

STABILITY AND REACTIVITY OF DIMETHYLETHOXYSILANE

Richard E. Johnson

LeTourneau University

Longview, TX 75607-7001

Phone: 903/753-0231, ext. 222; Fax: 903/237-2732

Douglas I. Ford

LeTourneau University

Longview, TX 75607-7001

Phone: 903/753-0231, ext. 378; Fax: 903/237-2732

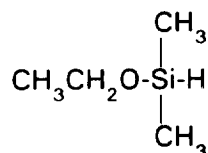
INTRODUCTION

In this paper, the chemistry of the compound dimethylethoxysilane (DMES) is discussed especially as it relates to waterproofing silica surfaces. Some of the desirable properties of this compound are that it readily reacts with silica in the vapor phase, it is a low boiling point liquid (54°C) and the by-product of its reaction with silica is the rather inert substance, ethanol. It is currently used by NASA to re-waterproof the HRSI shuttle tiles before relaunching the vehicle.

Very little information is available on this particular compound in the literature or even on related silane compounds that have both a hydride group and an alkoxy group. Since the close proximity of two groups often drastically affects the chemical behavior of each group, chemical reactions were carried out in the laboratory with DMES to verify the expected behavior of these two functional groups located on DMES. Some of the reactions tested would be potentially useful for quantitative or qualitative measurements on DMES. To study the reactions of DMES with silica surfaces, cabosil was used as a silica substrate because of its high surface area and the ease of detection by infrared spectroscopy as well as other techniques. (This paper cites references 1-11 and figures 1-10.)

CHEMICAL REACTIONS OF DIMETHYLETHOXYSILANE (DMES)

DMES has the following structure and physical properties.



Density 0.751 g/ml at 25°C

Boiling point 54°C

Refractive index 1.365

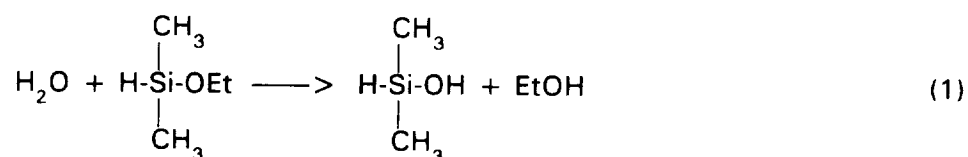
The methyl-silicon bonds are chemically inert toward ordinary chemical reagents (acids, bases, water, oxidizing and reducing agents). Most of the chemistry of this compound is due to the ethoxy and hydride groups. In contrast to carbon-ethoxy linkages, the silicon-ethoxy bond is readily hydrolyzed by water. The hydrogen of the Si-H linkage is a fairly strong reducing agent, whereas

the C-H linkage is quite inactive as a reducing agent. This is probably due to the smaller electronegativity of the silicon atom compared to carbon. DMES, then, has two fairly aggressive functional groups. These two groups account for most of its chemical reactions at ordinary temperatures and ordinary chemical environments.

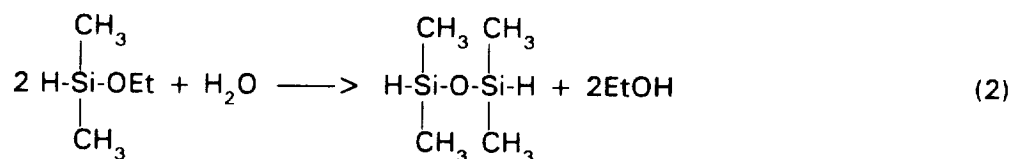
In the following section, reactions of DMES which were investigated are discussed. Various applications of each reaction are also given. Figures 1 and 2 summarize these reactions.

Water Hydrolysis

When water is added to DMES, separation in two layers occurs due to immiscibility. Agitation of the liquids for a few minutes produces a homogeneous solution. The obvious hydrolysis reaction would be



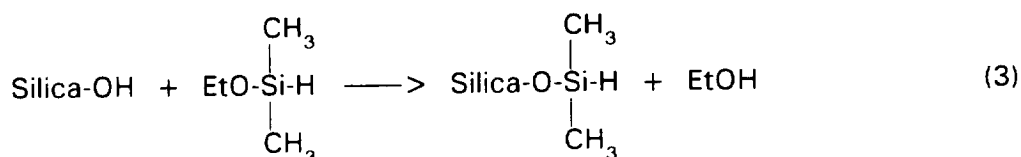
However, the resulting silanol has not been isolated (ref. 1). Indeed, the combination H-Si-OH does not occur in any known stable compound and is at best a very reactive intermediate. It is in this respect that DMES is unique compared to other common silylating agents. GCMS confirmed that the reaction of DMES and water produced ethanol and 1,1,2,2 tetramethylsiloxane. The net reaction is therefore



When DMES is applied to wet silica, this reaction will compete with the reaction of the DMES with silanol groups. However, infrared studies indicate that this is not a major factor for silica surfaces with physically adsorbed water, but could certainly be a major reaction if liquid water is present.

