

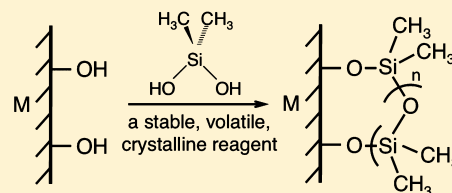
Hydrophobization of Inorganic Oxide Surfaces Using Dimethylsilanediol

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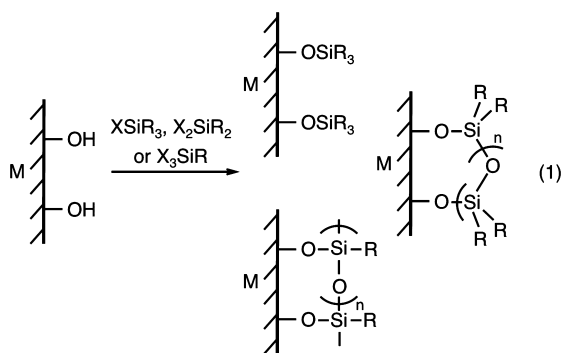
Supporting Information

ABSTRACT: Dimethylsilanediol is a stable crystalline solid that was described in 1953. As the monomer of an important class of commercial products (poly(dimethylsiloxanes)—silicones, PDMS) and as a simple molecule in its own right (the silicon analog of acetone hydrate), it has been neglected by several fields of fundamental and applied research including the hydrophobization of inorganic oxide surfaces. We report that dimethylsilanediol is a useful reagent for the surface modification (hydrophobization) of oxidized silicon and other oxidized metal surfaces and compare the wetting properties of modified solids with those of conventionally modified surfaces. That water is the only byproduct of this modification reaction suggests that this and likely other silanediols are useful surface-modification agents, particularly when substrate corrosion or the competitive adsorption of byproducts is an issue. We note that dimethylsilanediol is volatile with a significant vapor pressure at room temperature. Vapor-phase surface modifications are also reported.



INTRODUCTION

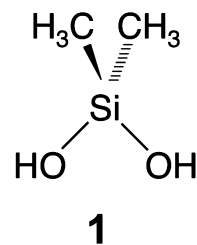
The modification of inorganic surfaces with self-assembled and covalently attached monolayers has a rich history and an enormous literature and is central to a wide range of technologies as well as current research programs.^{1–3} Silicon-based compounds containing groups that are reactive to metal oxides are by far the most important and versatile in this regard. Monofunctional, difunctional, and trifunctional reagents^{4,5} are useful (eq 1), and the R group can be varied in structure to control surface properties or reactivity for a plethora of different interface objectives.



The hydrolyzable groups in these reagents (X in eq 1) are generally halides (mostly chloro), amides (mostly dimethylamino), or alkoxides (mostly methoxy and ethoxy), and thus the byproducts of these reactions are acids, amines, and alcohols. The acid products are generally corrosive to inorganic substrates (amines are often added to reactions^{4,5}), and alcohols and amines compete for adsorption/reaction sites, affecting monolayer structure and properties. As solutions to this problem, we reported that hydrosilanes react with titanium and other metal surfaces to yield H₂ as an innocuous

byproduct⁶ and that siloxane polymers themselves can graft to oxide surfaces by equilibration (with no byproduct).⁷ A principal objective of these studies as well as those reported here was to develop modification reactions that rendered innocuous byproducts.

This Letter concerns reactions of dimethylsilanediol (1) with oxidized silicon and other oxidized metal surfaces. Several comments concerning this molecule and silanediols in general are warranted. This substance (the silicon analogue of acetone hydrate) was assumed to be unstable in the 1940s and early 1950s.^{8,9}



Sterically hindered silanediols were known to be stable and were reported^{10–12} by Kipping in the early 1900s; diphenyl, dibenzyl, ethylphenyl, and ethylbenzyl silanediols were described. Eaborn reported¹³ the diisopropyl-, diisobutyl-, and dicyclohexyl- derivatives in 1952. It must have been surprising to some when, in 1953, dimethylsilanediol (1) was reported^{14,15} in two nearly simultaneous publications as a crystalline solid that melts at ~100 °C.¹⁶ Hyde describes¹⁴ 1 as

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“no less stable under normal conditions than diphenylsilanediol.”

