Chemistry of Silane Coupling Reactions. 1. Reaction of Trimethylmethoxysilane and Triethylsilanol Studied by Gas–Liquid Chromatography

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ABSTRACT: The conditions under which reaction will occur and the products of reaction between trimethylmethoxysilane and a model for a glass surface, triethylsilanol, were studied by gas-liquid chromatography. Reaction occurred faster and under milder conditions than anticipated. Immediately after mixing at room temperature, methanol and the unsymmetrical disiloxane, 1,1,1-triethyl-3,3,3-trimethyldisiloxane, were formed; water formed soon thereafter. Simultaneously, the concentration of trimethylmethoxysilane decreased dramatically and the concentration of triethylsilanol decreased to a degree comparable to the amount of unsymmetrical disiloxane formed. The symmetrical disiloxanes were also present and their concentrations were monitored. After about 2 h an apparent equilibrium was attained with the unsymmetrical disiloxane as about 60% of the product, but at very long times, 5–10 days, the reaction mixture contained more than 90% 1,1,1-triethyl-3,3,3-trimethyldisiloxane. These reactions occurred readily either neat or in acetone, benzene, benzene–octane, or octane as solvent. Addition of acetic acid, *n*-propylamine, or phenyl-β-naphthylamine as possible catalysts may have increased the rate of redistribution slightly but did not alter the type or amount of products significantly. These studies of model reactions give new insight into the function of silane coupling agents in reactions on glass surfaces and suggest a three-stage reaction mechanism in which water is a by-product and not a primary catalyst.

Silane coupling agents are especially important for promoting bonding of various adhesives to glass and to metal. The formation of a siloxane bond between the silanol groups of glass and a silane coupling agent has previously been demonstrated by infrared and near-infrared analysis.[1-3] In principle, infrared analysis is a good way of following the progress of this condensation reaction; in practice, it is far from ideal because the concentration of the silanol groups is low and because infrared analysis does not distinguish between pure compounds and mixtures of siloxanes that probably are formed during these reactions. We were interested in forming siloxane bonds between glass and a silane under very mild conditions and needed detailed information about conditions under which these bonds can be formed and about their stability after formation. We therefore undertook a study by gas-liquid chromatography of reactions between a model for a glass surface, triethylsilanol (Et_3SiOH), and two model silanes, trimethylmethoxysilane (Me_3SiOMe) and dimethylmethoxysilane terminated poly(butadiene) [$(PB)\text{-}Me_2SiOMe$]. These studies form parts 1 and 2 of this series, respectively. The method has proven very useful for following these reactions. In previous reports the preparation of siloxanes from silanols and their redistribution (linearization) in the presence of other siloxanes were carried out at high temperature, in polar solvents, and/or were catalyzed by acids or alkalies.[1-8] Our studies show that the reactions occur just as readily at room temperature, in nonpolar media, and without catalyst. A revised three-stage mechanism for the reaction has emerged.

Experimental Section

(a) Materials. Me_3SiOMe from PCR was fractionated under nitrogen through a 5 in. Vigreux column (bp 55.5–57 °C). Gas-liquid chromatography (GLC) indicated that the main fraction consisted of 86% Me_3SiOMe and 14% hexamethyldisiloxane [$(Me_3Si)_2O$], the same as the undistilled product. Since fractionation did not lead to pure Me_3SiOMe or the sample immediately reacted to form some disiloxane, the apparently stable mixture was used. Its NMR spectrum was consistent with this composition. Et_3SiOH from PCR was used as received. GLC indicated that the sample contained 88% Et_3SiOH and 12% hexaethyldisiloxane [$(Et_3Si)_2O$]. The NMR spectrum was consistent with this composition. Tetraethylsilane (Et_4Si) from PCR, used as received, was greater than 99% pure by GLC. *n*-Octane (C_8H_{18}) and benzene (C_6H_6) were refluxed under nitrogen over CaH_2 for 2 h and then fractionated. Only the constant boiling center cut was used. Reagent grade acetone (AcMe), glacial acetic acid (AcOH), and phenyl-β-naphthylamine (PBNA), duPont's Neozone A, were used as received. *n*-Propylamine ($PrNH_2$) was distilled under nitrogen just before use (bp 48 °C).

(b) Reactions of Silanes. All reactions for GLC were carried out in 2 dram vials with polyethylene snap caps. With monomers the order of addition to the vial was always Et_3SiOH or Et_4Si, C_8H_{18}, C_6H_6 or AcMe, $PrNH_2$ or AcOH or PBNA, and Me_3SiOMe.

