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SYNTHESIS OF BONDED LAYERS FROM CYCLIC ORGANOSILICONS IN THE GAS PHASE

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SUMMARY

As a sequel to an earlier study of modifying silica gel 62 by reacting it with cyclic organosiloxanes or silazanes in a liquid-phase reaction, a similar formation of bonded layers has been attempted under a wide variety of conditions in a gas-phase type reaction. This attempt was successful and the resulting products were in many aspects similar. They often matched (however, they never surpassed) the earlier materials in gas chromatographic performance.

INTRODUCTION

Some time ago, our group described the syntheses of bonded phases from organosiloxane and organosilazane rings on typical silicic supports, and the performance of these materials in packed-column gas (GC) and liquid chromatography (LC)¹. The bonding process used a non-polar, inert, high-boiling solvent under reflux, similar to a technique developed earlier for bonding polyether layers².

In either case it seemed likely that the conditions characteristic of this type of synthesis had favored a sterically defined approach of the monomer/polymer onto the solid surface. In particular, the monomer/polymer was only sparingly soluble in the high-boiling alkane and, of course, there existed a large difference in polarity between the silanol-covered support and the hydrocarbon solvent. Furthermore, the high temperature promoted both chemical reactions and optimal chain orientation on the surface.

Thus it appeared that the condition of a solid-liquid interface may have exerted a decisive influence on the outcome of the synthesis. The question therefore arose whether a solid-gas interface would have resulted in a significantly different product. Could efficient chromatographic phases be obtained when the monomer/oligomer approached the solid support from the gas phase? Could the easier variation of temperature in a gas-phase reaction (as opposed to a liquid-phase reaction where the choice of solvent is limited to high-boiling alkanes and the temperature thus

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determined by their boiling points) bring significant benefits? Is there a fundamental difference between the two approaches?

This study was designed to answer precisely these questions, as well as to represent a direct sequel to the earlier report involving cyclic siloxanes and silazanes at the solid-liquid interface. Before describing the experiments, however, we should take note of the vast literature that, in one form or another, impinges on the question.

Silicic surfaces and organosilicon compounds—as well as the interactions between the two—have been extensively investigated (see, for instance, refs. 3–5); they serve a wide variety of purposes and are found in a wide variety of products. Even in the much more narrow chromatographic context, individual studies of silica and silicones are far too numerous to cite. Such studies cover primarily the deactivation of active surfaces and the formation of bonded layers. Similarly, the use of high temperatures—whether in column conditioning, deactivation of the inside of quartz capillaries, crosslinking of thicker films, or simply in day-to-day GC analysis—is commonplace.

The deliberate use of gaseous reagents, however, is far less common. GC columns can be brought back to life that way, and one could also argue that bleed from GC phases interacts with nearby surfaces. Deactivation and hydrophobization have been occasionally attempted with vapors of such compounds as dimethyldichlorosilane or hexamethyldisilazane. Nigh exclusively, though, conventional synthesis of bonded layers, whether destined for LC or for GC, is based on solution chemistry, *i.e.* on the solid-liquid interface.

In our own group, we have had some experience in using the gas phase for cleaning surfaces⁶, for coating materials with inorganic layers⁷, for transporting reagent to a polymerizing silicone⁸, or for collecting bleed constituents⁹. We have also had some experience with cyclic organosilicon compounds¹, which are rarely if ever used for conventional phase synthesis. (They figure prominently, however, as products of GC liquid-phase degradation. Furthermore, there are some reports in the non-chromatographic literature on their use as silica modifiers applied via the gas phase, *e.g.* ref. 10.)

Hence, despite the odds against producing a new, high-efficiency phase, we considered it worthwhile to use the cyclics for a synthetic comparison of solid-liquid *vs.* solid-gas interfacial systems. That the two could be very different appears obvious in light of their very different sorption and mass transfer characteristics, as well as their possible differences in the establishment of equilibria, the disposal of side-products, and the chances for reagent transmutation.

Of the various possibilities for bringing a support in contact with monomer vapor, we choose one of the simplest to control: we would expose loose support particles to diluted monomer vapor at different temperatures. The resulting materials would then be exhaustively extracted and characterized by carbon content and chromatographic behavior. Wide pore silica gel (neutral or acidified) would be used as the only support, and chromatographic tests restricted to gas chromatography. Besides the variation of temperature, inert gas (diluent) flow could provide different reagent concentrations/contact times and also allow the fluidization of the silica particles. A series of commercially available cyclic siloxanes, and one cyclic silazane, were to serve as silanizing reagents.

