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STRUCTURAL INVESTIGATIONS ON REVERSED-PHASE SILICAS DETERMINATION OF LIGAND FUNCTIONALITY

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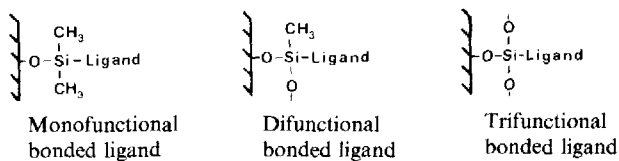
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SUMMARY

Hydrophobic derivatized silicas with octyl and octadecyl groups were treated with fused alkali in order to cleave the ligands from the polymeric matrix. The products were analysed by gas chromatography. Whereas silicas derivatized with trifunctional silanes showed mainly the free alkanes, difunctional substituted materials produced isomers of cyclic tri- and tetraalkylsiloxanes. Monofunctional ligands yielded trialkylsilanols and hexaalkyldisiloxanes after alkali fusion. Several commercially available reversed-phase silicas were thus analysed for their ligand functionalities.

INTRODUCTION

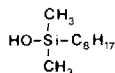
Structural investigations of chemically modified silicas have been the subject of several studies¹⁻¹³. Although their ligand structure of reversed-phase (RP) silicas could be determined unambiguously in most cases, the functionality of the silane used for derivatization was more difficult to identify. Pyrolytic degradation^{4,8,10} and



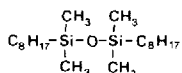
NMR investigations⁹ of RP silicas have previously been used for this purpose. Analytical methods based on the scission of the intact ligand from the polymeric matrix^{1,5,6,11-13} can be divided in two groups depending on whether the reagent cleaves the siloxane or the Si-C bond. In principle, only cleavage of the siloxane bond^{1,5,12,13} can yield information about the ligand functionality.

Our original intention in developing the alkali fusion reaction of RP silicas⁶ was to cleave the Si-C bond for ligand analysis, but although the siloxane linkage is destroyed under these conditions a statement about ligand functionality seemed to be impossible.

In a previous study of this reaction¹¹, however, it was found that a commercially available octyl-modified RP silica (RP-8), the monofunctional MOS Hypersil, produced the expected alkane in traces only, whereas mainly dimethyloctylsilanol and 1,1,3,3-tetramethyl-1,3-dioctyldisiloxane were formed, indicating exclusive siloxane bond splitting.



Dimethyloctylsilanol

1,1,3,3-Tetramethyl-
1,3-dioctyldisiloxane

The present study investigates how far the potassium hydroxide fusion method can be optimized and extended by utilizing the selective cleavage of the siloxane bond for ligand functionality identification.

EXPERIMENTAL

The gas chromatographic (GC) analysis was performed with a Sigma 1 gas chromatograph (Perkin-Elmer) and a Mikromat HR GC 412 (Orion Analytica, Espoo, Finland), both equipped with a flame ionization detector and helium gas supply.

The fusion products of RP-8 silicas were analysed on a 15-m fused-silica capillary column with a chemically bonded non-polar stationary phase (DB-1-15B, J&W Scientific) using a temperature programme from 50 to 310°C at a rate of 40°C/min.

The RP-18 silica fusion products were analysed on the same column, with a temperature gradient of 40°C/min from 160 to 310°C and a 10-min hold at 310°C.

The cyclic tri- and tetrasiloxanes obtained from difunctional RP-18 materials were analysed on a 6-m fused-silica SE 30 capillary column under isothermal conditions at 310°C. Injector and detector temperatures were set to 370°C.

Mass spectra were obtained with a CH 7A MAT mass spectrometer (Varian MAT) at 70 eV combined with a Aerograph 1400 gas chromatograph (Varian MAT) by open split coupling.

Mono-, di- and trifunctional RP-8 and RP-18 silicas were synthesized as described elsewhere¹⁴. The silanes used for synthesis were from Petrarch Systems (Bristol, PA, U.S.A.). References for the identification of organosilicon GC peaks were easily obtained by hydrolysis of the corresponding silanes.

All RP silicas tested for their functionality were commercially available products, and chemicals and solvents used were of analytical grade.

For determination of ligand functionalities, 20 mg of RP silica suspended in 100 μl triethylene glycol dimethyl ether (triglyme) were fused with 200 mg of dry solid potassium hydroxide in a small glass reaction tube (110 \times 5 mm I.D.) for 0.5 h at 150°C. For GC analysis 200 μl hexane were added after cooling down.

