J. Am. Chem. Soc. 1981, 103, 5303-5307 5303

remarks apply with especial force to calculations for nonclassical species and for potential surfaces for reactions, where the errors in the simple ab initio treatments can be very large.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008), the Robert A. Welch Foundation (Grant F-126), and The National Science Foundation (CHE-7803213). The calculations were carried out with a Digital VAX 11/780 computer, provided by grants from The National Science Foundation and The University of Texas at Austin, and with the CDC 66/6400 and Dual Cyber 170/150 computers at the University of Texas Computation Center.

Supplementary Material Available: Cartesian coordinated for all stationary points reported in this paper (14 pages). Ordering information is given on any current masthead page.

The Nature of Organosilane to Silica-Surface Bonding

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Received October 24, 1980

Abstract: Experimental evidence has been acquired leading to proposals concerning the nature of organosilane to silica-surface bonding. The yellow Schiff's base formed by reacting salicylaldehyde with (aminopropyl)silanes either in solution or on a silica surface has provided a means of measuring the relative stability of these silanes bonded to the surface. Studies of the effect of oven curing on silane-to-surface bonding stability and investigations into the rate of silane removal from the surface in ethanol have provided novel bonding information. Copper(II) ion uptake capacity studies on a series of (aminopropyl)silanes and trimethylsilyl chloride uptake experiments on the series $(CH_3O)_nSi(CH_3)_{4-n}$ (n = 1–3) complement the above experiments and suggest the bonding models proposed in this paper.

The numerous applications to chemistry of oxide-immobilized organosilanes are of unquestionable importance. Preconcentration of trace metals using chelating groups immobilized via silylation,[1,2] silica gel as a support for phase-transfer catalysis,[3] chemically modified electrodes,[4] immobilized enzymes,[5] and metal ion chromatography[6] are only some of the applications appearing in the recent literature. The vitality of interest in immobilized organosilanes is further illustrated by a recent symposium on silylated surfaces.[7] The literature on silica and on silane–silica interactions is vast and reflects the versatility that can be obtained by manipulation of the initial nature of the silica and of the silylation reaction conditions. This versatility has led to much confusion but also to many opportunities to create designed silane–silica structures. A number of useful spectroscopic and chemical tools have developed[8-13] to study the silane–silica interface. However, many relevant details remain speculative for thin silane coatings, such as the role of siloxane oligomerization and the number of covalent bonds to the surface. The results and methodology of our experiments is one approach to attempt to clarify important points related to these issues.

Experimental Section

Preparation of Silica-Immobilized (Aminopropyl)silanes. A 3.01-g sample of oven-dried Baker silica gel (60–200 mesh, 300 m^2/g) was slurried in 20 mL of 10% (v/v) silane ((3-aminopropyl)triethoxysilane, (3-aminopropyl)methyldiethoxysilane, or (3-aminopropyl)dimethylethoxysilane) in dry toluene. The reaction mixture was stirred frequently at room temperature for 30 min, filtered, and washed exhaustively with toluene. The air-dried solid silica product (**1**, **2** or **3**) turned bright yellow upon treatment with 0.5 mL of ethanol and 1 drop of salicylaldehyde. Percent carbon determination (Huffman Laboratories, Wheatridge, CO): **1** = 3.61%, **2** = 3.91%, **3** = 5.54%, all blank corrected for a blank equal to 0.71%.

The silica–silanes **1**, **2**, and **3** were similarly prepared from 5.00 g of Baker silica gel and 20 mL of 1% (v/v) silane in dry toluene.

Effect of Oven Curing on the Silane-to-Surface Bonding Stability. (Aminopropyl)silanes **1**, **2**, and **3** (from 10% solutions) were each divided into six 0.100-g samples to be oven cured at 80 °C for 0, 1, 3, 6, 12, and 20 h. At the appropriate time, each of these samples, in a test tube, was treated with 5.0 mL of 0.1% salicylaldehyde (excess) in ethanol. After 30 min of occasional stirring, the absorption spectrum (Cary 14) of the supernatant was taken noting the absorbance at λ_{max} 404 nm (salicylaldimine).