Despite the two 1953 reports, those of improved synthesis methods for **1**,^{17,18} the fact that **1** is found to be the major decomposition product of PDMS in at least seven different U.S. soils,¹⁹ and, in particular, that **1** can be considered to be the monomer of an important class of polymers (silicones), dimethylsilanediol and its stability are not currently appreciated by (at least certain groups of) chemical and materials scientists.^{7,20} This is not to say that silanediols have been neglected by all, and studies of their structure, stability, and chemistry are available in reviews of organosilanols.^{21,22} A recent report²³ of a sterically unencumbered silanediol (an α -amino acid with a δ -dihydroxymethylsilyl-*n*-butyl group) states that “dimethylsilanediol is unstable” and attributes the stability of the silanediol-containing amino acid to its water solubility. Sterically hindered silanediols have recently found use in hydrogen bond donor catalysis.^{24–28}

Our group was certainly guilty of an ignorance of silanediols and would have, more than a decade ago, used them in our studies on covalently attached monolayers^{4–6} had we been aware of their stability and ease of preparation. We describe here reactions of dimethylsilanediol with inorganic oxide surfaces and compare the resulting surface structures and wettability with those of samples prepared by reported (more standard) methods.

EXPERIMENTAL SECTION

Dimethylsilanediol (**1**) was prepared from $\text{Me}_2\text{Si}(\text{OEt})_2$ using essentially the same method¹⁴ reported by Hyde (Supporting Information). The procedure described in ref 19 suggests that the hydrolysis of $\text{Me}_2\text{Si}(\text{OMe})_2$ is significantly faster, but this was not studied. Kantor's method¹⁵ was also reproduced and is faster than Hyde's but involves heating. The recrystallization of **1** from toluene yielded platelets similar to those described¹⁴ by Hyde (from benzene). Samples stored in plastic vials are stable for months, and we observed mixed results in glass vials. Kantor notes¹⁵ reactivity with glass and suggests using quartz vessels. Hyde reports¹⁴ catalytic sensitivity to both acid and base and used Vycor vessels. We note that **1** sublimes in closed vials at room temperature and thus has a significant vapor pressure and a slightly sweet smell. We report the ¹H NMR and infrared spectra of **1** as Supporting Information. Sample preparation, handling, surface modification procedures, and characterization procedures were identical to the methods recently described.²⁹

RESULTS AND DISCUSSION

Reaction conditions for surface modification were chosen on the basis of procedures that were used for solution modification of silicon wafers (Si/SiO₂) with alkylchlorosilanes^{4,5} and direct modification of metal oxide surfaces (Ti/TiO₂, Al/Al₂O₃, and Ni/NiO) with PDMS.⁷ Table 1 shows water contact angle and

Table 1. Contact Angles and Ellipsometric Thicknesses for the Reaction of Si/SiO₂ with Me₂Si(OH)₂

| time | water contact angles (θ_A/θ_R) | ellipsometric thickness (nm) |
|--------|--|------------------------------|
| 5 min | 71°/57° | 0.29 |
| 10 min | 78°/64° | 0.42 |
| 20 min | 82°/67° | 0.40 |
| 30 min | 91°/84° | 0.56 |
| 60 min | 93°/85° | 0.61 |
| 5 h | 101°/86° | 0.62 |
| 18 h | 104°/89° | 0.62 |
| 72 h | 106°/92° | 0.64 |

