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Synthesis and characterization of bonded phases made via hydrosilation of alkynes on silica hydride surfaces

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Abstract

The use of the silanization/hydrosilation method for the modification of silica is extended to include the bonding of alkynes to hydride surfaces. Diffuse reflectance infrared Fourier transform and cross-polarization and magic-angle spinning NMR studies confirm the bonding of several different types of alkynes to the silica hydride and elemental analysis indicates high surface coverage ($>3.8 \mu\text{mol}/\text{m}^2$) for four of the five bonded phases. Static stability tests indicate good resistance to hydrolysis at both high and low pH. Preliminary chromatographic evaluations of the bonded materials demonstrate good separation characteristics in both the reversed- and normal-phase modes. © 1998 Elsevier Science B.V. All rights reserved.

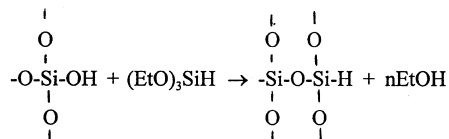
Keywords: Silanization; Hydrosilation; Stationary phase, LC; Alkynes; Silica hydride

1. Introduction

It has been shown that direct Si–C linkages are the most hydrolytically stable for bonding stationary phases to porous silica or for the modification of the inner wall of a capillary in HPCE [1–3]. The silanization/hydrosilation bonding method provides the most convenient approach for producing direct Si–C linkages on various types of silica surfaces [2,4,5]. Another advantage of the method is its synthetic versatility which allows a wide variety of functional groups to be bonded to the surface. In addition, the attachment of the organic moiety through hydrosilation can take place via a number of different multiple bond groups, the most common of which is a terminal olefin [6]. In this study the use of acetylenic compounds for the attachment of the

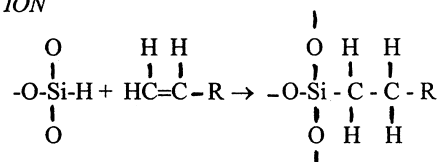
stationary phase is explored. The reaction sequence for attachment of an olefin is as follows:

SILANIZATION



$n = 1-3$ depending on extent of cross-linking

HYDROSILATION*

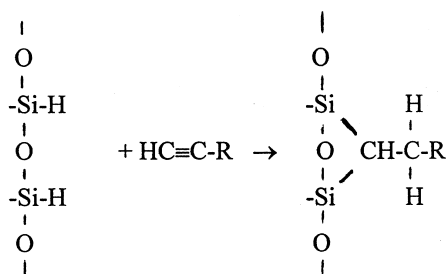


*Carried out in the presence of a catalyst such as hexachloroplatinic acid.

Another interesting possibility for the hydrosilation of acetylene compounds is the formation of a

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double Si–C linkage between the surface and the bonded organic moiety. One such bonded material which might result in a high degree of stability, but not the only product possible, is shown below.



Structure I

The objectives of this study are as follows:

(1) To determine the viability of bonding alkyne compounds to silica hydride surfaces through hydrosilation.

(2) To assess the presence, if any, of the double silicon–carbon linkage between the organic moiety and the surface.

(3) To test the hydrolytic stability of some materials under static conditions in acidic and/or basic media.

(4) To make some preliminary chromatographic evaluation of two of the new materials.

2. Experimental

2.1. Materials

Phenylacetylene, 1-phenyl-2-propyn-1-ol, propiolic acid, and 3,3-dimethyl-1-butyne were purchased from Farchan Laboratories (Gainesville, FL, USA) while 1-octyne was purchased from Aldrich (Milwaukee, WI, USA). All were used as received. A 5 mM solution of hexachloroplatinic acid (Strem Chemicals, Newburyport MA, USA) in 2-propanol was used as the catalyst for the hydrosilation reactions. For free radical addition, 2,2-azobisisobutyronitrile (AIBN, Aldrich) was used as the initiator. Triethoxysilane (Fluka, Milwaukee, WI, USA) was used for the synthesis of the silica hydride. The silicas used were Vydac TP 106 (The Separations Group, Hesperia, CA, USA) with a particle diameter of 6.5 μm , a pore diameter of 380

\AA and a surface area of 106.5 m^2/g , and Kromasil (Eka, Bohus, Sweden) with a particle diameter of 6.2 μm , a pore size of 100 \AA and a surface area of 349 m^2/g . Solvents for the syntheses were obtained in reagent grade, the organic mobile phase components utilized HPLC grade and the solutes for stationary phase characterization were obtained in the highest purity available. SRM 869 was obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). When water was required, it was purified by a Milli-Q apparatus (Millipore, Bedford, MA, USA).