Reaction With Silica-OH Groups

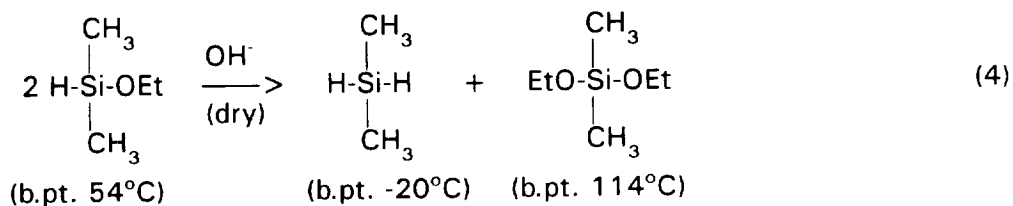
Silylating agents typically hydrolyze to silanols which then react with the fixed silanols of the silica surface to produce the Si-O-Si (siloxane) linkage. However, since DMES does not produce a stable silanol, it is likely that it reacts directly with the surface hydroxyls:



The reaction occurs reasonably fast even at room temperature, although it does not appear to replace all of the hydroxyl groups. The retention of the Si-H group during this reaction is confirmed by infrared spectra of cabosil treated with DMES (figures 3, 4).

Disproportionation

A major impurity in "old" DMES samples is found by GCMS to be diethoxydimethylsilane. For example, a bottle of DMES which was about two or three years old contained about 5% of the diethoxy compound. It has been noted in the literature that compounds containing H-Si-OEt disproportionate especially in the presence of a strong base which acts as a catalyst (ref. 2). Indeed, when dry NaOH is added to DMES, a vigorous reaction occurs accompanied by a small amount of heat released (which is characteristic of disproportionation) and also with the evolution of a gas. The disproportionation reaction is as follows.



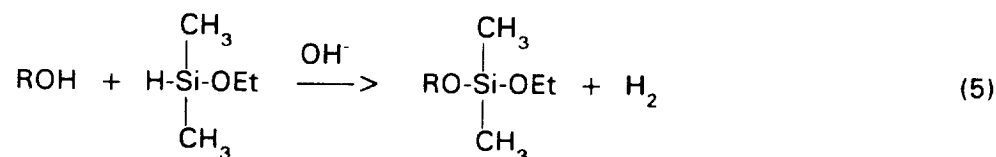
Both of the products have been confirmed by GCMS.

The above reaction might account for the slow pressure build up observed in containers of DMES and the presence of the diethoxy impurity. Reactions 5 and 6 (discussed in the next section) could also contribute H₂ gas as well. Figure 5 shows this pressure increase over a period of several days. The non-congruency of the lines of figure 5 is likely due to the absence of light during the night hours of the experiment, indicating a sensitivity of the reaction to light. Decomposition did continue to occur in an amber polypropylene bottle as well, indicating that some reaction occurs without catalytic effects of the glass surface or exposure to light.

The Si-H Group as a Reducing Agent

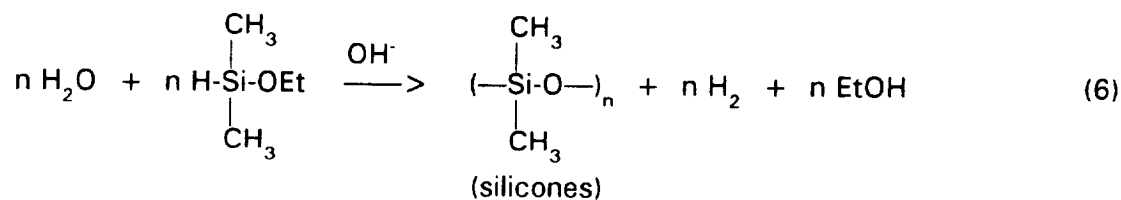
Hydrides of silicon are known to be good reducing agents. The -1 oxidation state of the hydrogen can be increased to 0 to produce H₂ gas or to +1 to produce water or hydrogen ions. Reactions which were examined involving the oxidation of DMES are given below.

1. Base catalyzed oxidation with alcohols.



This reaction was utilized to synthesize diethoxydimethylsilane in order to verify its peak as a decomposition product in the GC of DMES. Ethanol was used as the alcohol and the reaction was vigorous even at room temperature.

2. Base catalyzed oxidation with water.



Alkaline water reacts with both the hydride and ethoxy groups to give a bifunctional monomer which can then form silicone polymers.

3. Oxidation with $\text{Hg}^{+2}(\text{aq})$.

An aqueous solution of mercuric chloride is rapidly reduced by DMES to produce mercurous chloride and silicones. The combination of an oxidizing agent and water with DMES can always be expected to produce silicones. This reaction can be used to detect the Si-H group in silanes by the observation of the white precipitate, Hg_2Cl_2 .

4. Oxidation with aqueous I_2 or Br_2 .

Both I_2 and Br_2 oxidize DMES to produce silicones and either HI or HBr. The reaction with I_2 , as expected, is slower than with Br_2 . Both reactions have been used to perform quantitative oxidation-reduction titrations of DMES. Excess iodine or bromine was allowed to oxidize the DMES and then the excess halogen was determined using standardized sodium thiosulfate. The excess bromine was generated by using potassium bromate and excess potassium iodide.

5. Oxidation with Cu^{+2} .

When a saturated solution of CuSO_4 in methanol comes in contact with DMES in liquid or vapor form, it rapidly deposits a brown solid and produces hydrogen gas. The solid is probably metallic copper and Cu^+ salts. It provides a very sensitive test for DMES vapors.

6. Oxidation with Ag^+ .

A silver nitrate solution (0.1 M in 50/50 water-methanol) reacts rapidly with DMES to produce H_2 and metallic silver. Initially, a yellow color appears which then disappears or is masked by the gray to black silver precipitate. This was used to examine silica shuttle tiles which had been treated with DMES. When the tile was treated with DMES, spraying it with the silver nitrate solution produced a gray color, presumably due to the reduction of the silver ions by the Si-H.