(c) Chromatography. Most gas-liquid chromatograms were obtained using a Hewlett Packard 5750 chromatograph fitted with an SE30 column, a flame ionization detector, and a Perkin-Elmer Model 194B printing integrator. The usual program was 4 min at 60 °C followed by heating at 60 °C/min to 160 °C, and then 8 min at 160 °C. The injection port temperature was 220 °C. Some variations are described along with results. A few gas-liquid chromatograms, notably in experiment 6, Table I, were obtained using a Hewlett Packard 5710A chromatograph similarly equipped except that data were taken in real time by a computer and subsequently analyzed by computer. In this way we were able to eliminate subjectivity in analysis of the data and to show that the GLC results, although constant for any given program, depended somewhat on the program used.

Molecular weights of monomers were obtained on a Chemalytics MC-2 chromatogram with 10% DC 410 columns and gas density detectors using a programmed heating rate of 10 °C/min from 25 to 250 °C. Sulfur hexafluoride and carbon dioxide were used as carrier gases.

(d) NMR. A Varian T-60 NMR spectrometer was used to record NMR spectra of neat compounds.

Results and Discussion

(a) Formation of Methanol. One of the most striking features of all the reactions carried out between Et_3SiOH and Me_3SiOMe (Table I, experiments 1–9 and 12–15) was the appearance within 10–15 s of a cloudy solution which very soon separated into a clear solution with a small, more dense phase (a drop) in the bottom of the vial. Retention time, peak enhancement, and molecular weight determination indicated that this lower phase was mainly MeOH. Deliberately added MeOH was immisible in the mixtures and became part of the lower phase. The volume of this phase was approximately equal to the volume of

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Table I
Quantities Used for Gas-Liquid Chromatography Studies[a]

expt no.	Et_4Si[b]	Et_3SiOH[b]	Me_3-SiOMe[b]	C_8H_{18}[c]	C_6H_6[c]	AcMe	AcOH	$PrNH_2$	PBNA
1		96	83						
2		96	83	45					
3		96	83	35	96				
4		96	83	35	96		0.45		
5		96	83	35	96			2.2	
6[d]		96	83	35	35		0.45		
7		96	83	35	35				0.1 g
8		50	200	35	96				0.1 g
9		96	83	35	35				
10	113		83	35	35				
11	113		83	35	35				0.1 g
12		96	83		35		0.45		
13		96	166		35		0.45		
14		96	332		35		0.45		
15		96	83			35	0.45		

[a] All quantities are given in μL unless otherwise indicated. [b] 96 μL of Et_3SiOH = 83 μL of Me_3SiOMe = 113 μL of Et_3Si = 6.0×10^{-4} mol assuming reactants are pure. As stated above the Et_3SiOH contained 88% Et_3SiOH and 12% $(Et_3Si)_2O$ and the Me_3SiOMe consisted of 86% Me_3SiOMe and 14% $(Me_3Si)_2O$ by gas-liquid chromatography. Since the disiloxanes were also reactive and their densities were not very different from those of the parent compounds, the measured volumes used were calculated as if the compounds were pure. See Table II. [c] Concentrations were chosen so that usually C_8H_{18} but sometimes C_6H_6 could be used as internal standard. [d] This experiment was followed on both gas chromatographs described in the experimental section.

Table II
Properties of Materials in Reaction Mixtures of Me_3SiOMe and Et_3SiOH

compd	mol wt obsd	mol wt theor	d_4^{20}	ref
Me_3SiOMe	105.5	104.2	0.7560	9
C_6H_6	78.3	78.1	0.879	10
$(Me_3Si)_2O$	162.5	162.2	0.7636	9
C_8H_{18}	113.9	114.2	0.703	10
Et_3SiOH	139.6	138.3	0.8645	9
$Et_3SiOSiMe_3$	205.7	204.2	0.8443	9
$(Et_3Si)_2O$	246.0	246.2	0.8110	9
MeOH	35	32.0	0.792	10
AcMe	59.3	58.1	0.791	10
Et_4Si			0.7658	9
H_2O			0.9982	10

MeOH that would be expected to be formed in a given reaction according to eq 1 in the conclusions.