ellipsometric thickness data for Si/SiO₂ samples that were submerged in 0.1 M $\text{Me}_2\text{Si}(\text{OH})_2$ (**1**) in toluene at 65 °C for various times. Untreated wafers are wet by water ($\theta_A/\theta_R = 0^\circ/0^\circ$). The contact angle data indicate that a significant amount of reaction occurs during the first 5 min of exposure (contact angles increase from $\theta_A/\theta_R = 0^\circ/0^\circ$ to 71°/57°) but that the reaction continues and slows over tens of minutes, hours, and days. Reactive surface silanols are significantly depleted after only minutes of reaction but are not exhausted until after many hours. The same trend is observed in reactions of Si/SiO₂ with the monofunctional silane compounds (that cannot polymerize), $\text{Me}_3\text{SiNMe}_2$,⁴ and $(\text{Me}_3\text{SiO})_3\text{SiCl}$,³⁰ and this suggests a random covalent attachment mechanism³⁰ rather than graft polymerization, self-assembly, or polymerization followed by adsorption. The ellipsometry data mirror the kinetics assessed by contact angle analysis, are consistent with this mechanism, and indicate that a thin (~0.6 nm) oligomeric layer (about two molecular layers thick) is formed. X-ray photoelectron spectroscopy data are consistent with this analysis (Supporting Information). The contact angle hysteresis is lower during the intermediate stage of reaction (30 and 60 min data) than either prior to or subsequent to this stage. This minimum in hysteresis is also observed for the reaction of Si/SiO₂ with $\text{Me}_3\text{SiNMe}_2$,⁴ and we make identical interpretations: in early stages, surface silanols are present, and in late stages, steric congestion inhibits flexibility in the covalently attached monolayer. Samples prepared using 30 or 60 min reaction times contain dimethylsiloxane groups that are flexible. These surfaces are liquidlike and lower the barriers between metastable states of the three-phase contact line. We have discussed this effect in detail.^{4,5}

These oligomeric dimethylsiloxane layers prepared from **1** in toluene solution are different than other dimethylsiloxane/PDMS layers that we have prepared, and Table 2 summarizes

Table 2. Contact Angles and Ellipsometric Thicknesses for Various Si/SiO₂-Supported Dimethylsiloxane/PDMS Layers

| conditions | water contact angles (θ_A/θ_R) | ellipsometric thickness (nm) |
|---|--|------------------------------|
| $\text{Me}_2\text{Si}(\text{OH})_2$, toluene, 65 °C, 72 h | 106°/92° | 0.64 |
| Me_2SiCl_2 , toluene, EDIPA, 70 °C, 72 h ^a | 92°/85° | 0.35 |
| Me_2SiCl_2 vapor 70 °C, 72 h ^a | 104°/103° | 2.55 |
| PDMS ²⁰⁰⁰ 100 °C, 24 h ^b | 104°/102° | 1.15 |
| PDMS ²⁰⁰⁰ 150 °C, 24 h ^b | 104°/102° | 3.10 |
| PDMS ⁹⁴³⁰ 100 °C, 24 h ^b | 106°/105° | 5.05 |
| $\text{Me}_2\text{Si}(\text{OH})_2$ vapor room temp, 24 h | 86°/67° | 0.48 |
| $\text{Me}_2\text{Si}(\text{OH})_2$ vapor 65 °C, 24 h | 97°/78° | 0.64 |
| $\text{Me}_2\text{Si}(\text{OH})_2$ vapor 110 °C, 18 h | 105°/87° | 2.10 |
| $\text{Me}_2\text{Si}(\text{OH})_2$ vapor 150 °C, 18 h | 106°/96° | 2.48 |

^aReference 5. ^bReference 7.

data for comparison. A 0.35-nm-thick monolayer forms on silicon from dichlorodimethylsilane in toluene with ethyldiisopropylamine (EDIPA) present.⁵ This surface (prepared using a 72 h reaction time at 70 °C) exhibits a lower advancing contact angle ($\theta_A/\theta_R = 92^\circ/85^\circ$) than those derived from **1**. It is closer to a monolayer than the surface prepared from **1** in toluene. The reaction of Si/SiO₂ with dichlorodimethylsilane in the vapor phase yields⁵ a significantly thicker (2.55 nm thick)

