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INFLUENCE OF BONDING CHEMISTRY ON THE REORDERING/RESOLVATION OF SILICA IMMOBILIZED ALKYL CHAINS

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SUMMARY

The reordering/resolvation of silica modified with mono-, di-, and trireactive alkylsilanes has been studied. Under totally aqueous conditions, the onset for reordering has been found to begin at approximately the same temperature irrespective of the attachment chemistry. These results support the idea that bonding occurs heterogeneously in patches and that within a patch spacing is controlled by silanol concentration.

INTRODUCTION

The most popular means of preparing liquid chromatographic phases is by covalently binding organosilanes to porous silica. Chloro and alkoxy reagents are used most often. The bonding chemistry and resulting surface can be classified by the number of reactive groups in the silylating reagent.

Monoreactive silanes such as octyldimethylchlorosilane generate singularly attached structures. The degree and homogeneity of coverage are dependent on various parameters including surface silanol concentration, pore size and geometry, ligand size, shape and polarity, etc.

Surfaces prepared from polyreactive silanes such as octylmethyldichlorosilane and octyltrichlorosilane are even more complicated and less easily defined. Generally only one group in a polyreactive silane monomer will react with the surface. Depending on the existence of moisture, the remaining reactive groups can either cross-link or can be hydrolyzed and undergo further reactions with excess reagent. In the latter case, polymers are formed which are only loosely attached to the surface. Although polymeric bonded phases have greater hydrolytic stability than equivalent monomeric phases, they are more difficult to control and are less reproducible. If the surface silanization is performed under anhydrous conditions, the reactions are limited to the surface[1–4].

On a molecular level basis, the conformation and motional dynamics of bonded phases are dependent on chain length[5,6], solvent composition and polarity[7], temperature[5], etc. Under totally aqueous conditions, the immobilized chains undergo thermally induced reordering/resolvation. This process has been studied for both

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non-polar[8] and polar[9] phases. In the former case, reordering/resolvation has been explained in terms of chain–chain (cohesive), chain–solvent (hydrophobic), and solvent–surface (specific) interactions. However, in the latter case additional specific interactions arising from the functional group also must be considered[9]. The onset temperature (T_0) for reordering can be obtained from nonlinearity in a plot of ln k' *vs.* $1/T$. The experimental details have been discussed[5,8,9]. T_0 has been determined for a number of polar and nonpolar phases. For a particular homologous series of anchored groups, a linear correlation exists between the reordering/resolvation temperature and the boiling point of the corresponding nonimmobilized compunds[8].

Although the effect of chain length, surface coverage, and functionality on surface reorientation has been studied[5,8,9], the role of bonding chemistry (*e.g.*, the type of attachment between stationary phase and silica surface) has not been examined. In the current work, the reordering/resolvation of silica modified with mono-, di-, and trireactive alkylsilanes has been investigated. For comparative purpose, all silanization reactions were carried out under anhydrous conditions.

EXPERIMENTAL

Chemicals

n-Octyldimethylchlorosilane, *n*-decyldimethylchlorosilane, *n*-octyl-methyldichlorosilane, and *n*-decylmethyldichlorosilane were obtained from Petrarch (Levittown, PA, U.S.A.) and were used as received. LiChrosorb Si 60 ($d_p \approx 10$ μm and surface area 550 m^2/g) was purchased from Merck (Darmstadt, F.R.G.). Mobile phases were prepared (v/v basis) from HPLC-grade acetonitrile (Aldrich; Milwaukee, WI, U.S.A.) and deionized water which was purified using a Milli-Q reagent water system (Millipore; El Paso, TX, U.S.A.).

Preparation of bonded phases and columns

Each of the above organosilanes was used to chemically modify LiChrosorb Si 60 as previously described[5]. Toluene was used as the refluxing solvent. All reactions were carried out under dry nitrogen. The modified materials were thoroughly rinsed and then packed into 250 mm × 2.3 mm I.D. stainless-steel columns using a dynamic procedure[10]. A sample was removed from each reaction bath, dried and analyzed by combustion. The data obtained are summarized in Table I.

Chromatographic studies

All chromatographic studies were performed using a Laboratory Data Control (Riviera Beach, FL, U.S.A.) Model Constametric IIG liquid chromatographic pump with a UV detector. Column temperature was controlled in a water bath with a Tempunit (Techne; Princeton, NJ, U.S.A.) model TU-14 zero cross-over proportional controller and a Neslab (Neslab instruments; Portsmouth, NH, U.S.A.) Model EN-350 flowthrough liquid cooler. The flow-rate was monitored with a liquid flow meter (Model F1080A, Phase Separations; Queensferry, U.K.). A more detailed description of the hardware has been described elsewhere[5].