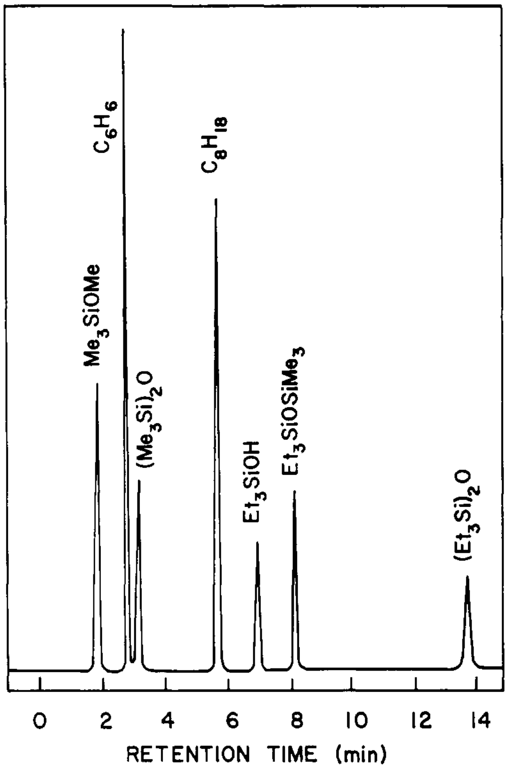

Figure 1. Typical gas-liquid chromatogram of the upper phase of a reaction mixture containing Me_3SiOMe (200 μL) and Et_3SiOH (50 μL) recorded 5 min after adding the Me_3SiOMe. (See experiment 8, Table I.)

(b) Formation of Water. At first it seemed strange that MeOH should appear in a more dense phase in these mixtures, especially when the densities of the various compounds possibly present in the mixtures are compared as in Table II. Repeating experiment 2, Table I, in the presence of white anhydrous copper sulfate, or adding the anhydrous copper sulfate to a similar reaction mixture after the appearance of the second phase, resulted in a bluish-green drop. When the copper sulfate was added at the beginning of the reaction, a yellow color appeared while the solution was cloudy and before the appearance of the green droplet. Neither neat C_8H_{18} nor neat Et_3SiOH had any effect on the color of the copper sulfate. Neat Me_3SiOMe gave the copper sulfate powder a yellow color, which turned green only on the addition of a trace of water. We concluded that some water was formed and that the relatively more polar MeOH was pulled out of the solution by that water even in the presence of acetone (Table I, experiment 15). Water does not show in gas-liquid chromatograms if flame ionization detectors are used, so it is not surprising that we did not see water in our gas-liquid chromatograms. Thus the very rapid appearance of MeOH is the first evidence that contrary to expectations based on the literature,[1-8] the reaction between Et_3SiOH and silanes is very fast even at room temperature and needs no catalyst. Proof that the Et_3SiOH is necessary for the formation of the second phase is given by the experiments between Et_4Si and the silanes (Table I, experiments 10 and 11), since no MeOH or water that could be detected by GLC or by anhydrous copper sulfate was formed in these reactions.

(c) Known Materials. A typical gas-liquid chromatogram of the upper phase from experiment 8, Table I, is shown in Figure 1. In contrast to the lower phase, which was principally MeOH, this phase contains seven different components. Four of them, two reactants and two solvents, were charged and the peaks associated with them were readily identified by retention time and peak enhancement

Table III

Effect of Time on Amounts of Materials in Reactions of Et_3SiOH (or Et_4Si) and Me_3SiOMe[a]

expt no.[b]	catalyst	time	Me_3SiOMe	$(Me_3Si)_2O$	Et_3SiOH	$Et_3SiOSiMe_3$	Et_4Si
9		0 s	0.660[c]		1.70[d]		
		10 s	0.137	0.575	1.37	1.16	
		30 min	0.052	0.322	0.595	1.80	
		2.6 h	0.123	0.227	0.225	1.93	
		24 h	0.086	0.358	0.245	1.78	
		10 days	0.201	trace	trace	2.89	
7	PBNA	0 s	0.660[c]		1.70[d]		
		2 min	0.167	0.506	1.00	1.15	
		28 min		0.552	0.668	1.32	
		24 h	0.092	0.288	0.282	1.76	
		10 day		trace	0.078	2.83	
10		0 s	0.660[c]				1.61[e]
		10 s	0.667	0.079			1.62
		67 min	0.617	0.248			1.62
		24 h	0.502	0.203			1.44
11	PBNA	0 s	0.660[c]				1.61[e]
		3.5 min	0.519	0.027			1.54
		20 min	0.617	0.248			1.62
		24 h	0.468	0.102			1.47

[a] All amounts are for the upper phase and are expressed as area ratios to octane. The GLC's were run on the Hewlett Packard 5750 chromatograph with the usual program except that the maximum temperature was 100 °C. [b] See Table I. [c] Taken from the calibration curve of area Me_3SiOMe/area C_8H_{18} vs. volume Me_3SiOMe/volume C_8H_{18}. [d] Taken from the ratio of area Et_3SiOH/area C_8H_{18} in the reaction mixture before addition of the Me_3SiOMe. [e] Taken from the ratio of area Et_4Si/area C_8H_{18} in the reaction mixture before addition of the Me_3SiOMe.