2.2. Synthetic procedure

The silica hydride was prepared via silanization according to a previously described procedure [4]. For hydrosilation, typically 2.3 g of silica hydride was dried under vacuum at 110°C for 12 h. Glassware was dried before use at 110°C overnight. At the start, the following materials were placed in a three-neck 250 ml round-bottomed flask and mixed for 1 h at 60–70°C: 161 ml of toluene, 23 ml of the alkyne compound and 2.3 ml of the 5 mM hexachloroplatinic acid solution. Attached to the round-bottomed flask which was sitting on a heating mantle and magnetic stirrer were a drying tube and a condenser tube. The silica hydride was slowly added by funnel through the open neck of the flask which was then fitted with a glass stopper. This mixture was heated to 100°C and the reaction was allowed to proceed for 96 h. After the reaction period, the solution was centrifuged at 1500 rpm ($\approx 1000 g$) for 10 min and the solid was collected. It was washed successively with 15–20 ml portions (3 times each) of toluene, methylene chloride and diethyl ether. The product was then allowed to dry overnight in a hood at room temperature and then further dried at 110°C under vacuum for an additional 24 h.

In the free radical procedure [7] 1.25 ml of propiolic acid, 10.6 ml of toluene and 0.0537 g of AIBN were added to the three-neck round-bottomed flask. The mixture was stirred at 60–70°C for 1 h. Then 0.5 g of silica hydride was added, the temperature was raised to 100°C and the reaction was allowed to proceed for 100 h. The same washing and drying procedure described above was used on the product from this procedure.

2.3. Hydrolytic stability tests

For acid hydrolysis, a 100-mg of sample was placed in 3 ml of a pH 2 (HCl) solution containing 10% methanol and stirred for 24 h. The material was centrifuged, the solid was washed with three 5-ml portions of diethyl ether and dried in a vacuum over at 100°C overnight. This process was repeated twice more. For base hydrolysis, the process outlined above was used with a pH 9 (NaOH) solution.

2.4. Instrumentation

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained using a Perkin-Elmer (Norwalk, CT, USA) Model 1800 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The sample consisted of a 50:50 mixture of the silica material and spectral grade KBr which was placed in a 2-mm diameter cup. Spectra consisting of 200 scans referenced against pure KBr over the range 4000–450 cm^{-1} were obtained at a resolution of 2 cm^{-1} . Spectra were then normalized to 100% transmittance.

Solid state NMR spectra by cross-polarization (CP) and magic-angle spinning (MAS) were obtained on a Bruker (Billerica, MA, USA) MSL 300 spectrometer. The silica sample (200–300 mg) was spun at 5 kHz in a double bearing ZrO_2 rotor. The ^{13}C and ^{29}Si CP-MAS spectra were acquired with a 3-ms contact time and a 5-ms contact time, respectively. The repetition rate was 5 s for both nuclei. ^{13}C spectra were referenced to external glycine and ^{29}Si spectra were referenced to external poly(hydridosiloxane).

Carbon analysis of the bonded materials was

obtained using the conventional combustion method (Desert Analytics, Phoenix, AZ, USA). Columns were packed using a slurry of the bonded silica in CCl_4 –methanol (9:1, v/v). The slurry was packed into a 15 cm \times 0.46 cm I.D. stainless steel tube with a Haskel (Burbank, CA, USA) pneumatic pump operating at 40 mP using methanol as the driving solvent. HPLC data was obtained on a Perkin-Elmer Model 200 liquid chromatographic system.

3. Results and discussion

Success of the bonding process is monitored by three types of information: elemental analysis, DRIFT spectra and CP-MAS NMR spectra. From the elemental analysis it appears that each of the five alkyne compounds which were tested in this study were successfully attached to the silica hydride surface. The results of the carbon analysis as well as calculation of the surface coverage [4,8] are shown in Table 1. The first four compounds in the table were bonded to Vydac silica while the last alkyne species was attached to Kromasil. The surface coverage for the first four compounds is quite high and corresponds to the best values which are usually obtained for monomeric phases [1]. Of these four alkynes, propiolic acid required the use of free radical initiation for the hydrosilation reaction in order to obtain high surface coverage. The last compound was prepared on Kromasil for better NMR spectral analysis (see discussion in Section 3.2). However, the low surface coverage is most likely due to the steric effects of the *tert.*-butyl groups at the end of the short alkyl chain.