PDMS layer with very low hysteresis. Trimethylsilyl-terminated PDMS reacts with Si/SiO₂ to form covalently grafted polymer monolayers with structures and properties that depend on the reaction temperature, reaction time, and polymer molecular weight.⁷ Data for the two molecular weight samples studied (2000 and 9430 g/mol, i.e., PDMS²⁰⁰⁰ and PDMS⁹⁴³⁰) are included in Table 2. The volatility of **1** noted above permitted vapor-phase reactions, and the results of these experiments are listed as the last four entries in Table 2. Kinetics studies were not carried out, but it is clear that thermally activated oligomerization/polymerization is operative at the Si/SiO₂–air interface that produces relatively thick (compared to the reaction in toluene) PDMS layers.

Attempts to modify Ti/TiO₂, Al/Al₂O₃, and Ni/NiO surfaces using **1** and the solution conditions described above for Si/SiO₂ (0.1 M **1** in toluene, 65 °C, 72 h) were not promising (first entry in Table 3); however, vapor-phase reactions at elevated

Table 3. Water Contact Angles (θ_A/θ_R) for Metal Oxide Samples Modified with Me₂Si(OH)₂

| conditions | Ti/TiO ₂ | Al/Al ₂ O ₃ | Ni/NiO |
|--|---------------------|-----------------------------------|----------|
| Me ₂ Si(OH) ₂ , toluene, 65 °C, 72 h | 54°/27° | 48°/21° | 65°/24° |
| Me ₂ Si(OH) ₂ vapor 65 °C, 24 h | 86°/55° | 65°/28° | 61°/30° |
| Me ₂ Si(OH) ₂ vapor 110 °C, 18 h | 100°/79° | 110°/64° | 103°/70° |
| Me ₂ Si(OH) ₂ vapor 150 °C, 18 h | 101°/85° | 114°/91° | 120°/79° |

temperature were successful at hydrophobizing these surfaces. Toluene likely coordinates with these more active (than silica) surfaces and competes with covalent attachment. Table 3 shows water contact angle data for surfaces prepared with titanium-, aluminum-, and nickel-coated silicon wafers and reaction with dimethylsilanediol vapor at various temperatures. The PDMS layers that form on these materials are similar in structure to those prepared using the direct reaction of PDMS oil with these surfaces.⁷ The high advancing values for aluminum and nickel on samples prepared at 150 °C suggest roughening. The polymerization of **1** likely occurs prior to or competitively with the surface reaction. The ellipsometric data for the last three entries in Table 2 indicate that this is likely for Si/SiO₂ surfaces as well. We note that the sensitivity to the reaction vessel composition that both Hyde¹⁴ and Kantor¹⁵ report tacitly predicts that reactions between **1** and metal oxide surfaces should occur.

OUTLOOK

We emphasize four points: (1) The silanediol structure, until now, has been neglected as a functional group for surface-modification reactions. (2) The simplest compound of this structure, dimethylsilanediol (**1**), the monomer of an important and unique class of materials, is an easily prepared, thermally stable, volatile crystalline solid. (3) **1** is an effective hydrophobizing agent for inorganic surfaces with the advantages that it is volatile and thermally stable (to at least 250 °C).¹⁹ (4) That the byproduct of the modification reaction (water) is innocuous to inorganic surfaces suggests that **1** and other silanediols will be useful reagents for surface modification, particularly when other choices (chlorosilanes and alkoxy-silanes) cause corrosion or competitive adsorption.

ASSOCIATED CONTENT

Supporting Information

X-ray photoelectron spectroscopy atomic composition data for Si/SiO₂ samples that were modified with **1** in toluene solution and in the vapor phase. Procedure for dimethylsilanediol synthesis (Hyde's method). ¹H NMR and infrared spectra for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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