RESULTS

Monofunctional bonded RP-18 silica was treated with molten potassium hydroxide in a triglyme suspension for various times and temperatures in order to

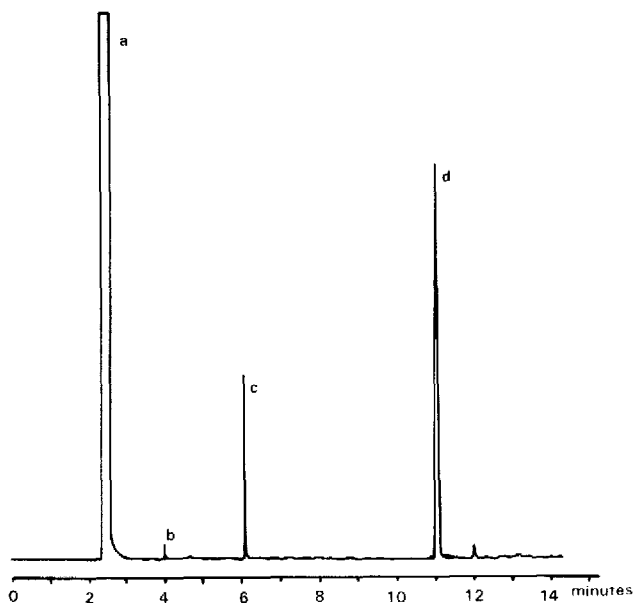
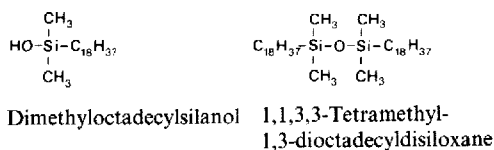


Fig. 1. Gas chromatogram of alkali fusion products from monofunctional derivatized RP-18 silica (0.5 h, 150°C, triglyme suspension). Peaks: a = hexane and triglyme (solvents); b = *n*-octadecane; c = dimethyloctadecylsilanol; d = 1,1,3,3-tetramethyl-1,3-dioctadecyldisiloxane.

optimize the reaction conditions for the exclusive siloxane bond splitting. The reaction products obtained were analysed by GC (Fig. 1). Besides some *n*-octadecane from Si-C bond cleavage, the reaction products were mainly dimethyloctadecylsilanol and 1,1,3,3-tetramethyl-1,3-dioctadecyldisiloxane, which were identified by GC-mass spectrometry (MS).



The amount of silicon-containing compounds was estimated by using *n*-hexacosane as internal standard. It was shown that relatively mild fusion conditions (0.5 h, 150°C) favour the destruction of Si-O-Si bonds and the generation of organosilicon compounds at comparably low alkane formation from Si-C bond cleavage.

Monofunctional RP-8 material treated with potassium hydroxide under these optimized conditions showed the same product distribution (Fig. 2) with dimethyloctylsilanol and 1,1,3,3-tetramethyl-1,3-dioctyldisiloxane as main compounds, as mentioned above.

Investigations with monofunctional aromatic RP silicas showed similar results for materials containing one or two phenyl groups attached to silicon. However, the

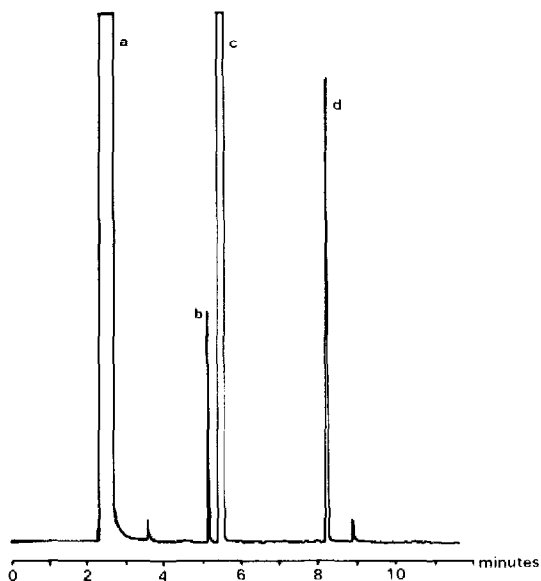


Fig. 2. Gas chromatogram of alkali fusion products from monofunctional derivatized RP-8 silica (0.5 h, 150°C, triglyme suspension). Peaks: a = hexane (solvent); b = dimethyloctylsilanol; c = triglyme; d = 1,1,3,3-tetramethyl-1,3-dioctyldisiloxane.