Table 1
Percentage carbon and surface coverage for the various alkynes bonded to silica hydride

| Compound | Carbon (%) | Surface coverage (α) ($\mu\text{mol}/\text{m}^2$) | |
|------------------------|------------|--------------------------------------------------------------|-----------------------|
| | | After acid hydrolysis | After base hydrolysis |
| 1-Octyne | 4.93 | 3.80 | |
| Propiolic acid | 1.71 | 4.61 | |
| 1-Phenyl-2-propyn-1-ol | 5.85 | 5.47 | 4.55 |
| Phenylacetylene | 4.14 | 4.23 | 4.02 |
| 3,3-Dimethyl-1-butyne | 2.00 | 0.81 | 4.11 |

3.1. Diffuse reflectance infrared Fourier transform

DRIFT spectra provide a spectroscopic confirmation of the bonding process as well as molecular information about the organic moiety attached to the surface [9]. The DRIFT spectrum of silica hydride has been reported previously [4] and its main feature is the Si–H stretching band near 2250 cm^{-1} . Fig. 1A shows the DRIFT spectrum of one of the alkynes, 1-phenyl-2-propyne-1-ol, bonded to Vydac hydride. In comparison to the spectrum of the hydride before the reaction, the Si–H stretching band at 2250 cm^{-1} has decreased in intensity. This result is a good indication that the bonding reaction is successful [2]. The other features observed in Fig. 1A which correspond to vibrational bands of the bonded organic moiety include aliphatic carbon–hydrogen

stretching between 3000 and 2750 cm^{-1} , aromatic carbon–hydrogen stretching from 3000 to 3200 cm^{-1} , and two aromatic bending bands just below 1500 cm^{-1} . Because of the aromatic component of the bonded moiety, it is not possible to determine from the DRIFT spectrum if the attachment to the surface is similar to structure I or if an olefin results from the hydrosilation reaction which would indicate a different mode of attachment (see discussion below). Fig. 1B is the DRIFT spectrum of 3,3-dimethyl-1-butyne bonded to Kromasil hydride. Because of the greater surface area of this material, the bands which result from the silanization and hydrosilation reactions are much stronger in intensity. However, similar to that observed in Fig. 1A, the intensity of the Si–H band has decreased in Fig. 1B in comparison to the spectrum for Kromasil hydride. The other intense feature associated with the bonded organic moiety is the aliphatic C–H stretching just below 3000 cm^{-1} . A weak band is also seen above 3000 cm^{-1} . Since there is no aromatic component in the molecule, this band is most likely the result of olefinic carbon–hydrogen stretching indicating at least some of the bonded moiety exists in a form different to structure I shown above. Similar weak olefinic bands are seen in the DRIFT spectra for 1-octyne and propiolic acid. The structures of three possible bonded species containing an olefinic group are as follows:

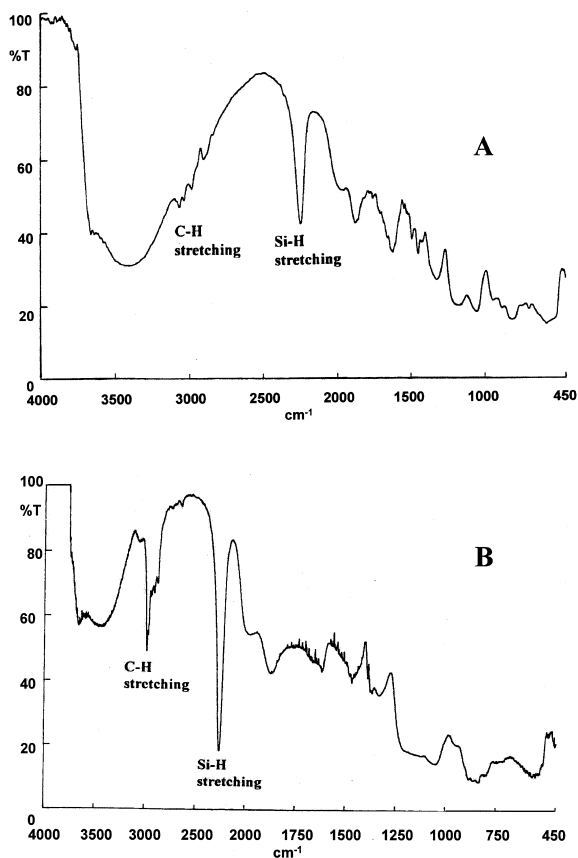
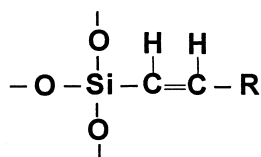
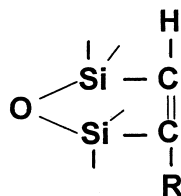


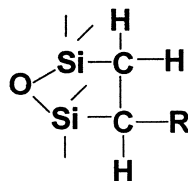
Fig. 1. DRIFT spectra of alkynes bonded to a silica hydride surface; (A) 1-phenyl-2-propyn-1-ol and (B) 3,3-dimethyl-1-butyne.