GAS CHROMATOGRAPHY STUDIES

Gas chromatograms were obtained for DMES in various stages of reaction with water and with sodium hydroxide. Dimethylsilicone stationary phases were employed on both packed and capillary columns in the chromatograph. The packed columns were operated isothermally at 50°C and utilized a flame ionization detector. The capillary columns utilized temperature programming and a mass spectrometer for the detector. All of the major peaks and many of the minor peaks were identified from the mass spectra obtained. Nearly all of the peaks could be accounted for in terms of expected hydrolysis and disproportionation products (reactions 2 and 4), with the disproportionation products then reacting with incidental moisture and the parent DMES molecule.

The following compounds are identified as major peaks coming off before twenty minutes on the capillary column (eight minutes on the packed column): $(\text{CH}_3)_2\text{Si}(\text{OCH}_2\text{CH}_3)_2$, $(\text{CH}_3)_2\text{HSiOSiH}(\text{CH}_3)_2$, $\text{CH}_3\text{CH}_2\text{OH}$, $(\text{CH}_3)_2\text{H}_2\text{Si}$, $(\text{CH}_3\text{CH}_2\text{O})\text{Si}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{SiH}$, $(\text{CH}_3)_2\text{HSiOSi}(\text{CH}_3)_2\text{OSiH}(\text{CH}_3)_2$. Many of the minor components were identified as being polysiloxanes, both linear and cyclic. The above mentioned components were also found in a DMES sample which was two to three years old.

INFRARED STUDIES OF DMES TREATED SILICA

Cabosil is a high surface area silica powder which is chemically similar to crystalline quartz and fibrous silica. Cabosil samples can be prepared for infrared spectroscopy studies by lightly pressing the powder sample between two salt plates of a demountable liquid cell. The apparatus used for room temperature studies of cabosil and DMES is shown in figure 6. After reacting in the apparatus, a portion of the cabosil powder was then pressed between the salt plates to a thickness of about 0.5 mm. Before discussing the results of infrared studies, a brief discussion of silica surfaces is given.

The Nature of Silica Surfaces

Silica is known to have a strong affinity toward water adsorption. This tendency is due to the silica surface hydroxyls of which there are two types, isolated hydroxyls and vicinal hydroxyls (ref. 4). The vicinal hydroxyls can form hydrogen bonds to each other and can retain water on the surface by forming hydrogen bonds to the adsorbed water. Surprisingly, it appears that isolated hydroxyls do not hydrogen bond to water molecules (no infrared shift) and therefore contribute

little to water adsorption (ref. 4). However, Lewis base compounds such as amines are preferentially adsorbed on the isolated hydroxyls. Also, other factors being equal, the isolated hydroxyls are more reactive than the hydrogen bonding hydroxyls (ref. 4, 5, 6).

Figure 8 shows the infrared spectrum of cabosil obtained by pressing the cabosil powder between two salt plates 0.5 mm apart. This sample technique was used previously and the absorption band assignments are as follows (ref. 3).

3750 cm^{-1} is the stretching vibrations of isolated surface hydroxyls
(sharp peak due to no interaction of isolated hydroxyls groups)

3660 cm^{-1} is due to vicinal hydroxyl groups which hydrogen bond to each other and thus give a broad absorption band

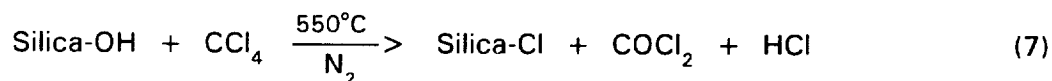
3450 cm^{-1} is a broad band due to water adsorbed on the silica surface

Typically, silica surfaces have from one to four hydroxyls per 100 square angstroms of surface (ref. 7). Raising the temperature destroys the vicinal hydroxyls by eliminating water. This occurs in the temperature range of 450 - 800°C and is known to be somewhat irreversible. The isolated hydroxyls (usually about one per 100 square angstroms) persist even at these elevated temperatures. Replacement of the surface hydroxyls by non-hydrogen bonding groups drastically reduces the wettability of the material.

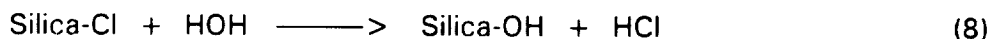
A Method for Determining Surface Hydroxyls

Fripiat and Uytterhoeven (ref. 7) determined the OH content of cabosil using the methyl-Mg Grignard reagent to generate methane gas with the surface OH groups. Cabosil was shown to contain one to four hydroxyls per 100 square angstroms of surface area depending upon the temperature. This value should be applicable to the shuttle tile surface as well since it is essentially pure silica except that it would have a much smaller surface area per gram than cabosil. The technique developed here to determine surface hydroxyls on silica is as follows.

1. Substitute Cl for surface OH groups (ref. 8).

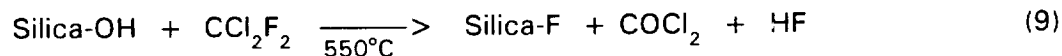


2. Hydrolyze the chloride (or fluoride) with water.



3. Titrate the liberated HCl (or HF) with standardized NaOH solution.

We were able to replace the hydroxyls of silica using freon 12, $\text{C Cl}_2\text{F}_2$. The reaction is conjectured to be



It was also found that freon 22, CHClF_2 , worked equally well to produce the fluorinated surface.