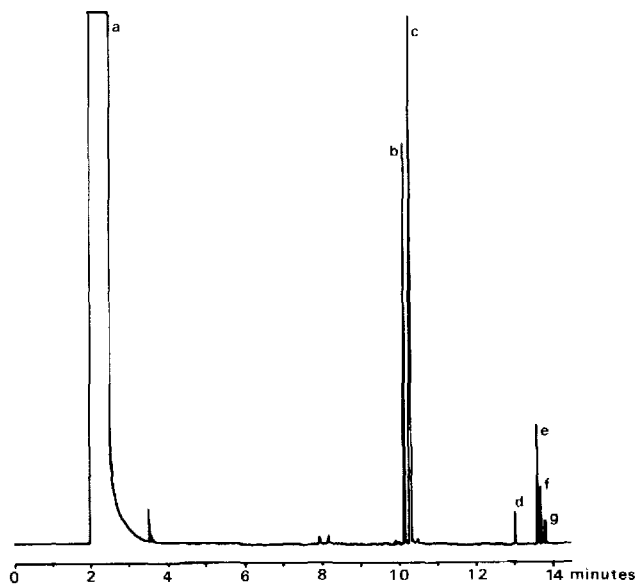
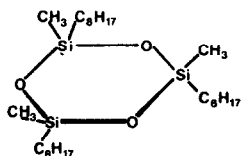


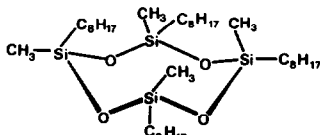
Fig. 3. Gas chromatogram of alkali fusion products from difunctional derivatized RP-8 silica (0.5 h, 150°C, triglyme suspension). Peaks: a = hexane and Triglyme (solvents); b and c = isomers of 2,4,6-trimethyl-2,4,6-trioctylcyclotrisiloxane; d-g = isomers of 2,4,6,8-tetramethyl-2,4,6,8-tetraoctylcyclotetra-siloxane.

Si-benzyl linkage turned out to be so labile under the fusion conditions applied that only toluene and no disiloxane could be detected.

Difunctional RP-8 silica was fused with potassium hydroxide under the same reaction conditions. A gas chromatogram of the fusion products shows only small amounts of *n*-octane followed by a peak doublet and a peak quadruplet (Fig. 3). GC-MS investigations showed these signals to be isomers of cyclic tri- and tetradialkylsiloxanes. It was not possible to allocate these peaks to particular isomers by MS.



2,4,6-Trimethyl-2,4,6-trioctylcyclotrisiloxane
(two isomers)



2,4,6,8-Tetramethyl-2,4,6,8-trioctylcyclotetrasiloxane
(four isomers)

Some chromatographic problems arose during analysis of the fusion products from difunctional RP-18 silicas. The expected six- and eight-membered siloxane rings substituted with octadecyl groups have molecular weights of 937 and 1249, respectively, with corresponding low volatility. A very short capillary column (6 m) therefore was used for analysis. Two products signals were observed (Fig. 4), which MS analysis showed to be 2,4,6-trimethyl-2,4,6-trioctadecylcyclotrisiloxane and 2,4,6,8-

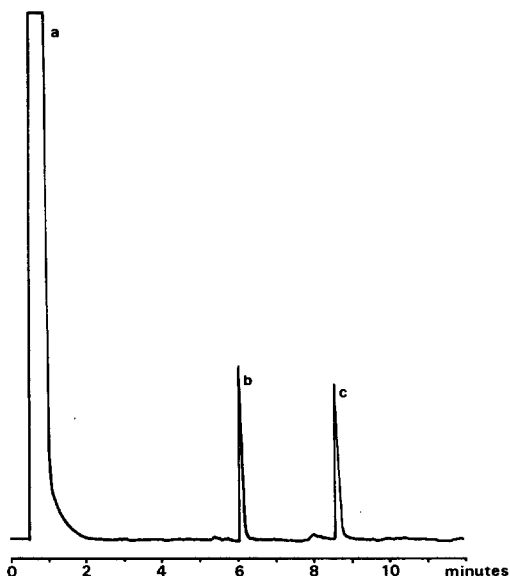


Fig. 4. Gas chromatogram of alkali fusion products from difunctional derivatized RP-18 silica (0.5 h, 150°C, triglyme suspension). Peaks: a = hexane and triglyme (solvents); b = 2,4,6-trimethyl-2,4,6-trioctadecylcyclotrisiloxane (two isomers); c = 2,4,6,8-tetramethyl-2,4,6,8-tetraoctadecylcyclotetrasiloxane (four isomers).

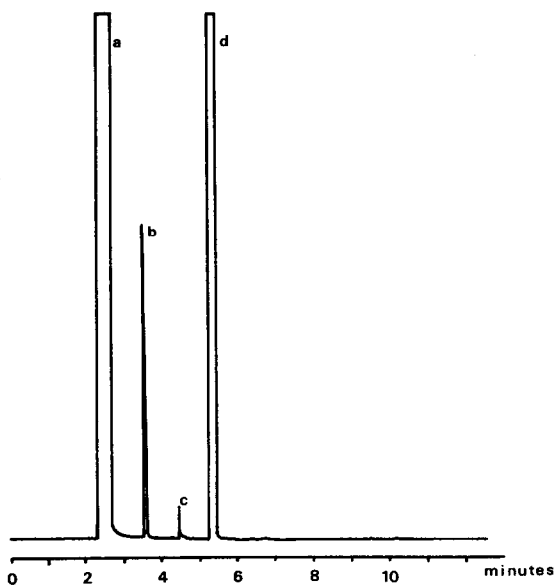


Fig. 5. Gas chromatogram of alkali fusion products from trifunctional derivatized RP-8 silica (0.5 h, 150°C, triglyme suspension). Peaks: a = hexane; b = *n*-octane; c = 1-octanol; d = triglyme.

tetramethyl-2,4,6,8-tetraoctadecylcyclotetrasiloxane. Separation of isomers was not achieved under these conditions.