Table IV

Effect of Time and GLC Conditions on Materials in Reactions of Et_3SiOH and Me_3SiOMe[a]

time, days	initial column temp, °C[b]	Me_3SiOMe	$(Me_3Si)_2O$	C_8H_{18}	$(Me_3Si)_2O + C_8H_{18}$	Et_3SiOH	$O(Me_3Si)Et_3Si$	$(Et_3Si)_2O$
1	80	0.072			0.83	0.22	3.61	0.49
2	80	0.059			0.79	0.07	3.02	0.58
5	80	0.050			0.69	0.05	2.30	0.72
5	80	0.049			0.79	0.05	1.99	0.71
5	70	0.050	0.247	0.447	0.69	0.05	2.30	0.72
5	60	0.052	0.313	0.523	0.83	0.15	2.81	0.85
5	60	0.053	0.253	0.603	0.86	0.16	2.88	0.85

[a] All amounts are for the upper phase and are expressed as area ratios to benzene. The GLC's were run on the Hewlett Packard 5710A chromatograph. Under some conditions this chromatograph did not resolve the $(Me_3Si)_2O$ and C_8H_{18} peaks. All data are derived from experiment no. 6, Table I, where HOAc was used as catalyst. The maximum column temperature was 160 °C. [b] 80 °C is the normal initial temperature for the 5710A chromatograph.

and were confirmed by molecular weight determination (see Table II). The first, second, fourth, and fifth peaks to appear were thus shown to be those of Me_3SiOMe, C_6H_6, C_8H_{18}, and Et_3SiOH, respectively.

(d) Impurities in the Starting Materials. As stated in section (a) of the Experimental Section Me_3SiOMe and Et_3SiOH each contained slightly more than 10% of an impurity. Their NMR spectra and well-established silane chemistry indicate that these impurities should be the corresponding symmetrical disiloxanes, $(Me_3Si)_2O$ and $(Et_3Si)_2O$. Retention time and molecular weights of the materials responsible for the third and seventh peaks in Figure 1 were consistent with this interpretation. (See Table II and Figure 1.)

(e) Products. The only peak that cannot be identified on the basis of the materials charged is the sixth peak. The most probable product from the reaction of Me_3SiOMe and Et_3SiOH is 1,1,1-triethyl-3,3,3-trimethyldisiloxane ($Et_3SiOSiMe_3$). Both retention time and molecular weight indicate that the sixth peak can be associated with $Et_3SiOSiMe_3$. Significantly a compound of molecular weight 90.2 corresponding to trimethylsilanol (Me_3SiOH) was not found among the products of our reactions, although we looked for it repeatedly. Once or twice a trace of material with molecular weight 86–91 was found in the tracings from the MC-2 chromatogram, but for all practical purposes, Me_3SiOH was absent. Its absence argues against a mechanism involving hydrolysis of Me_3SiOMe to the corresponding silanol before condensation with Et_3SiOH.

(f) The Role of Water. Further insight into the role of water in reactions of a silane and a silanol was obtained from an experiment in which water (10 μL) was added to a mixture of Me_3SiOMe (150 μL) and Et_3SiOH (50 μL). The effect of the water was to convert nearly all of both starting materials to their corresponding symmetrical disiloxanes and to increase the unsymmetrical disiloxane only slightly. Since, as will be seen below, the amount of $(Et_3Si)_2O$ hardly changed and Et_3SiOH decreased slowly during the first 24 h of our reactions, we believe that our reactions were initiated in anhydrous conditions and that the water that formed did not have an important effect.

(g) Effect of GLC Conditions. Tables III and IV show that GLC conditions have an important effect on the results obtained. The same time program was used throughout the study, but temperatures were varied. The data in Table III were obtained with a maximum column temperature of 100 °C and those in Table IV with a maximum temperature of 160 °C. The $(Et_3Si)_2O$ was eluted only with the higher column temperature. Table IV shows that if the initial column temperature is higher than 70 °C, $(Me_3Si)_2O$ and C_8H_{18} are not resolved. Since originally we intended to use the C_8H_{18} as the internal

