satisfied.

If the acid HB is H_3O^+, the reaction is specific-acid-catalyzed. Although water (the conjugate base of H_3O^+) plays an important role in the reaction mechanism,[31,32] it does not appear in the rate expression (7). This is consistent with our omission of the dependence of k_{app} on $[H_2O]$, even though the concentration of water varied significantly over the pressure range of interest. The bisulfate anion HSO_4^- could also act as a base in the second step of the mechanism;[31] however, its concentration is very low relative to water, and experiments revealed no influence of the anion on the reaction rate. The decrease in rate constant with increasing dielectric constant is consistent with the formation of an activated complex that is less polar than the reactants, which is the case of the concerted E2 mechanism displayed in Figure 5. Similarly, the lack of influence of the ionic strength of the medium on the rate constant is also consistent with the E2 mechanism, since the modified Brønsted–Bjerrum equation for ion–neutral molecule interactions predicts a negligible influence of ion strength on reaction rate. The large positive value of $\Delta V^{\ddagger}$ may be interpreted to be an artifact of electrostriction effects: the local electric field of the activated complex is weaker than that of the dipole and ion reactants, resulting in less electrostriction of the solvent molecules and a positive activation volume. Detailed numerical simulations of the acid-catalyzed disappearance of 1-propanol and the appearance of 2-propanol (with propene) in supercritical water also indicate the role of a concerted E2 mechanism in the dehydration of 1-propanol.[26] These simulations exploit the departures from first-order behavior emphasized earlier to discriminate between the E2 and E1 reaction mechanisms. Although discussions of the mechanism of propene hydration/propanol dehydration usually emphasize the role of a carbocation intermediate,[14-21] recent studies have given increasing attention to the possibility of a concerted mechanism that avoids the formation of the charged carbocation intermediate. For example, Dietze and Jencks[19] note "It is possible that the reaction mechanisms are concerted because simple secondary carbocations do not have a significant lifetime in the presence of water." Our findings are consistent with this viewpoint.

Conclusions

(1) The pK_a of sulfuric acid in supercritical water decreases from about 2.1 to 1.5 at 375 °C ($T_r = 1.003$) as pressure increases from 22.1 MPa ($P_r = 1.002$) to 34.5 MPa ($P_r = 1.563$). The bisulfate anion does not measurably dissociate under these conditions.

(2) The acid-catalyzed rate of disappearance of 1-propanol in supercritical water under these conditions is given by $k_H \cdot [H^+][C_3H_7OH]$, which is an example of specific-acid catalysis.

(3) These findings are consistent with an acid-catalyzed, concerted E2 dehydration mechanism.

(4) As pressure increases from 22.1 to 34.5 MPa, k_H decreases by about a factor of 3 at 375 °C. This decrease is linear in $1/D$, where D is the dielectric constant of water.

(5) From the linear dependence of k_H on $1/D$, the reaction rate in the close vicinity of water's critical point can be predicted by its behavior at higher pressures.

(6) Viewed in this context, we detect no abnormal behavior of the reaction rate in the close vicinity of water's critical point.

Acknowledgment. This work was supported by the National Science Foundation under Grants CBT85-14867 and CBT88-12954. We thank William Mok, Maninder Hunjan, and Tongchit Leesomboon (University of Hawaii) for assistance with the experiments; Professor Maitland Jones, Jr. (Princeton University), and Professor Geoffrey N. Richards (University of Montana) for many stimulating discussions concerning reaction mechanisms; and Dr. Duane Bruley and Dr. Maria Burka (NSF) for their continuing interest in this work. We also thank the two anonymous reviewers for their helpful comments.

Registry No. H_2O, 7732-18-5; $CH_3CH_2CH_2OH$, 71-23-8; H_2SO_4, 7664-93-9.

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Enhanced Silylation Reactivity of a Model for Silica Surfaces

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Contribution from the Department of Chemistry, University of California,
Irvine, California 92717. Received April 14, 1989.
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Abstract: The relative silylation reactivities of structurally similar silanols (**1–4a**) containing one, two, and three potentially hydrogen-bonded siloxy groups have been explored for the first time. In the absence of amine bases, silylation with TMSCl is sluggish and there is very little kinetic selectivity for silylation of either isolated silanols or intramolecularly hydrogen-bonded silanols. In the presence of Et_3N or pyridine, the rates for silylation of all types of silanols are greatly increased and there appears to be a slight kinetic preference for the silylation of vicinally hydrogen-bonded silanols over isolated, non-hydrogen-bonded silanols. Most significantly, there is remarkable selectivity for the monosilylation of **1** in the presence Et_3N. The experimental results suggest that the most reactive sites for silylation of hydroxylated silica surfaces may be those possessing at least three mutually hydrogen-bonded hydroxy groups.