(Aminopropyl)silanes **1**, **2**, and **3** (from 1% solutions) were each divided into three 1.01-g samples to be oven cured at 80 °C for 0, 1 and 3. At the appropriate time, each of these samples, in a test tube, was treated with 10.0 mL of 0.1% salicylaldehyde (excess) in ethanol. After 30 min of occasional stirring, the absorption spectrum of the supernatant was taken.

Kinetic Studies. Uncured 2.00-g samples of silica–silanes **1**, **2**, and **3** (from 10% solutions) were slurried in 100.00 mL of absolute ethanol. From slurries **1** and **2**, 3 mL aliquots were removed after 1 h, 4.5 h, 25 h, 3 days, and 6 days. Five drops of 1% salicylaldehyde (excess) was added to the cuvette and after 3–4 min the absorption spectra were recorded, noting the absorbance at λ_{max} = 404 nm. From slurry **3**, 1-mL aliquots were removed at the indicated time, diluted to 3 mL with ethanol, and mixed with 5 drops of 1% salicylaldehyde. After 3–4 min, the absorption spectra were recorded.

Copper(II) Capacity Studies. Approximately 0.2 g (accurately weighed) of silanes **1**, **2**, or **3** were dry packed into a stainless-steel chromatographic column. A microprocessor-controlled ALTEX high-performance liquid chromatograph 110A pump as utilized for cycling studies to determine copper capacity. A switching valve, before the pump, allowed water, acetate buffer at pH 5, 10^{-2} M copper(II) at pH 5, water, and nitric acid at pH 2 to be pumped through the column to

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† Visiting research professor, summer 1980, from the Department of Chemistry, University of Tennessee at Chattanooga, Chattanooga, TN.

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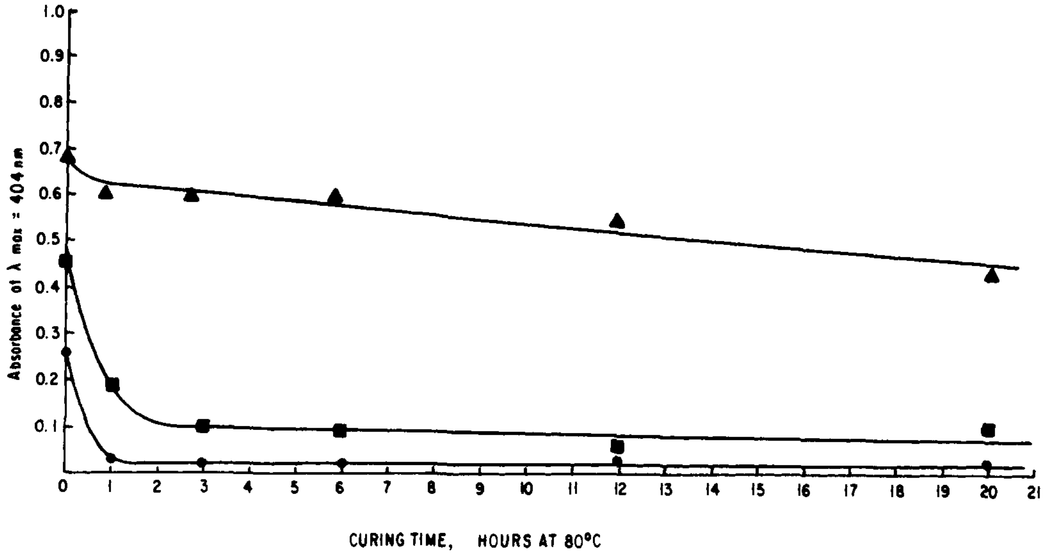


Figure 1. Absorbance at λ_{max} 404 nm of salicylaldehyde–ethanol supernatant as a function of curing time at 80 °C for silica–(3-aminopropyl)silanes prepared from 10% (v/v) silane in toluene solution: **1**, ●; **2**, ■; **3**, ▲.

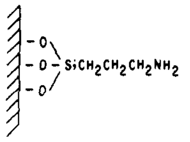
a mixing chamber. A colorimetric complexing reagent (1,2-cyclohexylenedinitrilo)tetraacetic acid (CYDTA) flowed from a peristaltic pump to the mixing chamber. The CYDTA reacted with the metal and flowed to a Hitachi Model 110 spectrophotometer set at 715 nm. Copper capacities of **1**, **2**, and **3** were determined at a flow rate of 1.00 mL/min by measurement of the Cu(II) complex absorption peak area obtained during acid elution of the column.

