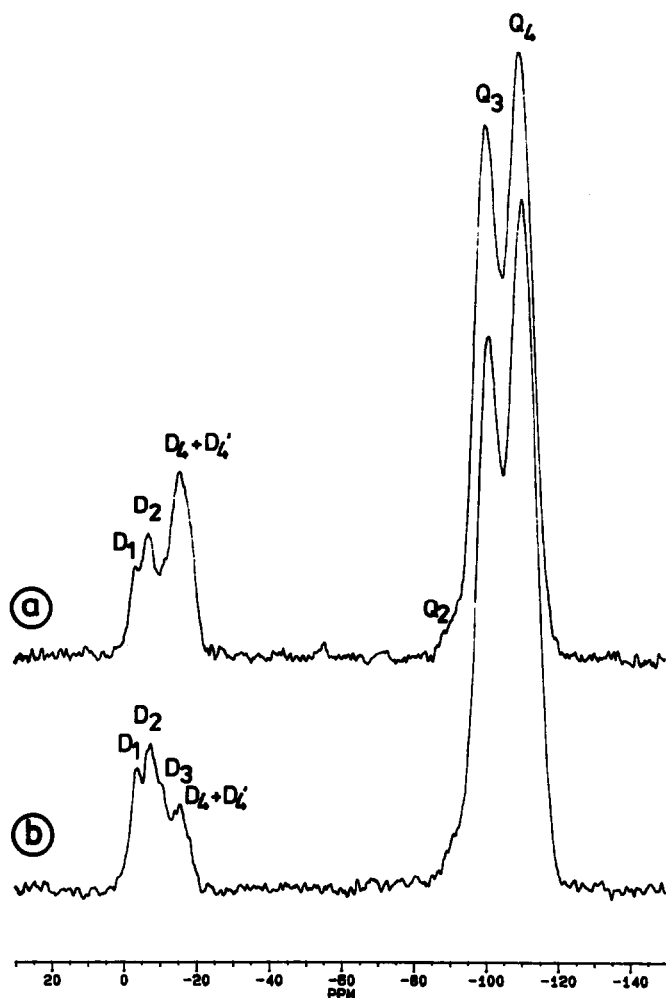
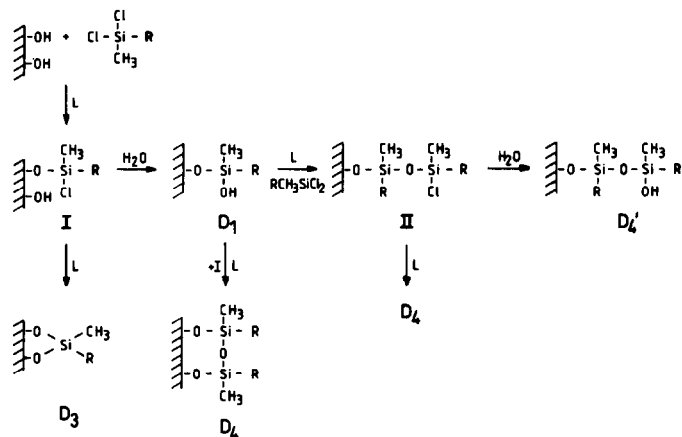


Fig. 5. ^{29}Si -CP-MAS-NMR spectrum of Nucleosil (Batch 4111) silylated with octadecylmethyldichlorosilane. The contact time was 5 ms. (a) After solvent exposure; (b) original phase.