Surface-modified silicas[1] are an important class of materials which have been used extensively as stationary phases in chromatography.[2] Modified silicas have also found a number of other useful applications, such as ion collection,[3] heterogeneous hydrogenation catalysts,[4] inorganic polymer fillers,[5] and drug delivery agents.[6] For all of these applications the surface properties of silica are specially tailored by chemically attaching organic groups

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(3) (a) Leyden, D. E.; Luttrell, G. H.; Sloan, A. E.; De Angelis, N. J. *Anal. Chim. Acta* **1976**, *84*, 97.

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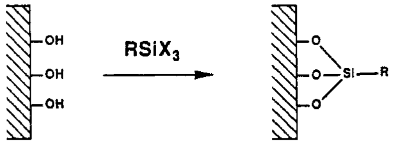
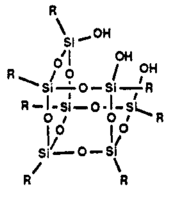
to surface siloxy groups, most commonly by silylation with methoxy- or chlorosilanes.

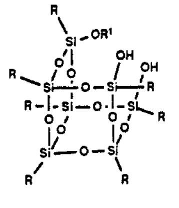


Despite its apparent simplicity, the silylation of silica is an enormously complex process. The structurally diverse nature of different silicas, the presence of surface impurities, and the existence of subsurface water and siloxy groups make definitive mechanistic studies extremely difficult. Consequently, many mechanistic studies on silica surfaces have been somewhat subjective and have painted oversimiplified pictures of very complex chemistry. The recent development of new analytical techniques for studying surfaces, especially solid-state NMR techniques,[7] provides powerful new tools for studying changes occurring at the molecular level during silylation, but the inherent complexity of the problem, compounded by a general lack of reactivity studies on intramolecularly hydrogen-bonded silanols,[8] leaves many unanswered mechanistic questions.

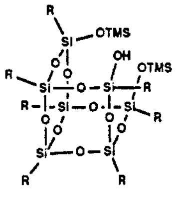
We recently described the syntheses of several incompletely condensed silsesquioxanes (e.g., **1**–**5**; R = cyclohexyl) which structurally resemble short-range molecular structures of known SiO_2 polymorphs.[9] The close proximity of hydroxy groups in these models for silica provides an excellent opportunity to explore the reaction chemistry of juxtaposed siloxy groups. In this paper we compared the relative reactivities of our models toward chlorotrimethylsilane (TMSCl). The implications of our results on the reactivity of silica surfaces are discussed.



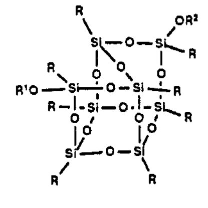
1



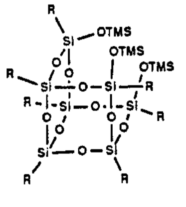
2a R^1 = $SiMe_3$
b $SiMe_2Ph$



3



4a R^1 = H, R^2 = H
b H $SiMe_3$
c $SiMe_3$ $SiMe_3$



5

Experimental Section

General experimental protocol and procedures for the syntheses of **1**, **2a**, **3**, **4a**, and **5** are described in ref 9. ^1H NMR spectra were recorded at 500 MHz in $CDCl_3$ unless otherwise specified. $CDCl_3$ was vacuum distilled (25 °C, 0.1 Torr) from CaH_2. C_6D_6 and THF-d^8 were vacuum distilled (25 °C, 0.1 Torr) from sodium benzophenone ketyl. Chlorodimethylphenylsilane was purchased from Aldrich Chemical Co. and used without further purification.