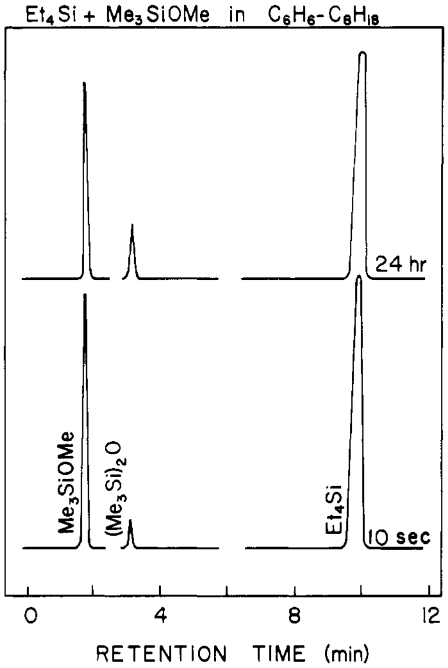

Figure 2. Gas-liquid chromatogram of a mixture of Me_3SiOMe (83 μL) and Et_4Si (111 μL) recorded at 10 s and 24 h after adding Me_3SiOMe. The C_6H_6 and C_8H_{18} peaks are omitted for simplicity. (See experiment 10, Tables I and III.)

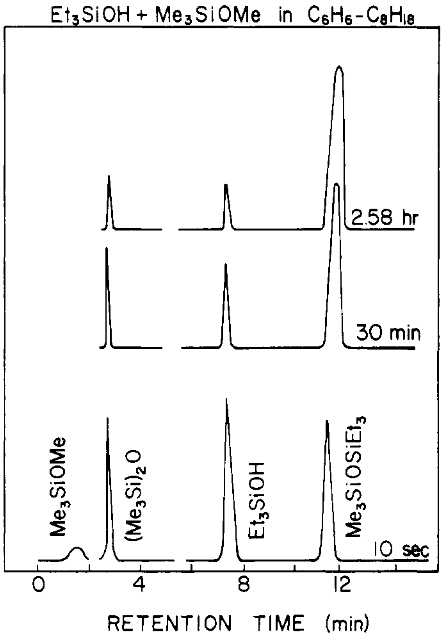

Figure 3. Gas-liquid chromatogram of the upper phase of a reaction mixture containing Me_3SiOMe (83 μL) and Et_3SiOH (96 μL) recorded 10 s, 30 min, and 2.58 h after adding Me_3SiOMe. The C_6H_6 and C_8H_{18} peaks are omitted throughout and the Me_3SiOMe peaks are omitted at 30 min and 2.58 h for simplicity. (See experiment 9, Tables I and III.)

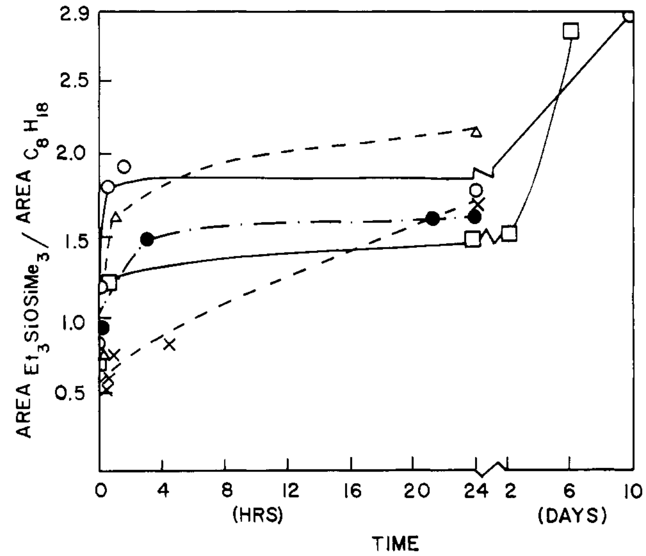

Figure 4. Variation of concentration of $Et_3SiOSiMe_3$ with time and catalyst in reactions of Et_3SiOH and Me_3SiOMe: ○, no catalyst, C_8H_{18} and C_6H_6 solvent; X, no catalyst, C_8H_{18} solvent; □, AcOH, C_8H_{18} and C_6H_6 solvent; △, $PrNH_2$, C_8H_{18} and C_6H_6 solvent; ●, PBNA, C_8H_{18} and C_6H_6 solvent.

standard, this is a serious deficiency. Both tables show some changes in composition that do not appear to be systematic or vary somewhat under identical conditions even when the data in Table IV were taken and analyzed by computer. The quantitative results clearly are very sensitive to GLC conditions. We concluded that reactions among silanes, disiloxanes, and silanols are very labile and restricted our analysis to gross changes.

(h) Effect of Time. Changes in the concentrations of the materials present in each reaction described in Table I were followed as a function of time. Some typical results are given in Tables III and IV and in Figures 3 and 4.