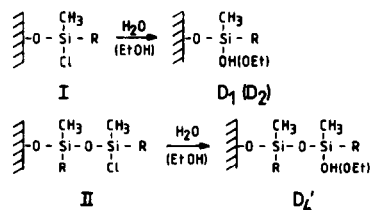
be correlated with a large amount of monodentate I. Hence the large amount of D_2 in reactions in an argon atmosphere reveal (Table II) that many of the monodentate I species neither have formed condensed species nor have reacted with the silica to form bidentate D_3 (Table III). However, the small amount of D_3 in the presence and absence of moisture clearly indicates that the bidentate D_3 formation is not favoured, but, as seen in Fig. 3, it still occurs. These findings are in contrast to those of Sindorf and Maciel⁵ and of Gilpin and Burke⁸, who described D_3 almost as hypothetical moieties. The ratio of monodentate (D_1 , D_2) to bidentate (D_3) after the washing step is in our example *ca.* 5 (Table II) and never < 3 . This indicates that the formation of the monodentates D_1 and D_2 , even in the presence of moisture, is always preferred.

In the trifunctional modification with trichlorosilane (Fig. 7A) the reaction also begins with the formation of an intermediate, I^5 , which can react further via two

A. Reactions with moisture



B. Washing



C. Condensation

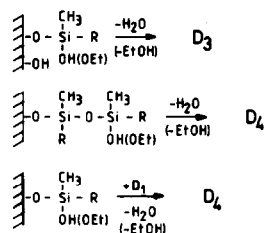


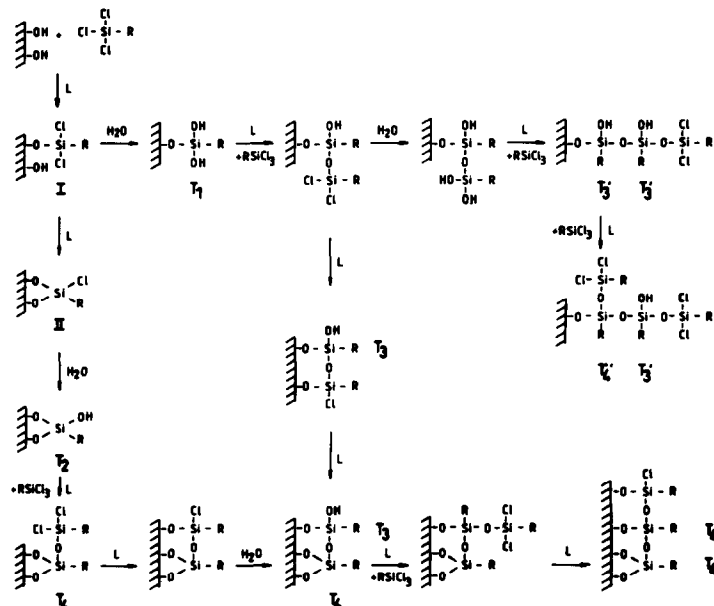
Fig. 6. Possible reaction pathways occurring after modification with octadecylmethylchlorosilanes. L = 2,6-lutidine (used as a catalyst); R = C₁₈H₃₇; Et = ethyl.

reaction pathways. One possibility is the reaction to bidentate II, which is hydrolysed during washing to bidentate T₂. The other possibility is the reaction with moisture to T₁ and further formation of cross-links (T₃ + T₃, T₄ + T₄). The monodentate I is hydrolysed during washing to monodentates T₁ and T₁' (Fig. 7B). In contrast to the difunctional modification, the formation of II is obviously preferred, as we obtained only a small amount of T₁ and T₁' after washing the samples, whereas the amount of bidentate T₂ is very high. Sindorf and Maciel⁵ also observed the most intense resonance at -53 to -55 ppm. However, they proposed for this resonance a structure resembling that of T₃ + T₃. In our opinion and that of other workers⁷, this resonance must be ascribed to a bidentate with chelate bonding (T₂). This argument is supported by the high stability of trifunctionally modified stationary phases in HPLC

because, owing to a chelate effect, a bidentate, (T_2 , D_3) should be more stable than a monodentate species¹⁴. These results agree with those of the recent investigations of Hetem *et al.*,¹⁵ who demonstrated in ageing experiments with various eluent compositions in the HPLC test that the trifunctional modified phases are the most stable.