Synthesis of 2b. Chlorodimethylphenylsilane (105 mg, 0.618 mmol) was added dropwise and with vigorous stirring to a solution of trisilanol **1** (500 mg, 0.514 mmol) and Et_3N (520 mg, 5.2 mmol) in THF (10 mL). After stirring overnight, the $Et_3N{\cdot}HCl$ was removed by vacuum filtration and the volatiles were evaporated in vacuo (25 °C, 0.1 Torr). The remaining white solid was extracted with hot hexanes, filtered to remove particulates, and then slowly cooled to room temperature. Upon standing for 20 h, the desired product crystallized as large colorless crystals, which rapidly desolvated upon isolation to afford 256 mg (45%) of white powder. For **2b**: ^1H NMR (500.1 MHz, $CDCl_3$, 23 °C) δ 7.63 (m, 2 H), 7.39 (m, 3 H), 3.53 (br s, 2 H, SiO*H*), 1.73 (v br m, 35 H), 1.23 (v br m, 35 H), 0.75 (v br m, 7 H, SiC*H*), 0.41 (s, 6 H, Si*Me*$_2$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, 23 °C) δ 139.43, 133.23, 129.53, 127.92 (phenyl); 27.62, 27.59, 27.55, 27.52, 27.47, 26.86, 26.81, 26.76, 26.63, 26.60, 26.52 (CH_2); 24.50, 23.90, 23.44, 23.11, 23.02 (s, 1:2:2:1:1 for CH); 0.43 (s, CH_3); mp 177–179 °C.

X-ray Diffraction Study of 2b. Crystals suitable for an X-ray diffraction study were obtained by allowing acetonitrile to slowly diffuse into a CCl_4 solution of **2b** (100 mg/mL) over several days. Crystal data for **2b**$\cdot(CCl_4)_{0.5}$ solvate [$C_{50}H_{90}Si_8O_{12}\cdot(CCl_4)_{0.5}$ (fw 2370.05)] are as follows: monoclinic $P2_1/n$, a = 14.9385 (23) Å, b = 17.0414 (20) Å, c = 26.1337 (29) Å, β = 93.250 (11)°; V = 6641.3 (15) Å^3; d_{calcd} = 1.18 g/cm^3 (Z = 4). A total of 8675 unique reflections with $4.0° \leq 2\theta \leq 45.0°$ were collected on a Syntex $P2_1$ diffractometer at −98 °C with use of graphite monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL PLUS). Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for Si, O, C, Cl) led to convergence with a final R factor of 0.085 for 676 variables refined against 5960 data with $F > 3.0\sigma F$. All other details regarding the crystal structure are reported in the supplementary material.

Silylation Studies. (a) Et_3N- and Pyridine-Catalyzed Silylation Reactions. Amine-catalyzed reactions were typically performed as described below for the reaction of **1** with TMSCl in 0.5 M Et_3N/THF. For reactions performed in neat Et_3N or pyridine, 1 mL of the amine was used as the solvent.

Chlorotrimethylsilane (6 μL, 0.047 mmol) was added slowly and with vigorous stirring to a solution of trisilanol **1** (49 mg, 0.05 mmol) and Et_3N (51 mg, 0.50 mmol) in 1.00 mL of THF at room temperature. The precipitation of $Et_3N{\cdot}HCl$ occurred within 2–5 min, but stirring was normally continued for 2 h to ensure complete reaction. Filtration through a fine sintered glass funnel and solvent removal in vacuo (25 °C, 0.001 Torr) afforded an amorphous white solid, which was completely dissolved in $CDCl_3$ for product analysis by ^1H NMR spectroscopy.

The reactions of incompletely condensed silsesquioxanes with TMSCl under these conditions are rapid and irreversible (no change in the distribution of kinetic products is observable after stirring for 24 h). The total amount of TMSCl that was actually added to the reaction mixture was therefore calculated from the ratio of integrated intensities for all trimethylsilyl (i.e., $SiMe_3$) resonances and all cyclohexyl methine (i.e., SiCH) resonances. Relative distributions of silylated products were calculated from the ratios of integrated intensities for trimethylsilyl resonances of **2**–**5**. These well-resolved resonances occur at δ 0.160, 0.135, and 0.115 for **2a**, **3**, and **5**, respectively.[9] Trimethylsilyl resonances for **4b** and **4c** occur as overlapping singlets at δ 0.110 and δ 0.107, respectively. The silylation of a remote siloxy group on **4a** has no apparent effect on the reactivity of the remaining siloxy group; therefore **4a** was treated in competition experiments as though it possessed two equally reactive siloxy groups. Great pains were taken to avoid contamination by silicon grease, which exhibits a narrow envelope of unresolvable singlet resonances centered at ~ δ 0.07. Resonances for unavoidably small amounts of grease do not overlap with resonances for **2**–**5** and do not interfere with our analyses.