The temperature studies were carried out as described previously using phenol and resorcinol as test solutes[8]. Prior to data collection, each column was conditioned with 100 ml of acetonitrile followed by 100 ml of the mobile phase, water. Acetonitrile was chosen as the organic conditioning solvent to minimize entrapment problems[11].

A complete evaluation consisted of three sequential steps: (i) initially, solute retention was measured every 5°C from 10°C to 80°C, (ii) the column was then cooled to the starting temperature and step i repeated, and (iii) the column cooled to the initial temperature and step i repeated a third time but retention measurements were made at 10°C increments. In all cases, the complete evaluation cycle was carried out twice for each column. Column void volume was measured with ^2H_2O.

RESULTS AND DISCUSSION

Summarized in Table I are the experimentally determined reordering/resolvation temperatures for equivalent bonded phases prepared using mono-, di- and trireactive reagents. T_0 was respectively 40.6°C, 41.6°C, and 40.7°C for the C_8 phases and 60.9°C, 61.5°C, and 60.1°C for the C_{10} phases. Also included in Table I are the standard deviations in the data. These values are based on multiple column preparations and at least four replicate measurements made on each batch. The data for trichlorosilane surfaces are from previously published work[5].

TABLE I

ONSET TEMPERATURE FOR SURFACE REORDERING/RESOLVATION

Silylating agents	*Reactive* groups*	*%Carbon***	*Temperature (°C)*
n-Octyldimethylchlorosilane	1	10.6	40.6 ± 0.49
n-Octylmethyldichlorosilane	2	10.5	41.6 ± 1.02
n-Octyltrichlorosilane	3	9.5	40.7 ± 0.71
n-Nonyltrichlorosilane	3	9.7	51.8 ± 2.10
n-Decyldimethylchlorosilane	1	12.0	60.9 ± 0.35
n-Decylmethyldichlorosilane	2	12.4	61.5 ± 0.48
n-Decyltrichlorosilane	3	12.3	60.1 ± 1.00

* Number of reactive chlorines in the silylating agent.

** Average values for preparations. All normalized carbon was within a range where T_0 has found not to vary with coverage (ref. 5).

The reordering began at approximately the same temperature for a given chain length (*i.e.*, within the experimental standard deviation of the current measurements) and a similar incremental change in T_0 was noted for each additional methylene group in the chain irrespective of the attachment chemistry.

The data in Table I suggest that within the range of coverages studied the controlling factor for group spacing is the silanol distribution not the bonding chemistry. This idea is consistent with previous studies[2] where the maximum surface concentrations of three silylating agents, octyltrichlorosilane, octylmethyldichlorosilane and octyldimethylchlorosilane, were identical within experimental error (2.35, 2.40, 2.35 μmol/m^2 respectively). The results from this latter investigation were explained on the basis of similarity in cross-sectional area of the silylating molecules irrespective of the number of reactive groups.

The current data along with data obtained in related studies, where T_0 also has been found to be independent of coverage once a certain minimum level is reached[5], are consistent with the idea that bonding occurs heterogeneously in patches or clusters of chains. Although surface coverage is dependent upon the number or size of patches, within a patch the closest spacing is controlled by silanol concentration. Likewise, the spacing of adjacent chains is similar from patch to patch. Therefore, for bonded phases with the same chain length, a similar degree of overlap is obtained regardless of differences in bonding chemistry. This thus gives rise to the same onset temperature.

A patch model for bonded groups immobilized on silica is also supported by various spectrometric measurements. For example, luminescence[12] and infrared[13] methods have been used to examine nonuniformity of bonding and spacing for [3-(3-pyrenyl)propyl]dimethylchlorosilane and cyanoalkyl groups respectively. In both cases, the bonded groups were found to be heterogeneously distributed in organically rich patches. Similar results were observed chromatographically[6] where longer bonded alkyl chains were found to form aggregates which exhibited liquid-like behavior.

The above results imply that the bonding chemistry has little if any effect on the onset temperature for reordering/resolvation at least when bonding is carried out under reaction conditions which limit attachment to the surface. For this condition to hold there must be a similar degree of chain–chain interaction irrespective of attachment chemistry. Thus the extent of overlap between two immobilized groups is determined by the distance between their points of attachment not the number of reactive groups in the silylating agent.

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