Preparation of Silica–Silanes (4–6). To 5.00 g of Baker silica gel was added 20 mL of a dry toluene solution containing 1 mL of methyltrimethoxysilane, dimethyldimethoxysilane, or trimethylmethoxysilane. The reaction mixture was stirred occasionally for 30 min, filtered, and washed thoroughly with toluene. Each sample (**4–6**) was oven dried at 84 °C for 18 h and vacuum dried at 84 °C for 3 h.

Reactions with Trimethylsilyl Chloride. Two-gram samples of silica–silanes **4**, **5**, and **6** and Baker silica gel were treated with occasional stirring with 20 mL of 10% (v/v) trimethylsilyl chloride in dry toluene. After 21 h, each mixture was filtered and the solid product washed exhaustively with methanol. Prior to submission for carbon determination, samples were vacuum oven dried at 84 °C for 3 h.

Results and Discussion

Preparation of Silica-Immobilized (Aminopropyl)silanes. The Salicylaldehyde Reaction. Silica-immobilized (3-aminopropyl)silane (**1**), (3–aminopropyl)methylsilane (**2**), and (3-aminopropyl)dimethylsilane (**3**) were prepared by reacting the corresponding (ethoxy)$_n$*silane* with Baker silica gel (60–200 mesh, 300 m^2/g) in dry toluene. Schematic structures are written below without implication of the nature of surface bonding. After thorough washing with toluene followed by methanol, samples of **1–3** were treated with salicylaldehyde in ethanol. Each solid immediately turned a bright yellow color as the salicylaldimine Schiff's base was formed.[14] The supernatant solution above **1** was not visibly colored, whereas the solution above **3** was a bright yellow. The supernatant of **2** was an intermediate yellow color. These qualitative observations are shown in Figure 1 (absorbance at curing time equals 0 h). The salicylaldimine chromophore detected in the solutions above (**1–3**) must have formed from aminosilane cleaved from the surface in the ethanol solvent. Since the silane loading (in mmol/m^2) is comparable for **1-3** (vide infra), the absorbances of **1-3** at λ_{max} = 404 nm[15] then reflect the relative stability of the bond(s) between these silanes and the silica surface (**1** > **2** > **3**).



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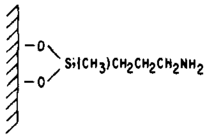

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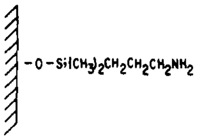

3

Effect of Oven Curing on the Silane-to-Surface Bonding Stability. Immobilized silanes **1–3** were prepared as usual from a 10% (v/v) silane in toluene solution at room temperature. Surface area measurements (N$_2$-BET) and carbon determination yielded the following loading figures in mol of silane/m^2 of silica gel: **1** = 0.0033, **2** = 0.0027, and **3** = 0.0030. One hundred-milligram samples of **1**, **2**, and **3** were removed from the curing oven (80 °C) at the times indicated in Figure 1 and treated with 5.0 mL of 0.1% salicylaldehyde (excess) in ethanol. After 30 min, the absorption spectrum of each supernatant solution was taken, noting the absorbance at λ_{max} = 404 nm. Listed below are some conclusions taken from these data and Figure 1.

(1) Curing times of 3 h at 80 °C are sufficient to achieve maximum silane-surface stability.

(2) At curing time equal to 0, the stability order is **1** > **2** > **3**. Since ethanol should rapidly solubilize all hydrogen-bonded species, it appears that the number of covalent bonds initially formed to the surface is related to the number of silanol groups and primarily determines the stability after silylation at room temperature without a heating step.

(3) Because oven curing does increase the stability of products, some of the silane must be merely hydrogen bonded to the surface prior to curing in each case and additional covalent bonds formed upon heating.

(4) Samples **1** and **2** are more similar in stability after curing than they are to the much less surface-stable **3** (see also Figure 3). This argues against the occurrence of long polymers of **1** on the surface since **2** can only form dimers by condensation (two covalent bonds to the surface) and long polymers of **1** should contain many more covalent bonds to the surface.