(b) Silylation Reactions Performed without Base Catalysis in $CDCl_3$ or THF-d^8. Reactions were typically performed as described below for the reaction of **1** with TMSCl in THF-d^8. Chlorotrimethylsilane (3.2 mL) was added via syringe to a solution of trisilanol **1** (26 mg, 0.027 mmol) in THF-d^8 (0.5 mL) in a 5 mmol NMR tube. The tube was fitted with a rubber septum. The course of the reaction was periodically analyzed as described above in part (a).

Results and Discussion

The salient feature of our silsesquioxane model for silica is the structural similarity between our incompletely condensed silsesquioxanes and known SiO_2 polymorphs.[9] Of particular significance are the short-range structural similarities between **1** and

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Table I. Selected Bond Distances and Angles for **2b**[a]

bond distances/Å		bond angles/deg	
O10–O11	2.722	O4–Si5–O10	109.5 (3)
O10–O11A	2.670	O5–Si5–O10	108.5 (3)
O10–O10A	3.981	O6–Si6–O11	104.8 (3)
O11–O11A	3.638	O7–Si6–O11	108.5 (3)
Si5–O10	1.629 (6)	Si1–O1–Si2	144.6 (4)
Si6–O11	1.620 (6)	Si1–O2–Si3	139.7 (4)
Si7–O12	1.605 (6)	Si1–O3–Si4	154.2 (4)
Si8–O12	1.630 (6)	Si4–O4–Si5	146.5 (4)
Si5–Si6	4.209	Si2–O5–Si5	143.1 (4)
Si5–Si7	5.292	Si2–O6–Si6	151.5 (4)
Si6–Si7	5.550	Si3–O7–Si6	155.8 (4)
		Si3–O8–Si7	160.6 (4)
		Si4–O9–Si7	139.7 (4)
		Si7–O12–Si8	142.7 (4)

[a] Within the Si–O framework Si–O distances are 1.606–1.627 (6) Å and O–Si–O angles are 107.5–110°.

geometrically comparable trisilanol sites available on idealized surfaces of β-cristobalite (111) and β-tridymite (0001), two SiO_2 polymorphs[10] that have been repeatedly suggested to resemble amorphous silica surfaces.[7f,11] Despite these similarities, which clearly provide excellent structural models for cristobalite-like and tridymite-like surface sites, the smaller "cubelike" framework of **1** could potentially manifest itself in very different reactivity patterns. This would be particularly true if adjacent siloxy groups on cristobalite-like and tridymite-like surface sites are capable of hydrogen bonding, but the smaller Si–O framework of **1** is sufficiently inflexible that intramolecular hydrogen bonding cannot occur. Although the structural details of surface sites that support hydrogen-bonded siloxy groups are not known, the presence of such sites is well-established. Useful models for silica surfaces should therefore be capable of intramolecular hydrogen bonding.

Evidence for intramolecular hydrogen bonding between adjacent siloxy groups in **1** and **2a,b** is provided by ^{1}H NMR spectra of very dilute $CDCl_3$ solutions of **1–4a**. Resonances for the hydroxylic protons of **1** (δ 6.04) and **2a** (δ 4.11) are substantially deshielded versus the non-hydrogen-bonded siloxy groups of **3** (δ 2.79)[12] and **4a** (δ 2.09). More conclusive evidence for intramolecular hydrogen bonding between juxtaposed siloxy groups comes from X-ray diffraction studies of both **2a**[13] and **2b**. The perspective plot from a single-crystal X-ray diffraction study of **2b** is shown in Figure 1a and selected distances and angles are collected in Table I.

Like trisilanol **1**,[9] disilanol **2b** crystallizes as a symmetry-related ($\bar{1}$), hydrogen-bonded dimer. In contrast to **1**, however, where hydroxylic O–O distances are approximately 4 Å and only intermolecular hydrogen bonding is observed,[9] the bond distances between adjacent hydroxy groups of **2b** are also consistent with strong intramolecular hydrogen bonding.[14] No hydroxylic hydrogen atoms could not be located in the final difference map, but the short O10–O11 (2.722 Å) and O10–O11a (2.670 Å) internuclear distances provide compelling evidence for hydrogen bonding as depicted in Figure 1b.