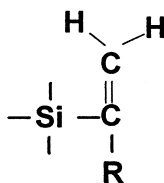
Structure II



Structure III



Structure IV



Structure V

3.2. CP-MAS NMR

In order to determine which of I–V are viable alternatives for the bonded phase, further spectroscopic evidence is necessary. Both ^{13}C and ^{29}Si CP-MAS NMR are often used to further elucidate the exact nature of a particular bonded moiety [9]. Fig. 2A shows the ^{13}C CP-MAS spectrum for 1-octyne bonded to a silica hydride surface. It is clear from the peaks at 120, 126, 144 and 152 ppm that some of the bonded organic moieties contain an olefin group. This observation confirms the result obtained above from the DRIFT spectrum. While it is not possible to absolutely rule out any of the olefin structures shown above, it is unlikely that V is a

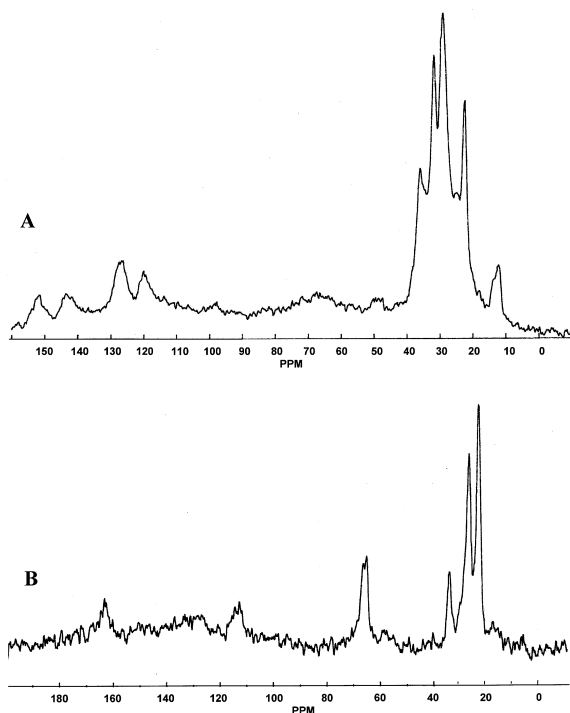


Fig. 2. ^{13}C CP-MAS spectra of alkynes bonded to a silica hydride surface; (A) 1-octyne and (B) 3,3-dimethyl-1-butyne.

reasonable choice because it would require bonding at the second carbon of the chain when it has already been shown for olefin hydrosilation that the reaction takes place almost exclusively at the terminal carbon in heterogeneous phase systems [2]. The four peaks could then be accounted for in one of two ways. Either the bonded material having an olefin component is a mixture of II and III, or most of the bonded phase could be II with the presence of four peaks accounted for by *cis* and *trans* isomers at the double bond. Another interesting feature of the spectrum is the peak at 12 ppm. Its low intensity and somewhat broad nature does not seem to indicate that it would be due to a methyl group. While structures I and IV might appear to be sterically unfavorable, they could account for a peak near 12 ppm. Because II, III and V all have olefin carbons which are bonded to silicon atoms at the surface and the nearest methylene groups to the surface would be near those olefin carbons so that a shift to lower field is more likely than the high field one observed for this peak. Another example of bonding of an alkyne is the ^{13}C CP-MAS NMR spectrum of 3,3-dimethyl-1-butyne shown in Fig. 2B. This spectrum displays only two peaks of low intensity in the aromatic region. Therefore, some of the organic moiety is bonded with an olefin structure but only one possible form exists because of the presence of only two peaks. Considering the position of the peaks at 113 and 163 ppm, structure II seems the most likely. However, the presence of two methyl peaks at 23 and 26 ppm and a methylene peak at 34 ppm indicate that a second form exists on the surface. The only structures which account for a methylene group in the bonded moiety are I and IV. The peak at 64 ppm which represents the quaternary carbon also appears to be split which would account for two different bonded structures on the surface. The only missing carbon in the spectrum would be the one which is attached to the surface in I. Because of the restricted motion expected from the carbon in this structure, the peak intensity would be expected to be low and the width broad. Therefore, it might be difficult to detect this peak in the spectrum although such a peak might be present between 10 and 20 ppm. The ^{13}C CP-MAS spectrum of phenylacetylene bonded to silica hydride contains a very large peak at 128 ppm which represents all of the protonated aromatic