EXPERIMENTAL

Materials

Hexamethylcyclotrisiloxane, hexaethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, octaphenylcyclotetrasiloxane, and octamethylcyclotetrasilazane were purchased from Petrarch Systems and used without further purification. Davison silica gel grade 62 was obtained from Grace Chemical and sieved to retrieve the 60–80 mesh fraction. This fraction was then extracted with azeotropic hydrochloric acid for four days in a Soxhlet, rinsed with distilled water to constant pH, and dried at 130°C and water-aspirator vacuum overnight (“neutral silica”). Some of the material was re-immersed in concentrated hydrochloric acid for 2 h and similarly dried (“acidic silica”).

Layer synthesis

Various models of simple reaction flasks were constructed from glass. The principal *modus operandi* remained the same, but the flasks differed in size and whether or not they allowed preheating of reagent vapors and collection of non-reacted cyclics to take place. Fig. 1 shows the latest and most “complex” of these flasks (and,

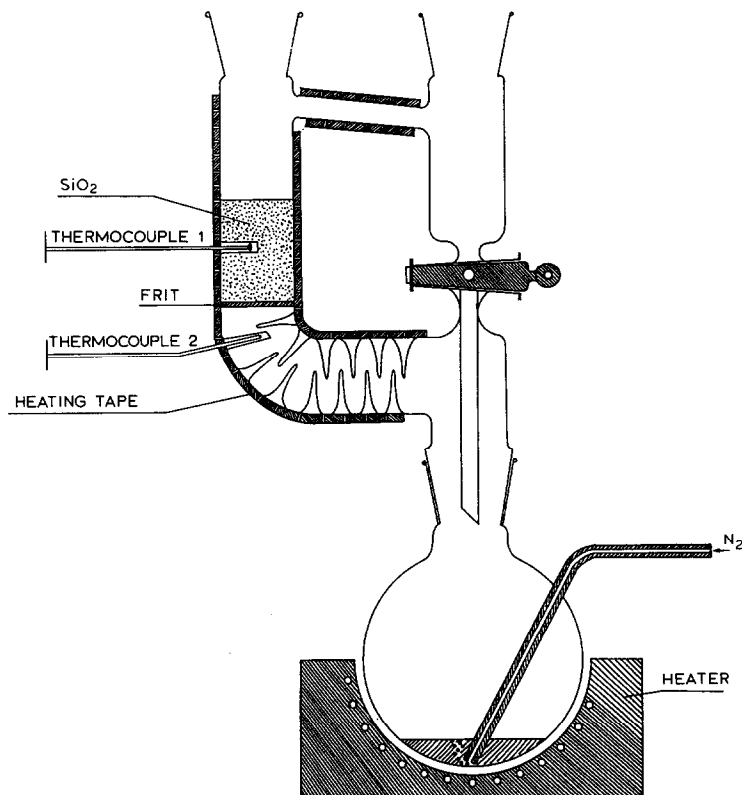


Fig. 1. Schematic of reaction flask. The top ground glass joints connect to a reflux condenser, an exhaust tube, and/or a stopper as required.

incidentally, the one that was used for most experiments). Silica is kept on a coarse frit in a separately heated section of the side arm and, depending on the nitrogen flow, awaits the arrival of reagent in either a fixed or a fluidized bed. The concentration of cyclic reagent in nitrogen gas is regulated by the temperature of the round-bottom flask. The carrier-reagent stream can be preheated by a separate section of heating tape. The combination of nitrogen flow, of volatility and temperature (as well as sorptivity on silica gel) of the cyclic, and of temperature in the reaction zone, determines the contact time. The effluents from the reaction can either be directly exhausted or stripped of most of the unreacted reagent by a condensor. Obviously, the apparatus can also work in a reflux mode. Except for some marginal experiments, however, care was taken to obey the gas-phase criterion to the extent that liquid reagent was not allowed to touch the silica gel and the silica gel was not allowed to look "wet".

The synthesis conditions varied to some degree with the nature of the cyclic reagent, but almost all procedures involved the following typical steps. About 2 g of cyclosiloxane or cyclosilazane were placed into the round-bottom flask and about 7 g of silica gel were poured onto the frit. The apparatus was closed and the silica (but not the cyclic) heated to reaction temperature with a very slow flow of nitrogen passing through to dispose of removable moisture. To start the reaction proper, the round-bottom flask was heated and/or a fast flow of nitrogen was turned on. The reaction was considered finished when all of the cyclic had vanished from the flask. After allowing the modified silica gel to cool down in the nitrogen stream, it was exhaustively extracted (usually for 10 h) in a continuous-flow apparatus¹¹ at the boiling point of the solvent (usually toluene).