Trifunctional RP-8 and RP-18 silicas showed no organosilicon compounds

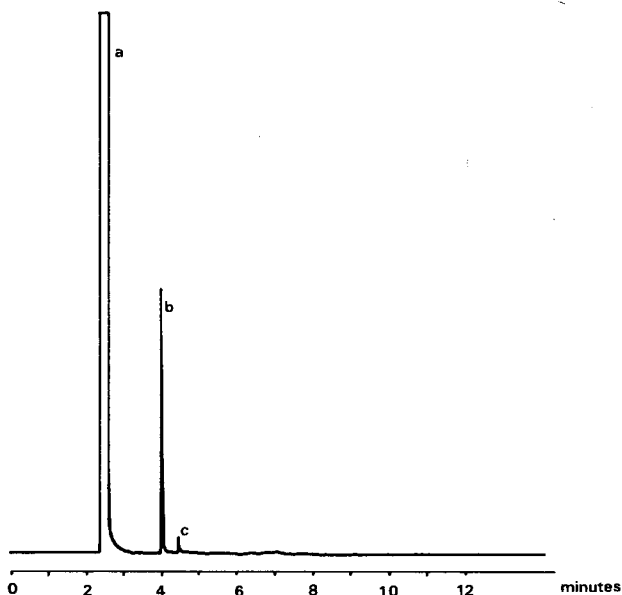


Fig. 6. Gas chromatogram of alkali fusion products from trifunctional derivatized RP-18 silica (0.5 h, 150°C triglyme suspension). Peaks: a = hexane and triglyme (solvents); b = *n*-octadecane; c = 1-octadecanol.

during GC analysis, but the corresponding *n*-alkanes and 1-alkanols were detected (Figs. 5 and 6). As the reaction products of mono-, di- and trifunctional derivatized model silicas with potassium hydroxide allowed a clear distinction between the three differently bonded types, several commercially available RP materials were analysed for their ligand functionalities. The results are shown in Tables I and II.

TABLE I

LIGAND FUNCTIONALITIES OF COMMERCIALY AVAILABLE RP-8 SILICAS

<i>Sample</i>	<i>Functionality</i>
HPTLC Fertigplatten RP-8 (Merck)	Di
LiChroprep RP-8 (Merck)	Di
LiChrosorb RP-8 (Merck)	Di
MOS Hypersil C8 (Shandon)	Mono
SIL-X 5 C-8 (Perkin Elmer)	Di
Kieselgel 60 HPLC C ₈ (Riedel)	Di

TABLE II

LIGAND FUNCTIONALITIES OF COMMERCIALY AVAILABLE RP-18 SILICAS

<i>Sample</i>	<i>Functionality</i>
HPTLC Fertigplatten RP-18 (Merck)	Di
LiChroprep RP-18 (Merck)	Di
LiChrosorb RP-18 (Merck)	Di
Nucleosil 7 C ₁₈ (Macherey-Nagel)	Tri
ODS Hypersil (Shandon)	Tri
ODS SIL-X 10 (Perkin-Elmer)	Tri
Sep-Pak (Waters)	Mono
Spherisorb S5 ODS C ₁₈ (Phase Separations)	Tri
Vydac 201 RP (The Separations Group)	Tri

DISCUSSION

Alkali fusion of RP silicas splits both the siloxane and the Si-C bonds. By varying the reaction conditions the ratio between the two types of cleavage can be altered. Cleavage of the Si-O-Si linkage produces trialkylsilanols with one or two methyl groups on silicon, according to whether mono- or difunctional bonded materials are involved. The reactive silanols condense very readily to form alkylsiloxanes until equilibrium is reached. However, at temperatures *ca.* 200°C Si-C bond scission also takes place, and these alkylsiloxanes are destroyed so that information about the ligand functionality is lost. However, at a temperature of 150°C good yields of organosilicon compounds are obtained.

The absence of silicon-containing GC peaks in the case of trifunctional materials is due to the formation of non-volatile cross-linked polymeric silicones. Trifunctional bonded ligands therefore are identified by deduction.

The analysis of several commercial RP silicas showed that only very few prod-

ucts are of the monofunctional type with its well-defined structure. A trend to monofunctional bonded ligands, as was assumed by Majors^{1,5}, cannot be established from the results obtained.

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