carbons. Several smaller peaks are found at 148, 141, 137 and 128 ppm. One of these peaks (probably the one at 141 ppm) is assigned to the unprotonated aromatic carbon and the rest are olefinic peaks similar to those discussed for the bonding of 1-octyne. It is quite likely that an additional olefinic peak is under the large aromatic resonance at 128 ppm. There is no readily identifiable methylene peak in the spectrum indicating the presence of **I** and **IV** are unlikely. Therefore, it would appear that the surface morphology is either a combination of two olefin structures or a single olefin with *cis* and *trans* isomers. The spectrum of 1-phenyl-2-propyne-1-ol has only two peaks in the low field region which are both characteristic of aromatic carbons: a large peak at 127 ppm for the protonated aromatic species and a small peak at 142 ppm for the one unprotonated carbon. More significant is the presence of a methylene peak at 30 ppm which can only occur if either **I** and/or **IV** are present. The methine carbon with the attached hydroxyl group appears at 75 ppm. The spectrum of the product from bonding of propiolic acid to silica hydride has only a broad peak centered at 127 ppm. This reaction was only successful via free radical addition. Therefore, one likely possibility is a polymerized bonded material which would lead to broad peaks in the spectrum.

Further characterization of these materials was done by ^{29}Si CP-MAS NMR. Fig. 3 is the spectrum for 3,3-dimethyl-1-butyne bonded to Kromasil silica hydride. It is characteristic of all the ^{29}Si NMR spectra except for propiolic acid bonded by AIBN. In comparison to the starting hydride, the peak at -85 ppm has diminished in intensity. In addition, there is

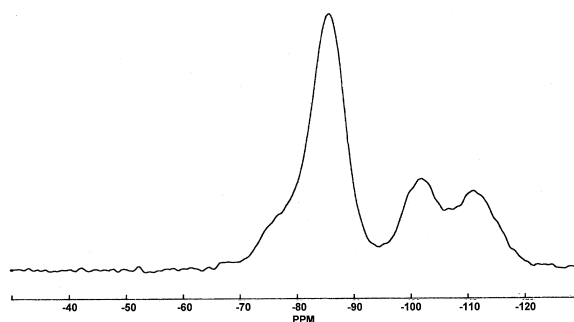


Fig. 3. ^{29}Si CP-MAS spectrum of 3,3-dimethyl-1-butyne bonded to a silica hydride surface.

a shoulder on the hydride peak with a maximum in the range of -75 to -80 ppm which is broader than the peak in the original spectrum at -75 ppm due to the surface moiety $(-\text{O})_2\text{Si}(\text{OH})\text{H}$. When an alkene is bonded to the surface creating a single Si–C linkage, a peak is seen near -65 ppm [2,9]. The differences observed in the ^{29}Si NMR spectrum for the bonding of an alkyne in comparison to an alkene might be explained by the different linkages shown in **I–V**. Either the double Si–C bond in **I** and **IV** or the various Si-olefin species in **II**, **III** and **V** are likely to lead to a 10–15 ppm shift upfield from the -65 ppm observed for the single Si–C species [10]. Therefore, the broad shoulder in the -75 to -85 ppm range observed in the spectrum could be the result of any one or a combination of **I–V**. For propiolic acid, only a slight decrease in the intensity of the Si–H peak at -85 ppm is observed.

3.3. Hydrolytic stability tests

In order to estimate the hydrolytic stability of these new bonded materials, one product, 1-phenyl-2-propyn-1-ol, was subjected to static testing in acid and base while another product, phenylacetylene, was subjected to base testing only. The results for these tests are also shown in Table 1. Some decrease in coverage is seen for 1-phenyl-2-propyn-1-ol under both acidic and basic conditions. The DRIFT spectra of this phase after both acid and base exposure show no appreciable change from the original spectrum including the intensity of the Si–H peak at 2250 cm^{-1} . For phenylacetylene there is a negligible decrease in α on exposure to base. Similar tests run on monomeric alkyl phases bonded by organosilanization generally result in a loss of 80–90% of the organic moiety on the surface [4]. While somewhat mixed, these results suggest that good hydrolytic stability may be present for at least some phases bonded by this method. In a recent study [11] on porous silicon wafers which were first modified to contain surface hydrogen groups (hydrides) and then subsequently reacted by hydrosilation with an alkyne, it was reported that these materials were stable in boiling aqueous KOH (pH 10). Extensive chromatographic testing is currently in progress to determine the relative stability of these bonded phases under more realistic operating conditions.