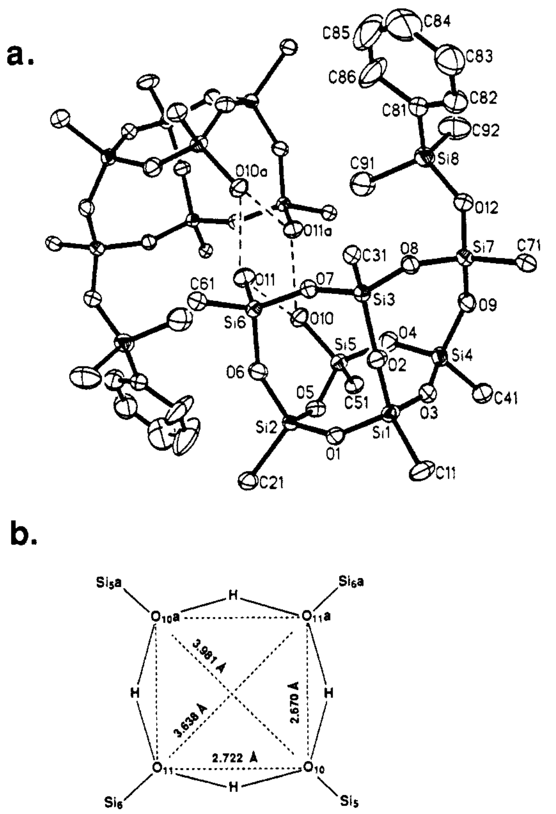

Figure 1. (a) Perspective plot of **2b**. The molecules crystallize as a hydrogen-bonded dimer in the space group $P\bar{1}$. The two molecules which comprise each dimer are crystallographically related by $\bar{1}$. For clarity, thermal ellipsoids are plotted at 20% probability and only C attached to Si are shown for cyclohexyl groups. (b) Representation of the most probable hydrogen-bonding arrangement for **2b**.

The contraction of the Si–O framework necessary to bring the siloxy groups in **2b** within hydrogen-bonding distance has surprisingly little effect on the bond distances and angles within the silsesquioxane framework. As expected, the biggest differences between the solid-state structures of **2b** and **1** are increases in the distances between Si7 and the hydroxy-bearing silicon atoms (Si5 and Si6). The Si7–Si5 and Si7–Si6 distances are 5.55 and 5.29 Å, compared to the average Si–Si separation of 4.9 Å for siloxy groups in **1**.[9] The oxygen atoms immediately attached to Si5, Si6, and Si7 are also displaced slightly due to the contraction, but most of the other atoms within the Si–O framework move very little. The bond distances and angles for atoms in the Si–O framework of **2b** are very similar to those observed in trisilanol **1** and are well within their accepted ranges.[9] Since four hydrogen bonds represent only 4–10 kcal/mol of **2b** (8–20 kcal/mol for the dimer),[14c] the "flexing potential" of the silsesquioxane framework must be quite broad and shallow. The hydroxyl groups of **2b** (and presumably **1**) can easily move to within hydrogen-bonding distance and are clearly not "pinned back".

Silylation Studies. Since the siloxy groups on **1** and **2a** are indeed capable of intramolecular hydrogen bonding, it is possible for the first time to compare the reactivity of structurally similar silanols with one, two, and three potentially hydrogen-bonded siloxy groups. The results from our studies on the reactions of **1–4a** with TMSCl are summarized in Table II.

In the absence of bases, the reactions of **1–4a** with TMSCl are sluggish and relatively nonselective at high conversions. (Table II, entries 1, 2, 14, and 17). For example, reactions performed in either $CDCl_3$ or THF-d^8 are less than 1% complete (based on TMSCl) after 15 min at room temperature and only 10–20% complete after 4 h. When THF-d^8 is the solvent, decomposition

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(10) (a) Although it has been argued[10b-d] that tridymite is not a pure form of SiO_2, it is nevertheless a very commonly observed form of "silica". (b) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: New York, 1982. (c) Sosman, R. B. *The Phases of Silica*; Rutgers University Press: New Brunswick, NJ, 1965; pp 50–65. (d) Barby, D. In *Characterization of Powder Surfaces*; Parfitt, G. D., Sing, K. S. W., Eds.; Academic Press: New York, 1976.

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(12) In ref 9 the hydroxylic proton resonance for **3** was incorrectly assigned an integrated intensity for two protons.