Immobilized silanes **1–3** were prepared from a 1% (v/v) silane in toluene solution at room temperature. Under these conditions the stoichiometry is controlled so that a maximum loading of only 6.7 × 10^{-4} mmol of silane/m^2 of silica gel is possible. Therefore, silane oligomerization, if it is occurring on the surface, should be less important than for the immobilized silanes prepared from 10% solutions. Indeed, the effect of oven curing at 80 °C on these silane-surface stabilities is strikingly different. Figure 2 summarizes the results and the list below points out some conclusions and observations.

(1) Immobilized silane **3** prepared from 1% and 10% solutions behave in a similar way toward oven curing.

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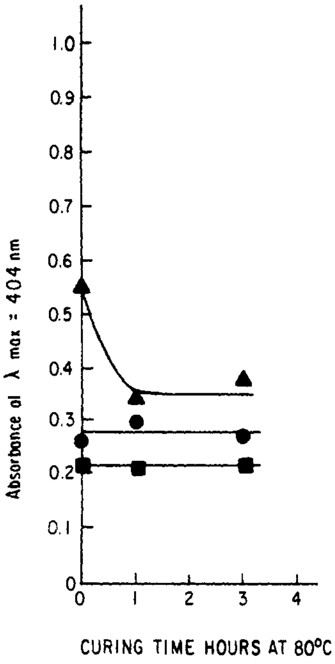


Figure 2. Absorbance at λ_{max} 404 nm of salicylaldehyde–ethanol supernatant as a function of curing time at 80 °C for silica–(3-aminopropyl)silanes prepared from 1% (v/v) silane in toluene solution: **1**, ●; **2**, ■; **3**, ▲.

(2) Oven curing for **3** has no apparent effect on the silane-surface stability of **1** and **2** which remain more surface stable than **3**. Apparently, for **1** and **2**, additional covalent bonds to the surface or to neighboring silane moieties are *not* formed during curing when these silanes are prepared from a 1% solution. This result supports the initial assumption that oligomerization is suppressed by silylation from a 1% solution. The surface stabilities of **1** and **2** appear to be reversed in this latter study (see Bonding Models below).

Kinetic Studies. Two-gram samples of the uncured silica–silanes **1–3**, prepared from a 10% silane in toluene solution, were covered with 100 mL of absolute ethanol. Aliquots were removed periodically and treated with 1% salicylaldehyde (excess). Figure 3 shows the results of the plot of reaction time vs. absorbance at λ_{max} = 404 nm. Conclusions and observations are listed below.

(1) Within seconds of ethanol treatment, some silane in each case was rapidly leached from the surface (**3** > **2** > **1**). This rapid initial loss was followed by a slower loss process which continued for the 6-day duration of the kinetic experiments. In no case did the loss exceed 15% removal of the silane.

(2) We interpret the rapid initial loss as being due to the facile removal of species which are merely hydrogen bonded to the surface. We interpret the slower loss process as being due to covalent bond cleavage of the silane attachments to the surface. Simple occlusion of the silanes in the surface pores would probably not show such a consistent and definite difference in leaching rates because the diffusion coefficient of the silanes investigated should be similar except for the surface interactions.

(3) Relative solvolysis rates are in the order **3** > **2** > **1**. This order probably reflects an increase in the number of covalent bonds to the surface and to neighboring bound silanes. Electronegativity and mechanistic consideration[16,17] suggest that in these amine-catalyzed systems, the solvolysis rate for a single siloxane bond should be in the reverse order (**3** > **2** > **1**) which supports the multiple bond interpretation.

(4) Silanes **1** and **2** are similar in solvolysis rate and very different from that of **3**. Again, this argues against the formation of long polymers on the surface from **1** since **2** can, at best, form dimers. This argument is more compelling as a result of the long-term study as the data is less obscured by the rapid initial loss of merely hydrogen-bonded silanes.

