Eds.; Pergamon Press: New York, 1958; p 24.

(3) Beredjick, N. In "Newer Methods of Polymer & Characterization"; Ke, B., Ed.; Interscience: New York, 1964; p 677.

(4) Jaffe, J.; Loutz, J. M. *J. Polym. Sci.* **1964**, *2*, 1669.

(5) Huggins, M. L. *Makromol. Chem.* **1965**, *87*, 119.

(6) Llopis, J.; Subirana, J. A. *J. Colloid. Sci.* **1961**, *16*, 618.

(7) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979.

(8) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.

(9) Vilanove, R.; Rondelez, F. *Phys. Rev. Lett.* **1980**, *45*, 1502.

(10) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95. *Phys. Rev. B: Condens. Matter* **1980**, *21*, 3976.

(11) Stephen, M.; McCauley, J. *Phys. Lett. A* **1973**, *44A*, 89.

Reinvestigation of the Reaction between Triethylsilanol and Trimethylmethoxysilane

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Recently, a report appeared concerning the reaction of triethylsilanol with trimethylmethoxysilane as a model for the reaction of a glass surface with a silane coupling agent.[1] A surprising result of that study was that Et_3SiOH and Me_3SiOMe reacted instantaneously upon mixing at room temperature in the absence of a catalyst. All previous reports had indicated that more vigorous conditions or the presence of a catalyst would be necessary to effect this reaction.[2,3]

We have reexamined the reaction between Et_3SiOH and Me_3SiOMe and have concluded that they do *not* react spontaneously at room temperature. We have shown that the presence of a chlorosilane contaminant, which may have been undetected in the previous study, will cause a fast reaction to occur.

Dreyfuss reported that within 10–15 s of mixing Et_3SiOH and Me_3SiOMe at room temperature, the solution became cloudy and phase separation soon occurred. The upper phase contained $Et_3SiOSiMe_3$ and the lower phase contained methanol (eq 1). When we repeated this experiment, no cloudiness or phase separation was observed and GC analysis indicated no reaction occurred over the course of several days at room temperature. Indeed, when equimolar amounts of Et_3SiOH and Me_3SiOMe were mixed, sealed in a glass ampule, and heated at 60 °C for a week, no reaction occurred.

$$Me_3SiOMe + Et_3SiOH \rightarrow Me_3SiOSiEt_3 + MeOH \quad (1)$$

A systematic investigation was carried out to discover the source of the discrepancy of observed reactivity. One possibility was that the reactants we used were contaminated with an inhibitor. Alternatively, the reactants employed by Dreyfuss may have been contaminated with a catalyst for the reaction.

The Me_3SiOMe, which was a commercial material distilled from K_2CO_3 prior to use in our studies, was >99% pure by GC analysis. Its elemental analysis was correct and established that it contained <0.1% Cl. The Et_3SiOH employed in our studies was prepared via the hydrolysis of Et_3SiH. The product contained 98% triethylsilanol and 2% hexaethyldisiloxane by GC analysis. The elemental analysis was correct and showed that the sample contained no Cl. The glassware used in our studies was new and was used as received. We conclude that our reactants were pure and did not contain an inhibitor for the reaction.

The reactants used by Dreyfuss were not pure. The Me_3SiOMe reportedly contained 14% $(Me_3Si)_2O$ even after distillation and the Et_3SiOH, which was a commercial material used as received, contained 12% $(Et_3Si)_2O$.

To determine whether a disiloxane could act as a catalyst in the condensation reaction, we added $(Me_3Si)_2O$ (14%) to Me_3SiOMe before mixing with Et_3SiOH. As expected, no reaction occurred even when the reactants were heated. Therefore it seems unlikely that a disiloxane acted to accelerate the condensation reaction in the Dreyfuss studies.

During earlier work in our laboratories, it was found that commercially available silyl ethers often contain impurities that make them highly reactive toward silanols. These impurities generally could not be removed either by simple distillation or by distillation from K_2CO_3. Since silyl ethers are prepared from chlorosilanes, the contaminants were likely to be residual chlorosilanes. Indeed, treatment of these impure silyl ethers with aqueous $AgNO_3$ gave an AgCl precipitate, indicating the presence of active chloride. HCl would be generated upon reaction of a chlorosilane impurity with silanols. HCl is known to be a catalyst for the reaction of silanol with methoxysilane and thus the high reactivity could be explained as a result of the in situ generation of a reaction catalyst.