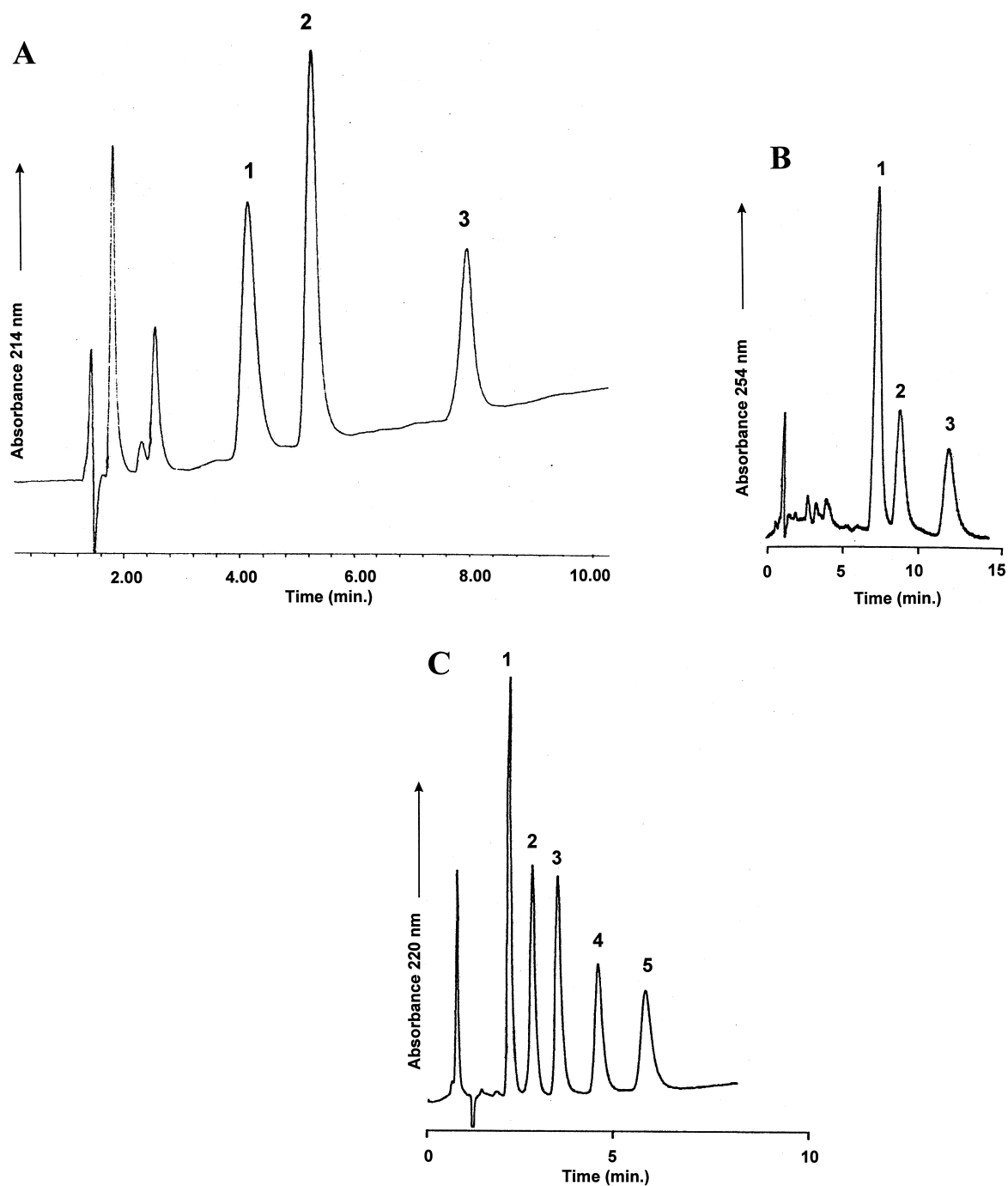


Fig. 4. Reversed-phase separations on C₈ column made from 1-octyne; (A) polypeptides; mobile phase: solvent A; 0.05% TFA in acetonitrile and solvent B; 0.05% TFA in water. Gradient: 20–35% A in 15 min. Flow-rate=1.3 ml/min. Detection at 214 nm. Solutes: 1=angiotensin III, 2=bradykinin, 3=angiotensin I. (B) Tricyclic antidepressants. Mobile phase: acetonitrile–methanol–10 mM phosphate buffer (35:25:40, v/v/v). Flow-rate 1.0 ml/min. Detection at 254 nm. Solutes: 1=desipramine, 2=imipramine, 3=clomipramine. (C) Barbituates. Mobile phase: methanol–water (37:63, v/v). Flow-rate 1.5 ml/min. Detection at 220 nm. Solutes: 1=butobarbital, 2=amobarbital, 3=secobarbital, 4=phenobarbital, 5=hexobarbital.

3.4. Chromatographic evaluation

Some preliminary chromatographic experiments on two of the bonded materials were also performed in order to further characterize them. For reversed-phase behavior, the C_8 material from 1-octyne was selected for evaluation. Elution of SRM 869 resulted in a chromatogram that is characteristic of highly loaded monomeric phases and the separation factor for two of the components in the mixture $\alpha_{\text{TBN/BaP}} = 1.35$ (TBN=1,2:3,4:5,6:7,8-tetrabenzonaphthalene and BaP=benzo[*a*]pyrene) is consistent with this conclusion [12,13]. The surface coverage ($3.8 \mu\text{mol}/\text{m}^2$) from elemental analysis is also in agreement with the chromatographic observations. A standard mixture of aromatic hydrocarbons (benzene, toluene, ethylbenzene, isopropylbenzene, *tert.*-butylbenzene and anthracene) is separated (baseline or better) in about 7 min with a methanol–water (57:43, v/v) mobile phase having an efficiency of $>28\,000$ plates/m for the last eluting component. This result is consistent with reasonable reversed-phase properties [14]. Some examples of reversed-phase separations are shown in Fig. 4. The first separation (Fig. 4A) is a mixture of three polypeptides each containing one or more basic amino acids. The peak shape is good ($A_s \cong 1.2$ and $N \cong 38\,000$ plates/m for peak 3) indicating little or no interaction with the surface under these conditions. The separation in Fig. 4B is an even more demanding test for surface silanols. The mixture contains three tricyclic antidepressants run at neutral pH. Again good peak shape ($A_s \cong 1.5$ and $N \cong 15\,000$ plates/m for peak 3) is obtained for all