Changes at very short times, *15–30 s after mixing*, are most readily perceived by a comparison of the 10-s results for mixtures containing Et_4Si and Et_3SiOH and shown in Figures 3 and 4, respectively. These samples were injected into the gas chromatograph as quickly after the addition of the Me_3SiOMe as the mixture could be sampled. In the mixture containing Et_4Si, no reactions were expected and none were observed. The Me_3SiOMe was charged in large excess over the $(Me_3Si)_2O$ (88/14 molar ratio) and the ratio changed only slightly even after 24 h. (Compare experiments 10 and 11 in Table III.) No new products were formed. In contrast, when Et_3SiOH was used instead of Et_4Si, most of the Me_3SiOMe disappeared immediately. Notice the large decrease in the Me_3SiOMe peak and the large increase in the $(Me_3Si)_2O$ peak in Figure 4 compared to Figure 3. Notice also that some of the new product, $Et_3SiOSiMe_3$, was formed. As can be seen by comparing the 0-s and 10-s data for experiment 9, Table III, and the 0-s and 2-min data for experiment 7, Table III, there was a simultaneous decrease in the Et_3SiOH concentration. This decrease corresponded closely to the amount of $Et_3SiOSiMe_3$ formed. From similar experiments with higher maximum column temperatures where the $(Et_3Si)_2O$ was eluted, we learned that at this stage there was no change in the $(Et_3Si)_2O$ concentration.

From the above observations we can conclude the following under our conditions: (a) The silanol is required to catalyze the rapid conversion of Me_3SiOMe to disiloxanes. (b) The Me_3SiOMe is converted partially to $Et_3SiOSiMe_3$ and partially to $(Me_3Si)_2O$. Very little Me_3SiOMe remains. (c) The Et_3SiOH reacts with the Me_3SiOMe or some intermediate derived from the Me_3SiOMe but hardly at all with itself. Since much Et_3SiOH remains unreacted at these short times, it appears that the Me_3SiOMe is as likely to react with itself as with the Et_3SiOH.

There were no significant changes in concentrations of components of mixtures containing Et_4Si at longer times and we will not discuss them further. In mixtures containing Et_3SiOH, during *the next 2 to 3 h*, the concentrations of $(Me_3Si)_2O$ and Et_3SiOH continued to decrease in favor of that of $Et_3SiOSiMe_3$, which increased until apparent equilibrium concentrations were achieved. The

Table V
Effect of Varying Ratio of Me_3SiMe/Et_3SiOH on Products[a]

expt[b] no.	Me_3SiOMe/Et_3SiOH	Me_3SiOMe	$(Me_3Si)_2O$	Et_3SiOH	$Et_3SiOSiMe_3$	$(Et_3Si)_2O$
12	1:1[c]	0.012	0.223	0.061	1.46	0.560
13	2:1[c]	0.333	0.776	0.420	1.68	0.199
14	4:1[c]	0.836	1.11	0.614	1.13	0.0

[a] The standard GLC conditions were used. The concentrations of products are expressed as area ratios to C_6H_6. The data are for the upper phase in each case. [b] See Table I. [c] In C_6H_6 no C_8H_{18} was added.

concentration of $(Et_3Si)_2O$ was fairly constant during this period.

Studies at much longer reaction times, *1–10 days*, revealed a slower reaction resulting in significant decreases in the concentrations of the symmetrical disiloxanes, $(Me_3Si)_2O$ and $(Et_3Si)_2O$, plus the virtual disappearance of Et_3SiOH and yielding about 90% conversion to the unsymmetrical disiloxane, $Et_3SiOSiMe_3$.

(i) Effect of Relative Concentration of Reactants. The results of a series of experiments (no. 12–14 in Table I) in which the ratio of Me_3SiOMe to Et_3SiOH was varied from 1:1 to 2:1 to 4:1 are given in Table V. In no case was the Et_3SiOH completely converted to $Et_3SiOSiMe_3$. Instead the amount of unsymmetrical product formed after 24 h was relatively constant and the amount of Me_3SiOMe increased. There was a notable decrease in the amount of $(Et_3Si)_2O$ and a corresponding increase in the amount of Et_4SiOH as the relative amount of Me_3SiOMe was increased but the total amount of Et_3SiOH and $(Et_3Si)_2O$ was fairly constant. Thus it is not possible to increase the rate of conversion of silanol to unsymmetrical disiloxane by using a large excess of silane.