Five grams of hydrolyzed cabosil halide neutralized about 35 ml of 0.1 M NaOH. The same amount of shuttle tile treated the same way only neutralized 0.4 ml of the same NaOH solution. From this, it can be calculated that the cabosil contains about 0.7×10^{-3} moles of surface hydroxyls per gram. This is consistent with previous data reported in the literature using a completely different method (ref. 7). The shuttle tile silica by the same calculations then has about two orders of magnitude less hydroxyl groups (due to less surface area) or about 1×10^{-5} moles/gram. From these data, it can be calculated that the stoichiometric amount of DMES needed to completely react with shuttle tiles is about one milligram of DMES per gram of tile. Cabosil is known to have a surface area of about $200 \text{ m}^2/\text{g}$ and therefore the shuttle tiles silica is estimated to have less than $10 \text{ m}^2/\text{g}$ silica of surface area. This low hydroxyl content of the shuttle tiles explains why it is difficult to see reacted DMES on treated tiles by infrared spectroscopy but it can be seen on cabosil surfaces.

Figure 7 shows the spectra of cabosil samples before and after treatment with CCl_4 and CCl_2F_2 (freon 12) at 550°C . Both reagents cleanly remove the surface hydroxyls and replace them with chlorine or fluorine atoms. Both chlorinated and fluorinated cabosil surfaces give essentially the same spectra, except for the weakly discernible SiF band at 900 cm^{-1} . The surface treated with CCl_4 was shown to be chlorinated by hydrolysis of the surface and treating the solution with AgNO_3 to obtain the white AgCl precipitate. The surface treated with freon 12 is likely to be fluorinated, since a negative test for chloride was obtained for the hydrolyzed product, and a band at 900 cm^{-1} is observed in freon-treated samples. Interestingly, both fluorinated and chlorinated cabosils and shuttle tile silica resisted wetting with water until hydrolysis took place, which was after about one hour of contact with water. Similar results for fluorinated porous glass were obtained using an entirely different process (ref. 9).

Infrared Detection of Attached Silyl Groups

Figure 3 shows the effect of reaction of the cabosil with DMES. As water adsorbency decreases, the hydroxyl peaks also diminish as well. Note, however, a new prominent peak at 2150 cm^{-1} which is due to the Si-H group. This peak persists even after heating the cabosil at 130°C under a vacuum. This indicates that the Si-H group does not significantly react with the surface hydroxyls. The small peaks at about 2900 cm^{-1} are due to methyl groups of the silane that have bonded to the surface.

Figure 4 contrasts cabosil surfaces reacted with DMES and hexamethyldisilazane (HMDS). The HMDS provides $(\text{CH}_3)_3\text{Si-O-}$ groups for bonding to the surface by replacing the surface hydroxyls. DMES provides $(\text{CH}_3)_2\text{Si(H)O-}$ groups for bonding. The differences can be seen in the infrared spectra. As expected, both HMDS and DMES treated cabosil give infrared peaks characteristic of C-H groups around 2900 cm^{-1} , but only the DMES spectrum has the Si-H band at 2150 cm^{-1} .

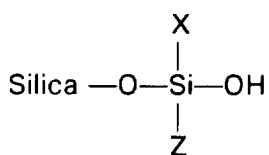
Thermal Stability of DMES Treated Cabosil

In order to examine the thermal stability of DMES treated silica, the specially constructed gas cell shown in figure 8 was used. A heating tape was wrapped around the center portion of the cell to control the temperature in the cell. A thin silica wafer was made by pressing cabosil powder between two stainless steel plates in a hydraulic press to a pressure of about 5000 lb/sq in. The resulting wafer was about 1.5 x 2.0 cm and weighed about 40 to 50 mg. The wafer could then be mounted into the holder which was then placed into the cell. Generally, the wafers were dried at room temperature by applying a vacuum and then reacted with DMES vapor at about 100 mm Hg pressure. The excess DMES was removed by vacuum again and the IR spectrum obtained. Subsequently, 50% R.H. air was admitted to the cell and then heated to various temperatures, held at the temperature for twenty minutes, and then the air was expelled and the cell cooled down to room temperature before the IR spectrum was taken. Representative spectra are given in figure 9.

The stability of DMES on silica is inferred by observing the Si-OH, C-H and Si-H peaks. It is evident that the groups C-H and Si-H begin to diminish in the $400 - 500^\circ\text{C}$ range while the Si-OH peaks begin to increase. This range for thermal breakdown is consistent with other work for silylated silica surfaces containing Si-H and Si-CH groups which also report decomposition of these groups in the $400 - 500^\circ\text{C}$ range in air (refs. 10, 11).

After heating to the highest temperature, 640°C , a silica wafer was retreated with DMES under the same conditions as previously described. Figure 10 indicates that there are qualitative differences in the silane bonded to silica upon retreatment as compared to initial treatment. The broad Si-OH peak was smaller in the retreated sample. This can be explained by the known phenomena of irreversible dehydration of silica surfaces at high temperatures (ref. 4). Adjacent Si-OH groups on the surface are converted to Si-O-Si bridges at high temperatures and these bridges persist even when the sample is recooled to room temperature.

More significantly, it is noted that even though the C-H and Si-H peaks reappear on the DMES for the retreated silica, the Si-H peak is diminished in size, suggesting that the thermally degraded surface has oxidized some of the Si-H groups of the reacting DMES. Also it is noted that in figures 9 and 10 the spectra of the samples that have experienced a temperature of 640°C indicate a new kind of surface hydroxyl may be forming. These results are consistent with the following representation of the thermal degradation of the silylated surface.



Here X and Z could be additional OH groups or partially oxidized methyl groups which could function as oxidizing agents. Certainly it is evident that repeated retreatment of partially degraded silylated silica surfaces is likely to give new surfaces which are not easily characterized.