three components. Finally, the separation of a five-component barbiturate mixture is shown in Fig. 4C. Baseline or better separation is achieved for all the compounds in less than 7 min with very good peak shape ($A_s \cong 1.3$ and $N \cong 30\,000$ plates/m for peak 3). These examples show that the C_8 phase made by hydrosilation of 1-octyne on a hydride silica surface produces an excellent reversed-phase material.

For testing in normal-phase operation, the bonded material made by the hydrosilation of 1-phenyl-2-propyne-1-ol on silica hydride was chosen. It has already been demonstrated that a mono-ol bonded phase is appropriate for use in the normal-phase mode [15,16]. The retention of some polycyclic

aromatic hydrocarbons (PAHs) using isooctane as the mobile phase is shown in Table 2. The retention on this mono-ol column is compared to the retention on another mon-ol column [16] and on two diol columns [17]. The capacity factors for the two mono-ol columns are quite similar but less than the values obtained on the diol columns. Such a result is consistent with the fact that the mono-ol is less polar than the diol and that the underlying surface on the two mono-ol columns is composed of hydrides while that of the diol columns has some remaining silanols. The effect of the unreacted surface hydrides on chromatographic properties of these and other materials is currently being investigated. As a further evaluation of the normal-phase capabilities of the mono-ol column prepared in this study, benzodiazepines were chosen as the test solutes. This group of drugs commonly used as sedatives is usually analyzed by reversed-phase HPLC [18–21] but the presence of at least one polar functional group (amine, carbonyl and/or aromatic nitrogen) in their structures indicates that they might be amenable to normal-phase analysis. In particular, the mono-ol column which possesses a low degree of polarity as shown above might be a suitable bonded material for the normal-phase separation of the benzodiazepines which also have moderate hydrophilicity. Fig. 5A shows the separation of a three-component mixture containing the compound diazepam, its decomposition product, oxazepam, and a metabolite, 2-amino-5-chloro-benzophenone. Good separation of this mixture is obtained and, as expected, the elution order is the opposite of that obtained in the reversed-phase analysis [19]. Fig. 5B shows another three-