The species T_1 , like the D_2 species, can only be formed during the washing step with ethanol, following the reaction procedure (Scheme 7B), and is therefore an indicator for the amount of intermediate I. Especially the derivatization in the presence of an argon atmosphere leads to an increase in bidentate species, T_2 (55.6%). The ratio of monodentate (T_1 , T_1') to bidentate (T_2) is 1:7 in an argon atmosphere and 1:9 in the presence of moisture (Table II). The reason for the large amount of bidentate may be that trichlorosilanes have three reactive groups, and hence a higher probability of having the appropriate steric form to react with two neighbouring surface silanols, in contrast to dichlorosilanes with only two functional groups. The

A. Reactions with moisture



B. Washing



C. Condensation

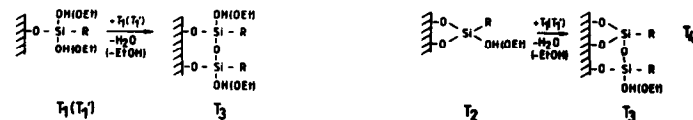


Fig. 7. Possible reaction pathways occurring after modification with octadecyltrichlorosilane. L = 2,6-lutidine (used as a catalyst); R = $C_{18}H_{37}$; Et = ethyl.

more moisture is available in the modification procedure, the more chlorine atoms of the trichlorosilanes are hydrolysed and therefore the formation of the T_2 species is not favoured, owing to the reduced amount of available reactive groups.

We believe that the concentration of the species polymerizing perpendicular to the surface (D'_4 , T'_3 and T'_4) should be relatively low, compared with the amounts of species polymerizing along the surface (D_4 , T_3 and T_4), owing to steric hindrance of the bulky octadecyl chains. Therefore, condensation of monodentates yields mainly D_4 , T_3 and T_4 species. Their amounts depend on the reaction procedure. Derivatization in the absence of an argon atmosphere causes increased condensation (Table II). The more moisture is available for the reaction, the more favoured is the competitive reaction of the monodentate I to D_1 or T_1 (Figs. 6A and 7A), which can react further with chlorosilane, catalysed by 2,6-lutidine, to form the condensation products $D_4 + D'_4$ or T_3 , T'_3 and $T_4 + T'_4$. Hence the reduced amounts of D_2 or T_2 without an argon atmosphere are easily explained by assuming that most of the monodentate I has formed $D_4 + D'_4$ or $T_4 + T'_4$ before washing.

The condensation reactions (Figs. 6C and 7C) seem to play a minor role in the modification procedure. This is indicated by the relatively small amount of D_3 or $T_3 + T'_3$ in all derivatized stationary phases (Table II). However, after flushing the stationary phases and storing in contact with solvent (Fig. 5, Table III), the amount of monodentates, D_1 and D_2 is reduced by almost 50%, whereas the $D_4 + D'_4$ species are correspondingly increased. The ethoxy species, D_2 , seems to form these condensed species preferentially, whereas the amount of D_1 species is hardly affected. These findings indicate that the condensation reactions play an important role in the ageing process of stationary phases in HPLC. We observed similar, but weaker, effects for dry samples that had been stored in the presence of air for 3 months. The amount of D_3 , $D_4 + D'_4$, $T_3 + T'_3$ and $T_4 + T'_4$ species is increased whereas that of the monodentates D_1 and D_2 or T_1 and T'_1 is decreased (not shown). The faster condensation in the presence of eluent may be due to an increased mobility of the surface groups in the solvated form.

At present, a complete assignment of all individual resonances is impossible. We are able to determine the relative amounts of the already known surface species, as a small amount of simulated intensity cannot yet be assigned. We believe that the unknown resonances of the D units at +1.6 ppm could be due to cracked silanes. Unhydrolysed chlorosilanes can be excluded, because the appropriate resonance would appear at *ca.* +9 ppm⁵.

Spectra of the modified phases (Figs. 2 and 4) indicate that silanediol groups are still present, despite the fact that they are thought to be very reactive and to react completely with the silanes¹⁶. This may be caused by a renewed hydrolysis of siloxane groups during the modification procedure.

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