CONCLUSIONS

Dimethylethoxysilane has a varied chemistry involving the hydride group which can act as a reducing agent and the ethoxy group which can react with water and silanol groups. These two groups can switch places intermolecularly by disproportionation under basic conditions. In view of this, it is not surprising that DMES readily produces a variety of products in the presence of small amounts of moisture or bases. A major impurity in aged DMES is diethoxydimethylsilane which can hydrolyze to produce silanols which in turn can react with itself and the parent DMES compound. Most of the products identified in an aged sample of DMES by GCMS can be accounted for in terms of this reaction scheme.

Using a high surface area form of silica called cabosil, infrared spectroscopy studies indicate that DMES reacts with the Si-OH groups by way of the ethoxy group. The silylated surface degrades in air beginning at temperatures of about 400°C which coincidentally is the same temperature the vicinal (adjacent) Si-OH groups of silica begin dehydrating to form Si-O-Si bridges. The infrared studies also suggest that the thermally degraded silylated surfaces which are retreated with DMES will produce attached silyl groups which are varied and not easily characterized. After many retreatments with DMES, the structure of the silylated surface could be much different from the initially treated surface.

ACKNOWLEDGMENTS

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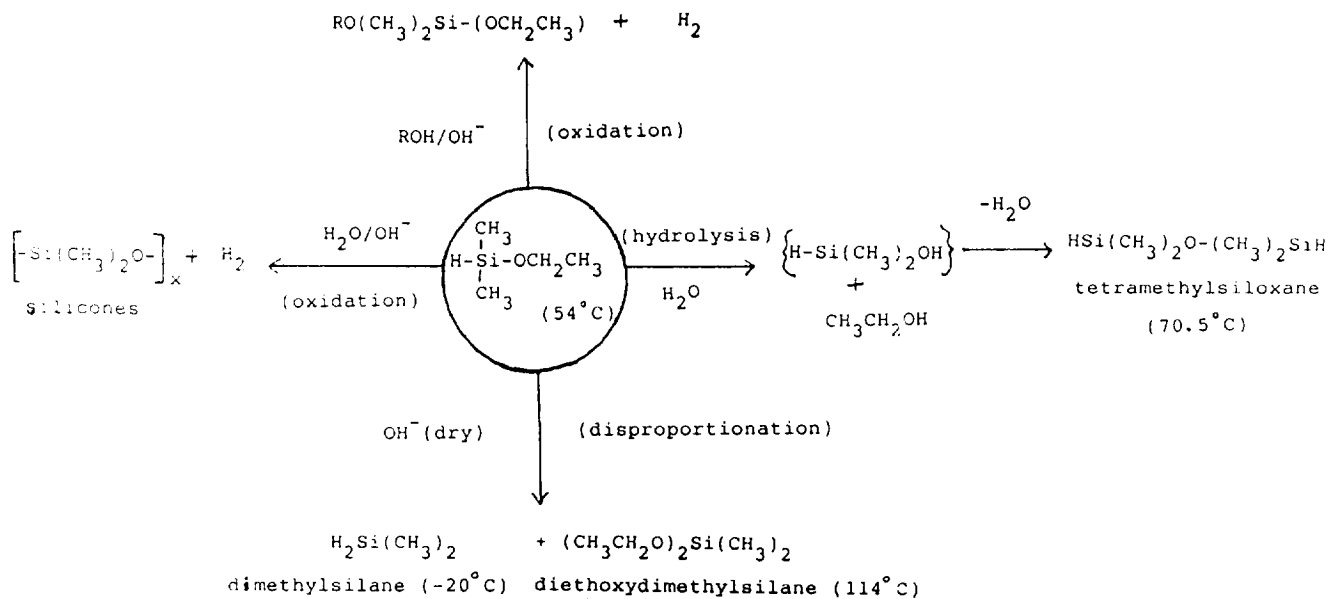


Figure 1. Reactions of dimethylethoxysilane in the presence of water or base.

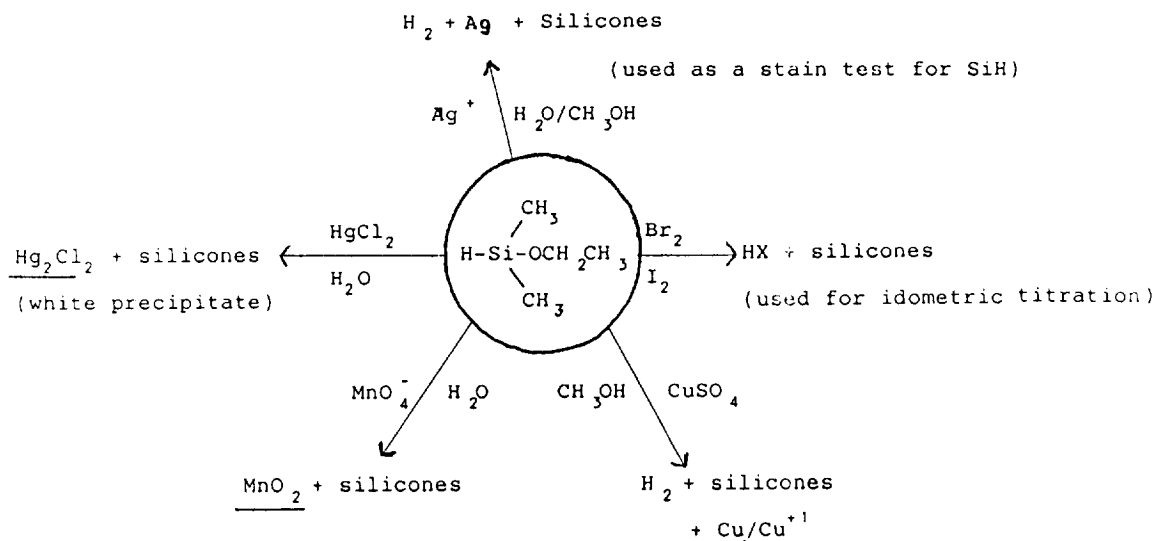


Figure 2. Miscellaneous oxidations of dimethylethoxysilane which can serve for qualitative and for quantitative determination of the Si-H group.