Table 2
Retention of polycyclic aromatic hydrocarbons (PAHs) on mono-ol and diol columns with isooctane as the mobile phase

| Compound | k' (1) | k' (2) | k' (3) | k' (4) |
|--------------|----------|----------|----------|----------|
| Fluorene | 0.21 | 0.14 | 0.49 | 0.68 |
| Phenanthrene | 0.27 | 0.24 | 0.67 | 1.00 |
| Pyrene | 0.33 | 0.29 | 0.91 | 1.44 |
| Chrysene | 0.44 | 0.33 | 1.24 | 2.20 |
| Perylene | 0.61 | 0.57 | 1.56 | 2.81 |

(1) Mono-ol from 1-phenyl-2-propyn-1-ol.

(2) Mono-ol from [16].

(3) Diol LiChrosorb from [17].

(4) Diol LiChrosphere from [17].

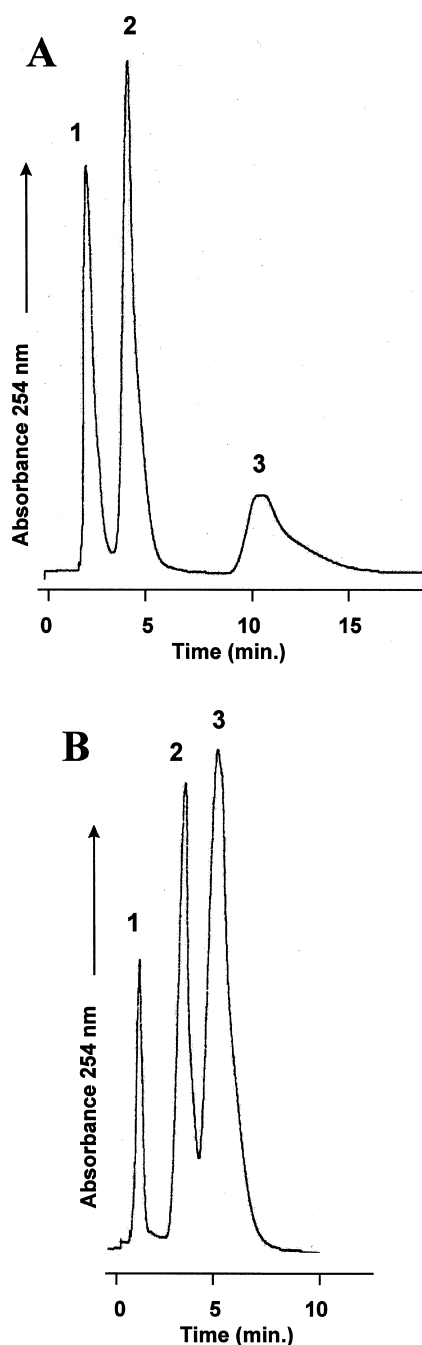


Fig. 5. Normal-phase separations of benzodiazepine mixtures on mono-ol column made from 1-phenyl-2-propyn-1-ol. Flow-rate, 1 ml/min. Detection at 254 nm. Mobile phase diethyl ether–heptane (25:75, v/v). (A) Solutes: 1=2-amino-5-chlorobenzophenone, 2=diazepam, 3=oxazepam. (B) Solutes: 1=2-methylamino-5-chlorobenzophenone, 2=diazepam, 3=temazepam.

component mixture with diazepam and a different decomposition product, temazepam, and its metabolite 2-methylamino-5-chlorobenzophenone. Again the elution order is opposite to that obtained in the reversed-phase mode [19]. In both of the separations in Fig. 5 the efficiency is lower ($N \cong 6000$ plates/m for peak 2 in A and $\cong 2000$ plates/m for peak 3 in B) and peak symmetry poorer ($A_s \cong 1.6$ and 1.5 for the peaks cited above) than for the reversed-phase separations described previously.

4. Conclusions

It appears that hydrosilation of alkynes on a silica hydride surface offers a new approach to bonding of organic moieties for chromatographic stationary phases. Preliminary stability testing indicates that resistance to hydrolytic degradation may be one of the advantages of these new materials. Chromatographic evaluation of materials made by this bonding method demonstrates that stationary phases suitable for both reversed-phase and normal-phase operation can be synthesized. Further studies to determine the exact structure of the bonded material made from alkynes and more rigorous chromatographic evaluation of hydrolytic stability of these phases are currently underway.

Acknowledgements

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