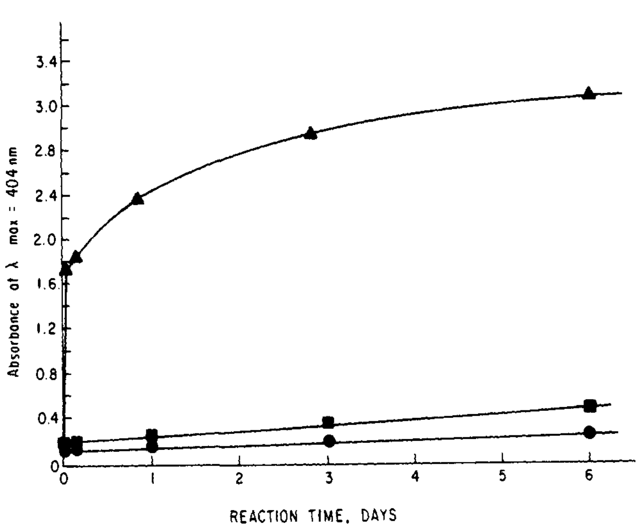
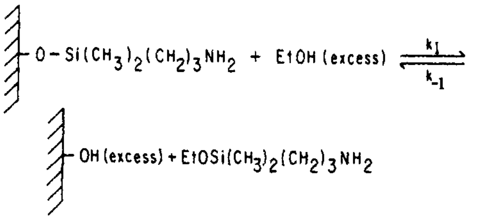


Figure 3. Absorbance at λ_{max} 404 nm of salicylaldehyde–ethanol supernatant as a function of reaction time for uncured silica–(3-aminopropyl)silanes: **1**, ●; **2**, ■; **3**, ▲.

(5) The five data points for **3** spanning reaction time of 0–6 days reflect reversible pseudo-first-order kinetics for **1** shown in reaction 1. With the absorbance at equilibrium (A_e) set at 3.0, a plot of log ($A_e - A$) vs. time is linear (r = −0.999) with a slope equal to −0.236 ($k_1 + k_{-1}$) and a y intercept equal to 0.102 (log ($A_e - A_0$)).



(1)

(6) After the 6-day reaction period, the solids **1–3** were isolated by filtration. Treatment of each with salicylaldehyde in ethanol produced the yellow Schiff's base color, confirming that some silane still remained covalently bound to the surface.

Copper(II) Capacity Studies. The relative silane surface stabilities for **1–3** have been measured by the quantity of silane released from the surface in ethanol. The results have been confirmed by a method which measures the relative amounts of **1–3** *remaining on the surface* after repeated treatment with aqueous solutions. Different aqueous solutions (acetate buffer at pH 5, 10^{-2} M copper(II) at pH 5, and nitric acid at pH 2) were pumped through a switching valve controlled by a microprocessor, through a HPLC column packed with silica–silane **1**, **2**, or **3** to a mixing chamber. A colorimetric complexing agent (1,2-cyclohexylenedinitrilo)tetraacetic acid (CYDTA) flowed from a peristaltic pump to a mixing chamber. The CYDTA reacted with the metal ion and flowed to a spectrophotometer.[6,18] Capacities of each silane for Cu(II), after cyclic metal ion–acid treatment, were determined by programming the microprocessor to set a flow rate of 1.00 mL/min and measurement of the Cu(II) complex peak area resulting from acid elution of copper from the column.

Figure 4 summarizes the relative capacity loss for **1–3** (i.e., column cycles vs. C/C_0, where C equals cycling capacity and C_0 equals initial capacity). The silane-surface stability order (**1** > **2** > **3**) obtains.

Trimethylsilyl Chloride Uptake Studies. In order to gain further insight into silane-to-surface bonding, we prepared silica–silanes

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Table I. Trimethylsilyl Chloride Uptake Results

sample	% C[a]	mol of initial silane[b]	% C from Me_3SiCl	mol of new Me_4Si[b]	mol initial silane + mol of new Me_4Si[b]
6 (reaction 4)	1.05	0.087 ± 0.012			
5 (reaction 3)	1.23	0.051 ± 0.006			
4 (reaction 2)	1.20	0.033 ± 0.004			
6 + Me_3SiCl	2.37		1.32	0.037 ± 0.004	0.124 ± 0.013
5 + Me_3SiCl	2.38		1.15	0.032 ± 0.004	0.083 ± 0.007
4 + Me_3SiCl	2.39		1.19	0.033 ± 0.004	0.066 ± 0.006
Baker silica gel + Me_3SiCl	2.44		2.44	0.068 ± 0.004	0.068 ± 0.004

[a] Huffman Laboratories, Wheatridge, CO. Includes subtraction of silica gel blank. [b] Mol/100 g of sample.