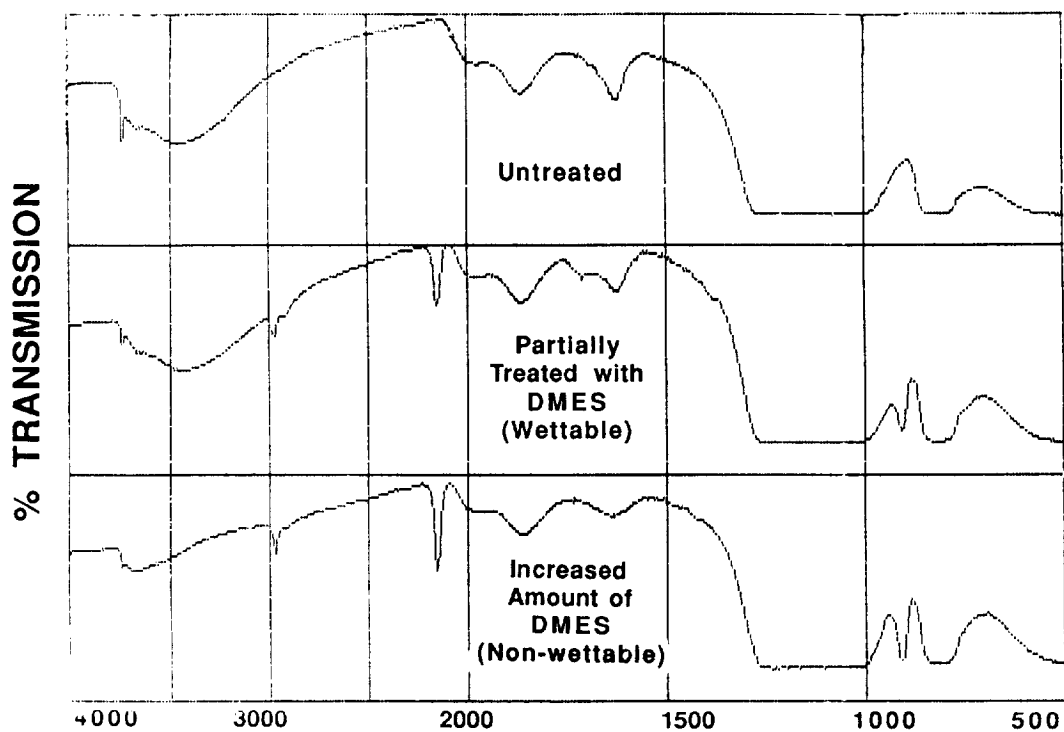


Figure 3. Infrared of cabosil powder in various stages of reaction with dimethylethoxysilane vapors at room temperature.

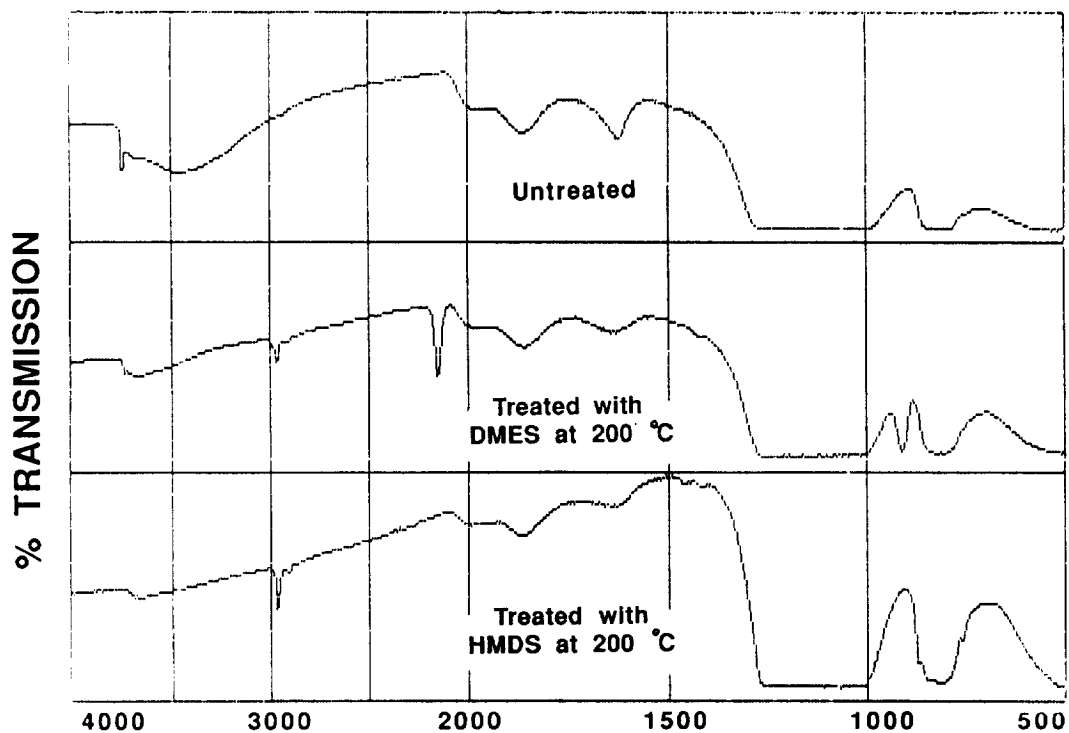


Figure 4. Infrared of cabosil powder before and after treatment with dimethylethoxysilane (DMES) and hexamethyldisilazane (HMDS) vapors.