Tests

The resulting materials were characterized by carbon analysis (Guelph Chemical Labs.), and by some standardized chromatographic runs. For the latter, the phases were filled into 1 m × 2 mm I.D. glass columns, conditioned at 230°C overnight (250°C for silica modified with octaphenylcyclotetrasiloxane), and tested with a variety of analyte mixtures (alkanes, alkenes, aromatics, oxygenates) in a standard temperature program starting at 40°C and rising at 8°/min. Nitrogen served as carrier gas (18–19 ml/min at 40°C).

RESULTS AND DISCUSSION

Effect of reaction conditions

Criteria. The effect of reaction conditions on the resulting product were judged by two criteria: carbon content (modifier load) and GC efficiency. As shall be seen later, the two appear related, but the precise reasons for this relationship are by no means obvious. Therefore they shall be treated separately in the following paragraphs. Furthermore, it should be understood that trends in behavior, as is not surprising in a complex system, will hold true for most, but not for each and every one of the experimental sequences.

Acidity. The reason for testing "acidified" versus "neutral" silica gel surfaces was the often-mentioned role of acids in the scission of siloxane bonds¹². All cyclics were reacted with "neutral" silica gel, while only octamethylcyclotetrasiloxane and

octamethylcyclotetrasilazane were reacted with the "acidified" surface. As judged by carbon content, the difference between the two surfaces approaches experimental variability. Chromatographic performance, again, was not significantly different for the two surfaces. (Silica gel itself is, of course, considered "acidic" in its pure form, and we did not treat its surface with alkali just for the sake of comparison.)

Temperature of reaction. This is the temperature measured in the thermocouple well protruding into the silica gel bed (Fig. 1). It is to some degree dependent on the flow-rate and the preheating of the diluent-reagent mixture and gives only a rough indication of the true reaction temperature.

Reaction temperatures were varied in the 200–400°C range with all cyclic reagents, depending, to some extent, on the vapour pressure of the cyclic. It should be realized in this context that two different reagents, even when present in the carrier stream at equal concentration, flow-rate and temperature, will not experience the same contact time with silica gel owing to different retention (adsorption) characteristics. And, of course, the rate of reaction increases, while the extent of adsorption decreases, with temperature.

In general, and not unexpectedly in light of the preceding comments and the limited support area, carbon content first increases strongly and then levels off as temperature is increased. At what temperature the levelling off (and perhaps slight downturn) occurs, depends on the nature of the cyclic as well as on the particular reaction conditions.

To mention some typical series: carbon contents of 0.26, 0.50, 0.75 and 1.42% were measured for octamethylcyclotetrasiloxane at reaction temperatures of 230, 300, 350 and 400°C, respectively, under fluidized-bed conditions and with preheating of reagent vapors. Hexaethylcyclotrisiloxane gave values of 1.40, 3.08 and 3.10 %C at 230, 300 and 350°C, while the values for hexamethylcyclotrisilazane were 3.20, 3.00 and 2.95 %C under similar and respective circumstances.

The fact that the silazane, in contrast to the siloxane, did not show a pronounced temperature dependence in that range, is simply a consequence of the much higher reactivity of the Si–N vs. the Si–O bond: the lowest temperature was already high enough to saturate the available surface. As a rule-of-thumb for the more extensively investigated cyclosiloxanes, the optimum temperature is generally in the range of 300 to 350°C.

Nitrogen flow. The flow of the carrier gas nitrogen serves to transport cyclic reagent to, and to remove unreacted reagent plus side products from, the silica gel. When the flow is large, it can also serve to fluidize the silica gel bed and thereby remove any spatial discrimination (as may occur in a fixed bed depending on whether a particular particle is situated at the entrance or the exit of the reagent gas stream, and in what position/contact it finds itself in regard to its neighbors).

Almost all of the fifty-odd experiments that were carried out needed between 3 and 5 h to come to "completion", *i.e.* to reach the stage where all of the cyclic reagent had evaporated from the round-bottom flask. However, this overall reaction time says little about the actual contact time between silica gel and cyclic reagent. Clearly, the faster the flow under otherwise similar conditions, the shorter the contact time. Of particular relevance here is the very fast flow necessary to fluidize the solid bed. Thus, experiments carried out under these conditions, some thirty-odd runs, produced in general lower carbon contents. However, these runs often (particularly with phases

made from octamethylcyclotetrasiloxane) lead to somewhat better-looking chromatograms (less tailing, sharper peaks). It is not immediately obvious whether this was caused primarily by spatial factors (the fluidized *vs.* the fixed bed) or by surface chemistry (the type and frequency of retention centers, removal of reaction products, etc.) or both. For instance, one could argue that the improved access to all surface areas, which is characteristic of the fluidized bed, allowed a more uniform coating and favored the reaction of the most active types of silanols (*c.f.* ref. 13), thereby creating, in terms of activity and space, a chromatographically more homogeneous surface.