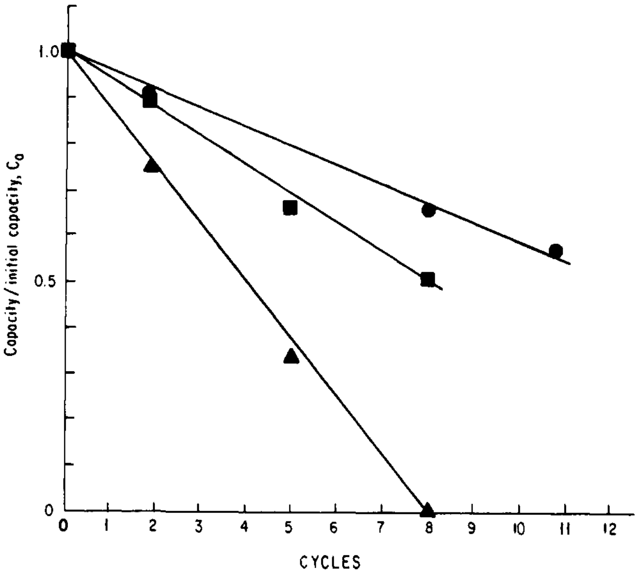
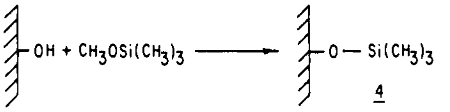


Figure 4. Relative capacity change, $\Delta C/C_0$, as a function of cycle number. Capacity is measured in mmol of Cu(II)/g of substrate: **1**, ●; **2**, ■; **3**, ▲.

4–6 from 5.00 g of Baker silica gel and 5% (v/v) toluene solutions according to reactins 2–4. Product structures **4–6** are drawn to



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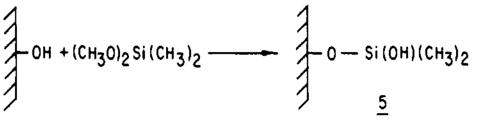

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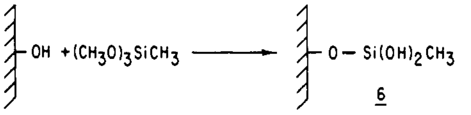

(4)

indicate the potential of each silane to generate a different number of silylatable hydroxyl groups from hyrolyis by trace water.[19] This bonding concept might be tested by comparing **4–6** with regard to uptake of trimethylsilyl groups when each silica–silane is subsequently treated with excess trimethylsilyl chloride in toluene. Table I presents the results of this event with organosilane uptakes measured by percent carbon analyses.

It is first noteworthy that the silica gel treated only with Me_3SiCl (blank) contains the same number of mol of Me_3Si/100 g as does sample **4** treated with Me_3SiCl. This is expected since the initial silane reagent in **4** is itself a Me_3Si grouping although less reactive than trimethylsilyl chloride. Samples **5** and **6** then take up more Me_3SiCl than expected, with **6** taking up more than **5**. These results are in accord with reactions 2–4. However, these reactions apparently do not proceed quantitatively as written. A silica sample containing 0.051 mol of **5** and hence 0.051 mol of possible "new" Si–OH from the organosilane should take up 0.051 mol of Me_3SiCl more than sample **4**. The actual difference is about 0.017 mol, indicating that only one-third of the "new" OH groups are free and reactive to Me_3SiCl. Similarly, a silica sample containing 0.087 mol of **6** and hence 2(0.087) = 0.174 mol of possible "new" OH should take up 0.174 mol of Me_3SiCl over sample **4**. The actual difference is about 0.058 mol, indicating, again, that only one-third of the "new" OH groups are free and silylatable by Me_3SiCl.