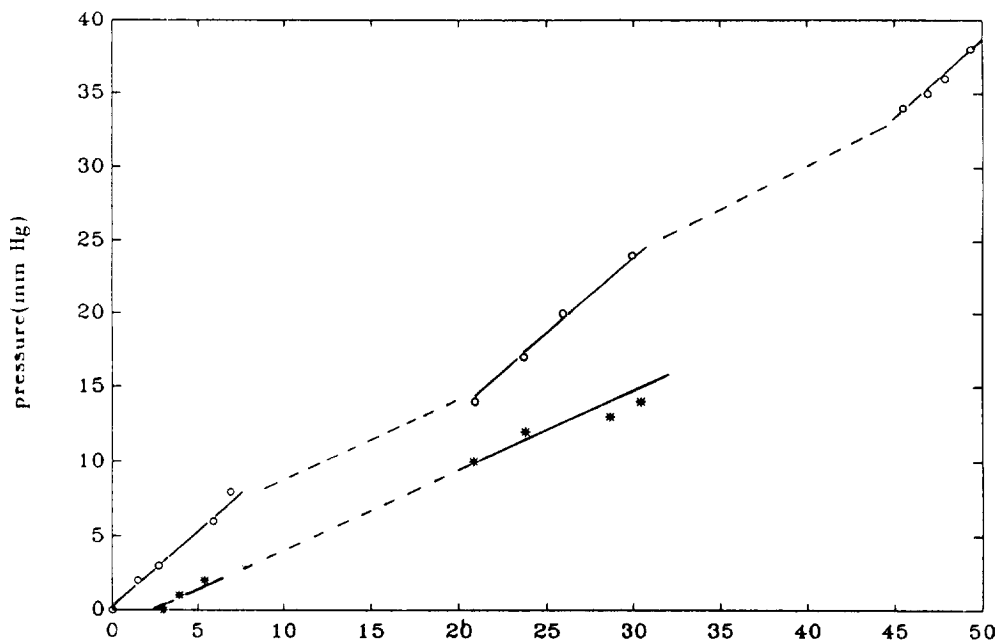


Figure 5. Pressure build-up over DMES in a closed container immersed in a 26°C water bath. Circles denote data collected when using a clear pyrex glass container. Asterisks denote data collected when using an amber polypropylene container. Dashed lines are periods when the lab lights were off.

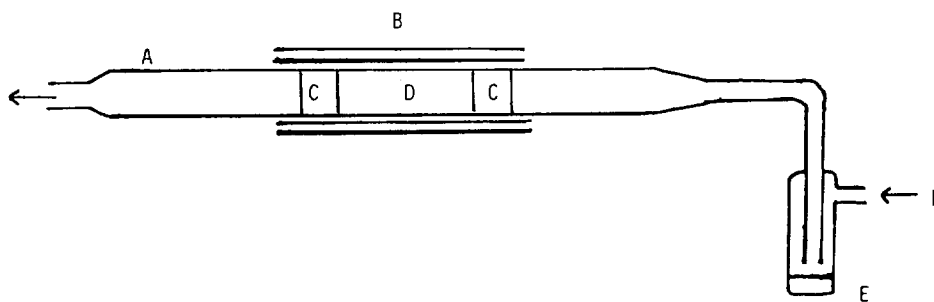


Figure 6. Apparatus for chemical treatment of cabosil powder. Legend: A - quartz tube, B - furnace, C - porous silica plugs, D - cabosil sample, E - DMES or other agents, F - nitrogen gas.