(j) Effect of Catalyst. In experiments 3–7 of Table I and in Figure 4 the effectiveness of AcOH, $PrNH_2$, PBNA, and nothing as catalysts for the coupling of Me_3SiOMe and Et_3SiOH was compared. The course of the reaction in each case was qualitatively the same as described above in section c. There was very little difference in the initial rate of formation of the disiloxane mixture. Possibly $PrNH_2$ and AcOH did increase the rate of subsequent redistribution of the disiloxane mixture to form the unsymmetrical disiloxane but the reaction was relatively slow in all cases and proceeded nearly to completion at very long times even in the absence of catalyst.

(k) Effect of Solvent. Previous workers have used either neat silanes or solutions of silanes in polar solvents such as ethanol or acetone to carry out coupling reactions with silica or glass surfaces.[1–8] Since ultimately we were interested in carrying out coupling reactions between silanated poly(butadiene) and glass, polar solvents are unacceptable because they do not dissolve the poly(butadiene). Therefore we compared reactions of Me_3SiOMe and Et_3SiOH neat and in acetone, benzene, octane, and benzene–octane mixtures (experiments 15, 12, 2, 6, and 4 in Table I, respectively). Methanol formed as a separate phase in every case and the same products were observed in each case. After 24 h, compared to benzene, the change to acetone resulted in increased amounts of unreacted Me_3SiOMe (12% compared to 0.5%) and of unreacted Et_3SiOH (3.0% compared to 2.0%). The amount of unsymmetrical disiloxane was also decreased from 63% for benzene to 47% for acetone. At least at the concentrations used, benzene was a better solvent for the coupling reaction.

Conclusions

Our studies with model compounds indicate that silane coupling agents should interact with glass surfaces to form primary chemical bonds. The reactions can occur at room temperature, without catalyst, neat or in a variety of solvents ranging from acetone with a dielectric constant of 20.7 to octane with a dielectric constant of 1.95. The reactions do not go to completion even at very long times and there appears to be a dynamic equilibrium among the siloxanes that are formed, although the unsymmetrical disiloxane is formed in the largest quantity.

The mechanism by which the interaction occurs is less certain. Water does not seem to be a necessary and primary catalyst that acts by hydrolyzing the silane to a silanol, which then condenses with existing silanol groups as has been suggested previously.[1] Any mechanism that is written must account for the following experimental observations:

(a) *Immediately after mixing* $Me_3SiOMe/(Me_3Si)_2O$ (86/14 molar ratio) and $Et_3SiOH/(Et_3Si)_2O$ (88/12 molar ratio), MeOH, $(Me_3Si)_2O$, and $Et_3SiOSiMe_3$ are formed. Water forms rapidly also but the slightly delayed change in the color of anhydrous copper sulfate suggests it is a secondary product. Most but not all of the Me_3SiOMe is converted to products. Much Et_3SiOH persists and the amount of $(Et_3Si)_2O$ hardly changes.

(b) During *the next 2–24 h* the concentration of $Et_3SiOSiMe_3$ increases while $(Et_3Si)_2O$ remains fairly constant. The concentrations of $(Me_3Si)_2O$ and Et_3SiOH decrease.

(c) *From 1–10 days* the concentrations of the remaining $(Me_3Si)_2O$ and $(Et_3Si)_2O$ decrease gradually until about 90% of the possible $Et_3SiOSiMe_3$ is formed after 10 days. Detectable amounts of Me_3SiOMe, $(Me_3Si)_2O$, Et_3SiOH, and $(Et_3Si)_2O$ persist even after 10 days.

Our data suggest that a three-stage reaction occurs. Et_3SiOH is sufficiently acidic to react directly with Me_3SiOMe in a very fast *first-stage* reaction that results in the formation of methanol and the unsymmetrical disiloxane:

$$Me_3SiOMe + Et_3SiOH \rightarrow MeOH + Et_3SiOSiMe_3 \quad (1)$$

The MeOH that forms then equilibrates with the $(Me_3Si)_2O$ present in the Me_3SiOMe to regenerate Me_3SiOMe and to form trimethylsilanol, Me_3SiOH, which is unstable with respect to $(Me_3Si)_2O$ and HOH:[4,13]

$$(Me_3Si)_2O + MeOH \rightleftharpoons Me_3SiOH + Me_3SiOMe \quad (2)$$

$$2Me_3SiOH \rightarrow (Me_3Si)_2O + HOH \quad (3)$$

These two reactions account for the persistance of Me_3SiOMe and $(Me_3Si)_2O$ in our reaction mixtures and for the formation of some water, which combines with the methanol to form a separate lower phase. The first stage is complete in 15–30 s.