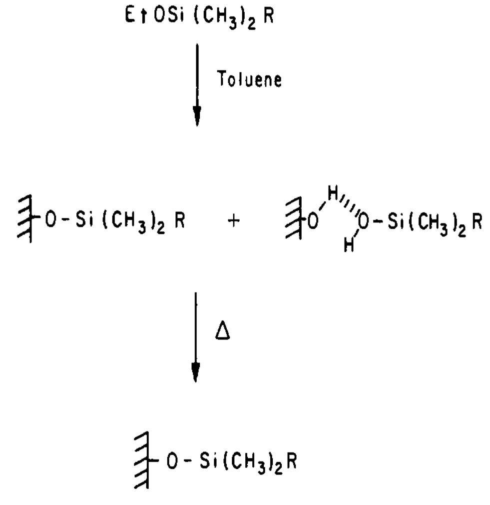

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Figure 5. Bonding model: (3-aminopropyl)dimethylsilane (R = 3-aminopropyl).

One may readily observe that the total percent carbon on all Me_3SiCl treated samples is very similar. However, this is not directly significant because of the conversion of percent carbon to moles of silane. The important values are the differences given in the last two columns of Table I, all of which are much larger than the expected error reported as one standard deviation. The possibility that the silanes bonded to the surface prior to the Me_3SiCl treatment may be hydrolyzed by HCl and released during the course of the reaction has been investigated in two experiments. First, primary amines have an NH_2 deformation absorption near 1600 cm^{-1}. The exact frequency of this band depends on the type (donor or acceptor) and strength of hydrogen bonding present. (Aminopropyl)silane bonded to silica gel show this absorption when the treated silica is mulled in a halocarbon solvent and the Fourier transform infrared spectrum is taken. After the reaction with Me_3SiCl, the absorption is still present with about the same intensity.

In a second set of experiments, thermometric enthalpy titration of the amino function on the silica gel–immobilized amino silanes reported here shows that the Me_3SiCl treatment does not affect the number of amino silane groups on the surface.[20] Samples of Me_3SiCl-treated products were allowed to stand in water 20

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(20) Grime, J. K.; Sexton, E. D.; Waddell, T. G.; Leyden, D. E., unpublished results.

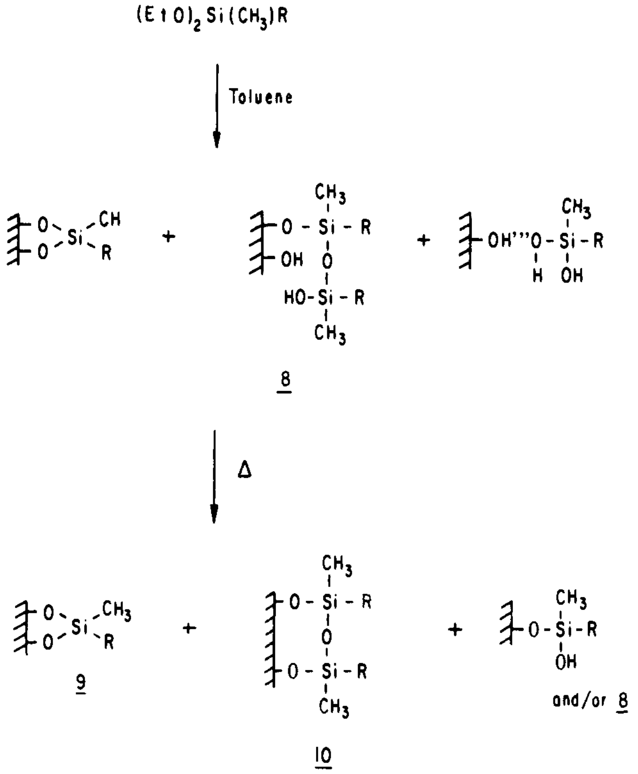

Figure 6. Bonding model: (3-aminopropyl)methylsilane (R = 3-aminopropyl).

min. The supernatant liquid was then removed and replaced with fresh solvent. Subsequent titration of the amine function with perchloric acid revealed amino group capacities consistent to within 2–5% with capacity and elemental carbon determinations obtained on non-Me_3SiCl treated samples.

Bonding Models. Figure 5–7 present silica-to-silane bonding structures which contain features supported by these stability, kinetic, and Me_3SiCl-uptake experiments on samples prepared from 5.00 g of silica gel and 20 mL of 10% (v/v) silane in toluene. It is tempting to generalize these features to all silica–silanes. However, reaction conditions, stoichiometry, and silane class can affect the nature of the bonding.