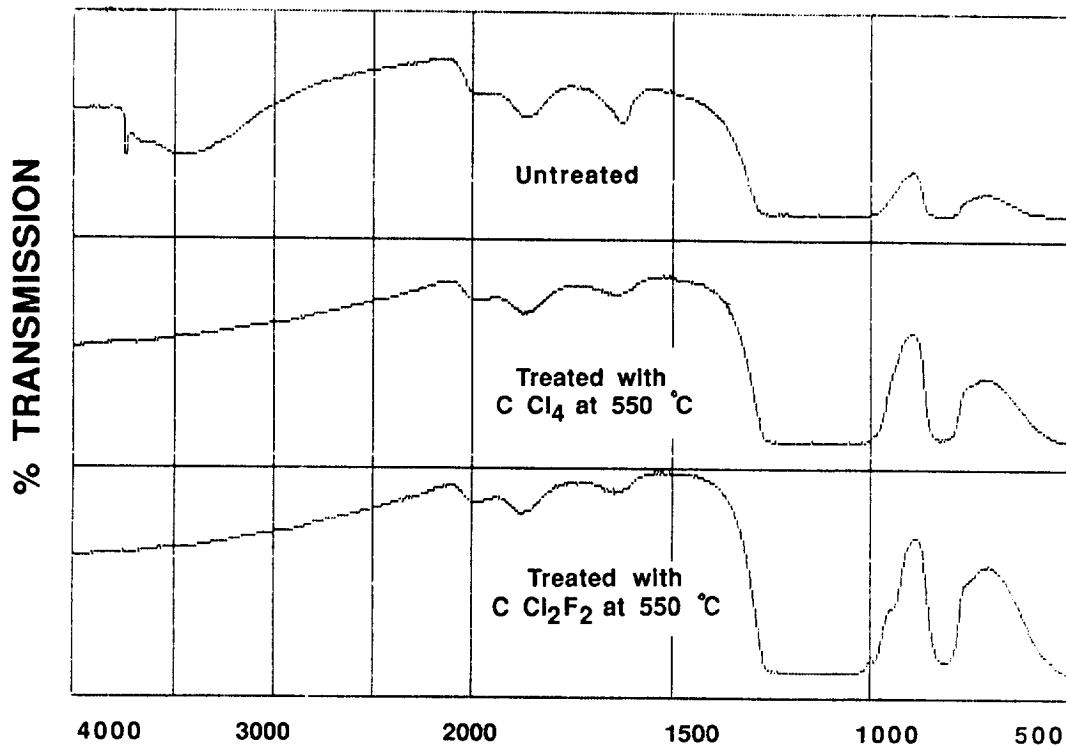


Figure 7. Infrared spectra of cabosil before and after treatment with carbon tetrachloride or freon 12.

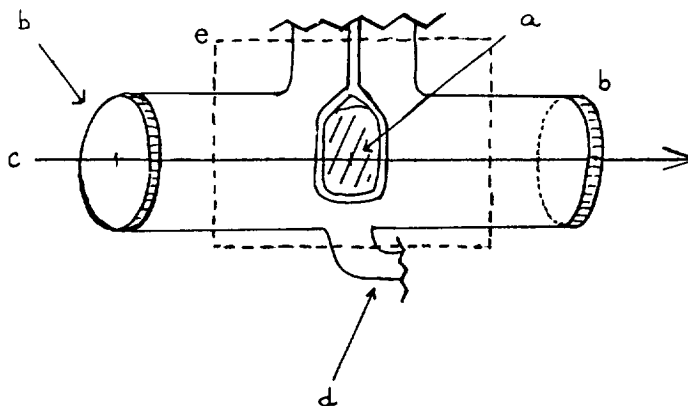


Figure 8. Infrared cell used for thermal studies of DMES-treated cabosil. Legend:
 a - silica wafer ($\approx 3 \text{ cm}^2 \times 0.25 \text{ mm}$, $\approx 45 \text{ mg}$, 5000 lb/in^2),
 b - sodium chloride plates, c - infrared beam, d - access port,
 e - heated area.

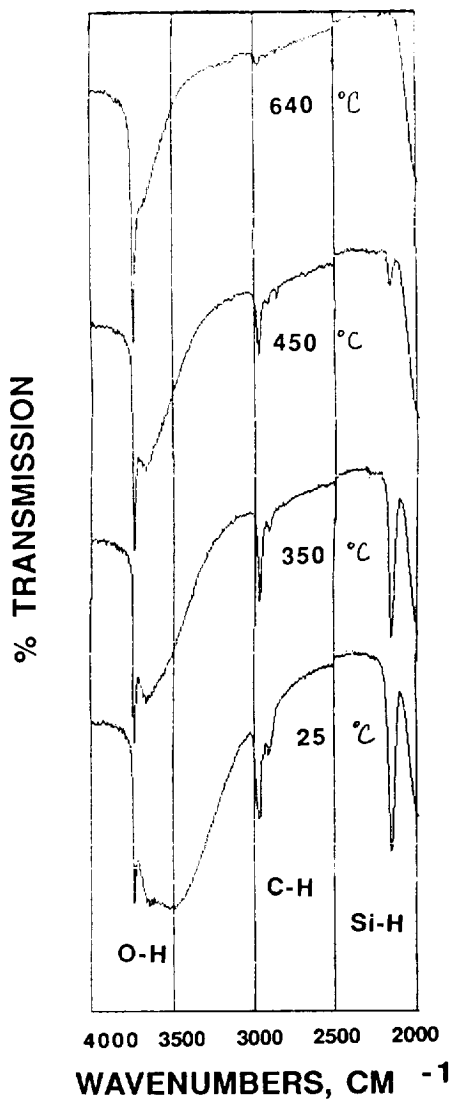


Figure 9. Infrared spectra of DMES-treated cabosil wafers at various temperatures.

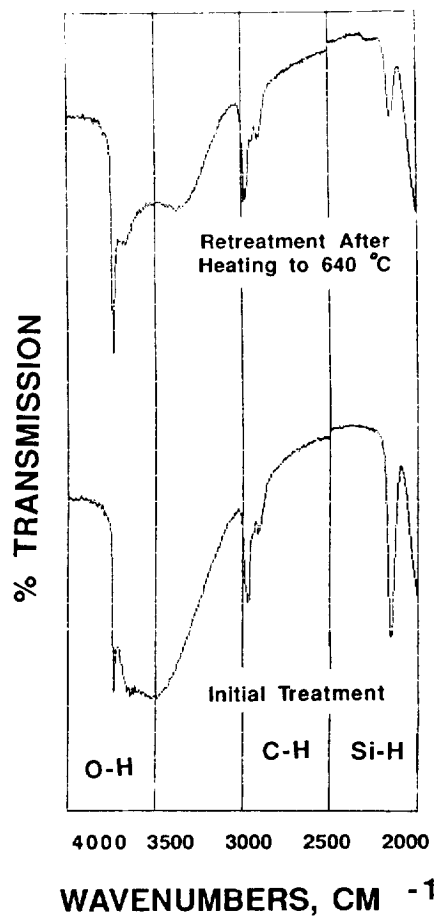


Figure 10. Infrared spectra of DMES-treated cabosil wafer showing the difference in silylation for a new sample as opposed to a sample which had been treated and then thermally degraded before retreatment.