Reactions of Et_3SiOH analogous to eq 2 and 3 probably also occur but they are much less important than with Me_3SiOH because Et_3SiOH is known to react in this way only $^1/_{600}$ as fast as Me_3SiOH under similar conditions.[11] The reactions do provide a mechanism for the persistance of Et_3SiOH and $(Et_3Si)_2O$ at long times. Et_3SiOH probably reacts faster with Me_3SiOMe and $(Me_3Si)_2O$ than it does with itself.

During the *second stage* additional unsymmetrical disiloxane is formed by reaction of $(Me_3Si)_2O$ with Et_3SiOH

$$Me_3SiOSiMe_3 + Et_3SiOH \rightarrow Et_3SiOSiMe_3 + Me_3SiOH \quad (4)$$

Again the Me_3SiOH that forms is removed rapidly by the reactions shown in eq 2 and 3. The net result of reactions 3 and 4 is to convert 1 mol of $(Me_3Si)_2O$ and 2 mol of Et_3SiOH to 2 mol of $Et_3SiOSiMe_3$ and 1 mol of HOH. This stage takes 2–3 h and accounts for the observed simultaneous disappearance of $(Me_3Si)_2O$ and Et_3SiOH.

The much slower *third stage* begins after most of the Et_3SiOH is gone and is the redistribution (linearization) reaction of the symmetrical disiloxanes that gives the unsymmetrical disiloxane as the product

$$(Me_3Si)_2O + (Et_3Si)_2O \rightarrow 2Et_3SiOSiMe_3 \quad (5)$$

Catalysts are not necessary for the first stage reaction but they may speed up the second and third stage reactions.

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Chemistry of Silane Coupling Reactions. 2. Reaction of Dimethylmethoxysilanated Poly(butadiene) with Triethylsilanol and with Glass

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ABSTRACT: Poly(butadiene) having a dimethylmethoxysilane end group has been found to react with a model silanol, triethylsilanol, in the same way as a simple silane does, yielding the addition product, methanol, and dimers of the two starting materials. This reaction takes place readily at room temperature in benzene solution. A corresponding addition reaction between silanated poly(butadiene) and the OH groups present on the surface of glass has therefore been inferred. This is corroborated by a greater degree of retention of silanated poly(butadiene) compared to unsilanated poly(butadiene) on glass slides subjected to thorough washing, and by direct observation of polymer particles, about 0.3 μm in size, adhering to the glass treated with silanated poly(butadiene).

In studying the effect of chemical bonding on the adhesion of elastomers to various substrates, it is important to separate the effects of two reactions: chemical bonding to the substrate, and cross-linking the elastomer to form a coherent solid. The first reaction can in principle be achieved by silane coupling[1-5] and the second by free-radical processes, so that it seems possible, at least in principle, to carry them out independently. In order to study the first reaction, a poly(butadiene) sample with a silane end group has been prepared. The reactions of this material with triethylsilanol, a model substance containing OH groups comparable to those on glass, and with glass itself, are reported here. To avoid cross-linking the poly(butadiene) these reactions have been carried out under mild conditions, at room temperature and in the presence of a stabilizer.

Experimental Section

(a) Materials. Sample I of silanated poly(butadiene) was prepared by anionic polymerization of butadiene in benzene using *sec*-butyllithium as initiator[6] and then terminating the reactive chain end by adding an excess of dimethyldichlorosilane. The resulting dimethylchlorosilanated poly(butadiene) was then converted to the corresponding methoxysilane $(PB)Me_2SiOMe$ by adding excess methanol. The polymer was isolated by precipitation in methanol. The product was purified by dissolving in benzene and reprecipitating again with methanol. Gel permeation chromatography (GPC) tracings indicated a bimodal molecular weight distribution with approximately half the product having a number-average molecular weight $\overline{M}_n$ of 1.5×10^5 and the other half having $\overline{M}_n = 3.0 \times 10^5$, Figure 1. We surmise that about half the poly(butadiene) had combined by end linking to form the disiloxane $(PB)Me_2SiOSiMe_2(PB)$. On this basis the silicon content of the polymer is computed to be $\sim 6.7 \times 10^{-6}$ mol of silicon per g of polymer.

Sample II of silanated poly(butadiene) was similarly prepared except that the reactive chain end was terminated by adding dimethylmethoxychlorosilane, which gave $(PB)Me_2SiOMe$ without further addition of methanol. This polymer had a unimodal molecular weight distribution with $\overline{M}_n \simeq 1.8 \times 10^5$.

A sample of poly(butadiene) of similar microstructure, but with unreactive end groups (Diene 35NFA), was obtained from the Firestone Tire and Rubber Co. It was dissolved in benzene and

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