GC retention

It is reasonable to expect carbon content and chromatographic retention to correlate in some way. Whether retention increases or decreases with carbon content depends generally on the chemical nature of the support and the liquid phase (or bonded layer), on the amount of liquid phase present, and on the chemical nature of the solute probe. Most often, one speaks of gas-liquid chromatography when retention increases, and of gas-solid chromatography when retention decreases, with an increase in carbon load.

In this study, carbon loads varied from very small values to about 3% for the methyl phases, 5% for the ethyl phase and 9% for the phenyl phase (no deliberate attempts were made to drive carbon contents to their upper limits). It is instructive to calculate the nominal layer thickness and the molar coverage that corresponds to the largest values. If, purely for purpose of estimate, the organic material is assumed (1) to cover evenly the total BET surface (which is treated as flat), (2) to have unit density, and (3) to consist of silyl units (*i.e.* R_2Si), then the nominal layer thickness d is given in Ångstroms by

$$d = \frac{\%org \times 10^4}{(100 - \%org) \times S} \text{ \AA}$$

where %org is percent organic matter, calculated for silyl units from %C data without correction for blank values, and S is the BET surface of silica gel 62 (about 300 m²/g with nitrogen). The estimate considers the pore radius large enough to be neglected at low loadings. Similarly, the micromoles of silyl groups per square meter of support can be estimated by

$$\alpha_{exp} = \frac{\%org \times 10^6}{MW_{org} \times S \times (100 - \%org)} \mu\text{mol/m}^2$$

where MW_{org} is the gram molecular weight of the silyl unit R_2Si .

When this is done, 3% carbon from dimethylsilyl translates to about 2.6 Å and 4.5 μmol/m², 5% carbon from diethylsilyl to 3.3 Å and 3.8 μmol/m², and 9% carbon from diphenylsilyl to 4.3 Å and 2.4 μmol/m².

In comparison, a liquid phase synthesis in refluxing hexadecane yielded a value of 3.1 Å for diphenylsilyl from diphenyldiethoxysilane¹⁴. Values of that magnitude are quite comparable to literature values of good bonded phases, particularly when the correlation of pore size and nominal layer thickness, and the different calculation methods employed by different researchers, are taken into account¹⁴.

Gas chromatographically speaking, maximum nominal thicknesses for the organic layer between 2 and 5 Å suggest that the materials best be designated modified solids, not bonded liquids (if such a distinction, indeed, makes much sense under the circumstances).

As an aside, this does not mean that systems could not be found where similar reactions would lead, directly or indirectly, to what might be considered typical "bonded liquids". For instance, it appears possible to "bond" silicones to the surface of Chromosorb by a simple heat treatment¹⁵, a reaction that found some application in the commercial production of capillary columns. It is well known that thermal degradation of silicones leads to cyclics and it is tempting to speculate that it are these cyclics that are involved in some of the necessary surface bonding/crosslinking that stabilizes the liquid layer and makes it resistant to extraction. Cyclics have also been used directly for deactivating quartz capillaries¹⁶.

To return to the problem at hand: if the obtained phases are to be characterized as "modified solids", retention should decrease with carbon content. That this is indeed so is shown in Fig. 2 for all retention data obtained for hexylbenzene on silica gel modified with octamethylcyclotetrasiloxane (the most frequently used cyclic). It should be borne in mind that this graph combines data from materials obtained in different vessels, at different reaction temperatures, at different flow-rates, etc. Given this fact, the correlation with carbon content appears as good as can be expected. Clearly, retention is based, exclusively or predominantly, on inorganic (not organic) surface features. Similar dependencies are found for all other test compounds.

The star in Fig. 2 marks a phase synthesized in a solid-liquid system, *i.e.* by using octamethylcyclotetrasiloxane in refluxing *n*-hexadecane¹. Retention appears slightly higher but is still considered within experimental variability. A similar situation was found with materials derived from hexaethylcyclotrisiloxane. It also appeared that, for equal carbon load, the peak-to-peak differences in retention temperatures (*e.g.* between adjacent *n*-alkanes) were slightly larger for the solid-liquid than for the solid-gas phase syntheses. However, the differences could have conceivably arisen from experimental variability, and a more detailed and closer controlled study of this minor aspect was not considered necessary in the present context.