It appears that the Me_3SiOMe used by Dreyfuss was contaminated with a chlorosilane, probably Me_3SiCl, in addition to the $(Me_3Si)_2O$ contaminant. In an attempt to verify this, various amounts of Me_3SiCl were added to Me_3SiOMe before mixing with Et_3SiOH, and the time lapse from mixing to appearance of cloudiness was noted. When the Me_3SiOMe contained 20–25% Me_3SiCl, a cloudy solution formed within 10–15 s after mixing with Et_3SiOH, just as Dreyfuss described. To see if the same result would be obtained when the Dreyfuss experimental procedure is followed, we fractionally distilled a mixture of 65% Me_3SiOMe, 20% Me_3SiCl, and 15% $(Me_3Si)_2O$ through a 5-in. Vigreux column. The fraction boiling at 58–60.5 °C (uncorrected) was combined with Et_3SiOH, and a cloudy solution formed after about 15 s. When the concentration of Me_3SiCl in Me_3SiOMe was lower, the time lapse between mixing with Et_3SiOH and appearance of cloudiness was longer.

It may seem surprising that 20–25% Me_3SiCl in Me_3SiOMe would not have been detected, but we have found that Me_3SiOMe and Me_3SiCl have the same retention time when Dreyfuss' GC conditions (SE-30 column, 60 °C) are used or when an SE-52 column at 60 °C or even at 30 °C is used. Furthermore, the average molecular weight of a 25% Me_3SiCl in Me_3SiOMe mixture is 105.3, which is within experimental error of the 105.5 value obtained from the MC-2 chromatogram in the previous study. On the basis of this evidence, we conclude that the Me_3SiOMe used in that study must have contained a high concentration of Me_3SiCl contaminant, which caused the Me_3SiOMe to appear highly reactive.

In a previous study carried out in our laboratories, an impure sample of Me_3SiOMe that reacted with Me_3SiOH upon mixing at room temperature was purified by refluxing over and distillation from NaOMe. After distillation from NaOMe, the Me_3SiOMe did not react with Me_3SiOH. Distillation of the impure Me_3SiOMe from K_2CO_3 yielded a sample of Me_3SiOMe that still reacted spontaneously with Me_3SiOH. Presumably, K_2CO_3 would remove any acidic impurities but NaOMe would be required to convert chlorosilane impurities to methoxysilane.

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Table I

% Me_3SiCl in Me_3SiOMe	result
0.1	no reaction after 30 min
1	~10% $Me_3SiOSiEt_3$ [a] formed in 30 min
5	solution became hazy in 5 min
10	solution became hazy in 75–90 s
20	solution became hazy in 15 s
25	solution became hazy in 10 s
50	solution became hazy in 5 s

[a] M^+ = 204 in chemical ionization mass spectrometer.

To further illustrate the lack of reactivity between a silanol and silyl ether in the absence of a catalyst, we carried out the following experiment. Me_3SiOH, which reacts 600 times as fast as Et_3SiOH in condensation reactions with silyl ethers,[2] was combined with $MeSi(OMe)_3$, which is more reactive than Me_3SiOMe.[3] After 30 min of heating at vigorous reflux, no reaction had occurred as shown by GC analysis.

Experimental Section

General Procedures. The silanes and hexamethyldisilazane were purchased from Silar Laboratories and were purified as described below. Gas chromatographic analysis was carried out with either a Hewlett-Packard 5830A gas chromatograph equipped with a 6 ft × $^1/_4$ in. glass column containing 10% SE-30 on Chromsorb 80/100 W-HP or a Hewlett-Packard 5750 equipped with 4 ft × $^1/_4$ in. stainless steel columns containing either 15% SE-52 on 80/100 W-HP 5750 or 15% SE-30 on 80/100 W-HP 5750. Infrared spectra were recorded as thin films on salt plates on a Perkin-Elmer 598, and NMR spectra were recorded using $CDCl_3$ solutions on a Varian T-60 spectrometer. Mass spectrometry was done with a Varian MAT 311A equipped with a combination chemical ionization–electron impact source.

Synthesis of Et_3SiOH. Et_3SiH (51.8 g, 0.45 mol) was dissolved in diethyl ether (96 g), and a mixture of H_2O (25 g, 1.4 mol), CH_3CN (13.3 g), and a small amount of Pd/C was added. The reaction was stirred at room temperature and monitored by GC. After 2 days, the reaction was complete. The top layer was decanted, filtered through Celite, and dried over $MgSO_4$, and solvent was removed by rotary evaporation. The last traces of CH_3CN were removed from the Et_3SiOH by adding toluene and then distilling the toluene/CH_3CN azeotrope and the excess toluene. The product obtained was 98% Et_3SiOH and 2% $(Et_3Si)_2O$ as established by GC analysis. The IR and NMR spectra were consistent. Anal. Calcd for $C_6H_{16}OSi$: C, 54.48; H, 12.19; Si, 21.24; Cl, 0. Found: C, 54.77; H, 12.00; Si, 20.16; Cl, <0.01.