The preparation of silica–(3-aminopropyl)dimethylsilane (**3** and **7**) follows the reactions of Figure 5. Oven curing does improve surface stability and hence the inclusion of the hydrogen-bonded species. The more rapid solvolysis of this silane than the others from the surface, and the chemical structure of the silane itself, suggests one covalent bond per group.

In Figure 6, the situation of silica–(3-aminopropyl)methylsilane (**2**) is more complex. Oven curing has a significant effect on surface stability. Therefore, uncondensed OH groups are included prior to heating (as in **8**). Solvent ethanol immediately removes a small quantity of silane from the uncured surface, implying the hydrogen-bonded species is prevalent. That **2** is more stable on the surface than **3** requires more than one covalent bond to the surface as in **9** and **10**. Finally, the Me_3SiCl uptake experiments are suggestive of some uncondensed OH groups remaining after curing (as in **8**). The reaction model shown in Figure 6 is very similar to that proposed by Gilpin and Burke for the bonding of dimethyldichlorosilane to silica surfaces.[21]

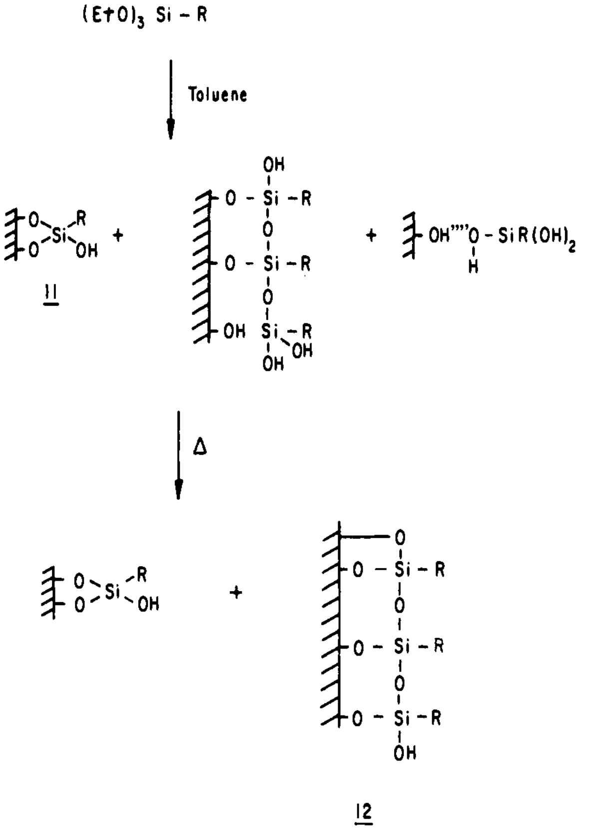

Figure 7. Bonding model: (3-aminopropyl)silane (R = 3-aminopropyl).

The behavior of the most surface stable of the silica–(aminopropyl)silanes (**1**) implies bonding as in Figure 7. Oven curing has a significant effect on surface stability. Therefore, uncondensed OH groups are included prior to heating. Solvent ethanol immediately removes a small quantity of silane from the uncured surface, implying the hydrogen-bonded species. That **1** is more surface stable than **2** requires more than two covalent bods to the surface as in **12**. And, as discussed, the smaller surface stability difference between **1** and **2** than between **1** or **2** and **3** suggests that dimers and trimers exist for **1** on the surface (as in **12**) but not long polymers.

This last point is supported by the properties of **1**–**3** prepared from 1% (v/v) silane in toluene (see Figure 2). In this situation, where oligomerization is suppressed, the concept shown in Figure 5 still holds since **3** is affected by oven curing. The surface bonding models for **1** and **2** must change, however, since oven curing does not affect their surface stabilities which now appear to be reversed. We propose that these observations can be understood in terms of monomeric structures **9** and **11** where, in both cases, two covalent bonds are formed during the silylation reaction and persist during curing. The apparent reversal in surface stability (**2** > **1**) may be related to differences in solvolysis rate between **9** and **11**.

Acknowledgment. We wish to thank Douglas Kendall, Peter Carr, and Dwight Williams for numerous valuable discussions and critical comments on this paper. The financial support of the National Science Foundation (Grant No. CHE-78-23123), the AMAX Foundation, and the Dreyfus Foundation is gratefully acknowledged.

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