A comparison of the retention data for all synthesized materials showed that the polarity of the retention medium, as expressed in the difference of retention temperatures between alkanes on one hand and alkenes or alkylbenzenes on the other,

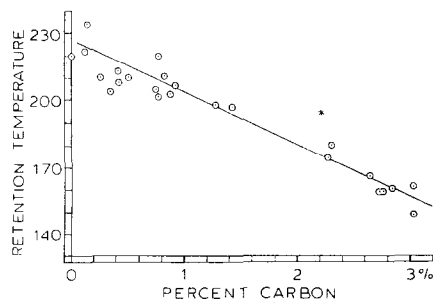


Fig. 2. Retention temperature of *n*-hexylbenzene in a standard temperature program on various octamethylcyclotetrasiloxane-modified silica gels vs. their carbon contents. The star denotes a similar phase synthesized in refluxing hexadecane¹.

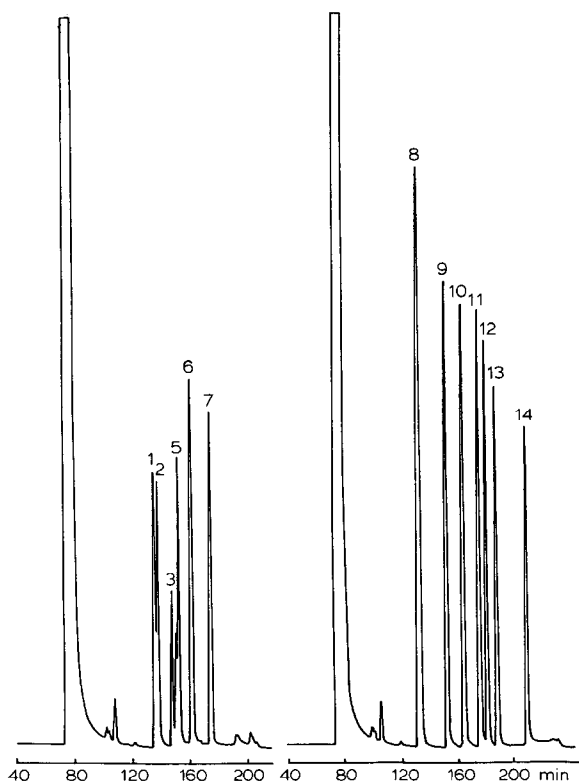


Fig. 3. Temperature-programmed GC of mixtures of olefins and alkylbenzenes on silica gel 62, 60–80 mesh, modified by hexaethylcyclotrisiloxane at 350°C in a fluidized bed. Compounds: 1 = *trans*-2-heptene, 2 = *cis*-2-heptene, 3 = 1-octene, 4 = *trans*-2-octene, 5 = *cis*-2-octene, 6 = 1-nonene, 7 = 1-decene; 8 = benzene, 9 = toluene, 10 = ethylbenzene, 11 = *n*-propylbenzene, 12 = mesitylene, 13 = *n*-butylbenzene, 14 = *n*-hexylbenzene.

did not vary to a great extent. This is to be expected if the silica gel surface (as opposed to the modifying groups) provides most or all of the retention.

The comparison of liquid- and gas-phase syntheses thus shows little differences in the retention of solutes of low polarity, and the peaks are of similar width and symmetry. On the other hand, highly polar, hydrogen-donor type materials such as alcohols had better peak shapes on the materials derived from a liquid-phase synthesis and hence were not used for testing purposes in this study.

Two sample chromatograms, of alkenes and alkylbenzenes on a silica gel modified in fluidized bed with hexaethylcyclotrisiloxane at 300°C (3.1% C), are shown in Fig. 3. They are comparable to chromatograms from a corresponding material (*i.e.* same cyclic, similar load) synthesized in boiling hexadecane, except that the latter did not resolve *n*-propylbenzene and mesitylene.

Taking into account all synthesized materials, which represent a wide range of reaction conditions, the following conclusions can be drawn: (1) It is possible to produce modified silica gel surfaces of chromatographically acceptable quality from organocyclsiloxanes and -silazanes in a gas-phase type synthesis. (2) Conditions for

the synthesis of these materials are not overly critical: most products of this study yielded reasonably looking chromatograms. (3) However, while the materials obtained by gas-phase synthesis have often come close to, and sometimes matched, those obtained by liquid-phase synthesis, they have never clearly surpassed the latter in terms of general GC performance.

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