Synthesis of Me_3SiOH.[4] $(Me_3Si)_2NH$ (17.5 g, 0.108 mol) was dissolved in 50 g of diethyl ether and the solution was added to a 500-mL flask containing 12.5 g of H_2O to which several drops of methyl orange indicator had been added. The mixture was stirred vigorously and cooled in a methanol–ice bath. Aqueous HCl (2 N) was added dropwise just until the indicator remained pink (about 70 mL). A small amount of $NaHCO_3$ was then added until the indicator was orange again. The aqueous and ether layers were separated, the aqueous layer was extracted with 50 mL of ether, and the combined ether fractions were dried over $MgSO_4$. After filtration, the ether was removed under vacuum to yield 18.6 g of Me_3SiOH (95%), which contained ca. 1% $Me_3SiOSiMe_3$ by GC analysis. The IR and NMR spectra were consistent.

Purification of Me_3SiOMe. Me_3SiOMe obtained from Silar Laboratories was distilled from anhydrous K_2CO_3, bp 56–57 °C, to yield pure Me_3SiOMe in which no impurities could be detected by GC. Anal. Calcd for $C_4H_{12}SiO$: C, 46.09; H, 11.61; Si, 26.95; Cl, 0. Found: C, 46.32; H, 11.70; Si, 26.42; Cl, 0.04.

Purification of $MeSi(OMe)_3$. Unpurified $MeSi(OMe)_3$ reacted spontaneously with Me_3SiOH at room temperature. Even after the $MeSi(OMe)_3$ was distilled from K_2CO_3, spontaneous reaction with Me_3SiOH occurred. However, after 20 g of $MeSi(OMe)_3$ was combined with 1 g of CH_3OH and 0.1 g of NaOMe and fractionally distilled through a 5-in. Vigreux column, bp 102–103 °C, to yield $MeSi(OMe)_3$ that was pure by GC analysis, no reaction with Me_3SiOH was observed after 30 min at reflux.

Reaction of Me_3SiOMe with Et_3SiOH. Me_3SiOMe (0.39 g, 3.8 mmol) and Et_3SiOH (0.50 g, 3.8 mmol) were mixed and the solution was analyzed by GC. The solution was sealed in a glass ampule and heated at 60 °C for 1 week. The ampule was opened and GC analysis of the solution showed that no reaction had occurred.

In another set of experiments, various amounts of Me_3SiCl were added to Me_3SiOMe before admixture with an equimolar amount of Et_3SiOH, and the room-temperature reaction was followed by GC or by the time required for a hazy solution to form. Results were as in Table I.

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References and Notes

(1) Dreyfuss, P. *Macromolecules* **1978,** *11* (5), 1031.

(2) Grubb, W. T. *J. Am. Chem. Soc.* **1954,** *76,* 3408.

(3) Noll, W. "Chemistry and Technology of Silicones"; Academic Press: New York, 1968; pp 94–101, 211–233.

(4) MacLaury, M. R.; Schroll, A. L., private communication of their modification of a synthesis first reported by: Sauer, R. O. *J. Am. Chem. Soc.* **1944,** *66,* 1707.

Reaction between Triethylsilanol and Trimethylmethoxysilane

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A few years ago we reported that products of the reaction between triethylsilanol (Et_3SiOH) and trimethylmethoxysilane (Me_3SiOMe) can be observed by gas chromatography (GC) immediately after mixing at room temperature.[1] We noted that the reaction occurred faster and under milder conditions than anticipated on the basis of earlier studies. White and Olson report that, contrary to our earlier observations, Et_3SiOH and Me_3SiOMe do not react spontaneously at room temperature and their mixtures can be stored for long periods without any products being formed.[2] White and Olson attribute the rapid reaction observed by us to the probable presence of the catalytic impurity trimethylchlorosilane (Me_3SiCl) and further suggest that the level of impurity is 20–25%. They argue that because Me_3SiOMe and Me_3SiCl have nearly identical boiling points, 57–58 °C and 57 °C, respectively, and similar molecular weights, 104.3 and 108.7, respectively, the presence of the Me_3SiCl could have gone undetected in our study.

Fortunately, we still have on hand a sample of the Me_3SiOMe used in our previous study and were able to characterize it further. Now, measured 6 years after the sample was received, the sample shows the presence of Me_3SiCl by mass spectrometry (direct analysis) (MS) but not by GC–MS. The presumption is that the Me_3SiCl is such a reactive compound that it does not survive intact even under relatively mild GC conditions. Duplicate chlorine analyses by Galbraith Laboratories, Inc., gave

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