(13) Compound **2a** crystallizes as a hydrogen-bonded dimer in the space group $P2_1/m$ (or $P2_1$) (a = 17.7633 (27) Å, b = 17.5963 (27) Å, c = 20.3531 (35) Å, β = 107.83 (1)°). Although the Si–O framework could be clearly identified and refined, problems with disorder prevented a satisfactory completion of the structure.

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Table II. Summary of Reactions of Silanols **1–4a** with Chlorotrimethylsilane (TMSCl)

entry	substrates	solvent	equiv of TMSCl added[a]	extent of reaction (%)[b]	products (% yields)[c]
1	**1**	$CDCl_3$	0.56	<1 (15 m)	**2a** (trace)
				9 (4 h)	**2a** (9), **3** (trace)
				66 (24 h)	**2a** (81), **3** (19), **5** (trace)
				84 (72 h)	**2a** (67), **3** (27), **5** (6)
2	**1**	THF-d^8	0.76	<1 (15 m)	**2a** (trace)
				23 (4.5 h)	**2a** + dec[d]
3	**1**	Et_3N	0.75	100	**2a** (90), **3** (9.5), **5** (0.5)
4	**1**	pyridine	0.71	100	**2a** (78), **3** (16), **5** (6)
5	**1**	5% $Et_3N/CHCl_3$	0.62	100	**2a** (97), **3** (3), **5** (trace)
6	**1**	5% Et_3N/THF	0.80	100	**2a** (>99), **3** (trace), **5** (trace)
7	**1**	5% Et_3N/THF	1.74	100	**2a** (30), **3** (51), **5** (19)
8	**1**	5% Et_3N/Et_2O	0.70	100	**2a** (>99), **3** (trace), **5** (trace)
9	**1**	5% Et_3N/C_6H_6	0.90	100	**2a** (95), **3** (5), **5** (trace)
10	**1**	5% pyr/$CHCl_3$	0.61	100	**2a** (78), **3** (15), **5** (7)
11	**1**	5% pyr/THF	0.90	100	**2a** (84), **3** (13), **5** (3)
12	**1**	5% pyr/Et_2O	0.78	100	**2a** (88), **3** (11), **5** (1)
13	**1**	5% pyr/C_6H_6	0.73	100	**2a** (93), **3** (7), **5** (trace)
14	**2a**	THF-d^8	0.40	<1 (4 h)	**3** (trace)
				40 (24 h)	**3** + dec[d]
15	**2a**	5% Et_3N/THF	0.87	100	**3** (72), **5** (28)
16	**2a**	5% pyr/THF	0.71	100	**3** (62), **5** (38)
17	**1** (1.0) and **4a** (0.5)	THF-d^8	1.0	72 (16 h)	**2a** (62), **3** (6), **4b,c** (32), **5** (trace)
18	**1** (1.0) and **4a** (0.5)	5% Et_3N/THF	0.78	100	**2a** (>99), **3** (trace), **4b,c** (<1)
19	**1** (1.0) and **4a** (0.5)	5% pyr/THF	0.75	100	**2a** (81), **3** (8), **4b,c** (5), **5** (6)
20	**2a** (1.0) and **4a** (0.5)	5% Et_3N/THF	0.57	100	**3** (54), **4b,c** (43), **5** (3)
21	**2a** (1.0) and **4a** (1.0)	5% pyr/THF	0.69	100	**3** (43), **4b,c** (53), **5** (4)
22	**3** (1.0) and **4a** (0.5)	5% Et_3N/THF	0.18	100	**4b,c** (~75), **5** (~25)

[a] Determined by ^1H NMR spectroscopy to compare the relative integrated intensities of TMS resonances vs the methine resonances of the cyclohexyl groups. [b] The extent of reaction refers to the percentage of TMSCl consumed in the reaction. [c] Product yields are based on TMSCl consumed and are expressed as percent mole fractions. [d] Approximately half of the reacted TMSCl exists as **2a** and small amounts of **3**. Extensive decomposition of the mixture, presumably due to the reaction of THF with TMSCl and/or HCl, prevented a more complete analysis.

of the reaction mixture occurs within an hour, presumably due to the reaction of solvent with HCl and/or TMSCl.[15] In $CDCl_3$, however, silylation is still incomplete after 72 h at room temperature. The use of other solvents was not extensively explored because of the poor solubility of **1** in most common NMR solvents that do not react with chlorosilanes, but based on the reactions of **1**, **2a**, and **4a** with TMSCl in $CDCl_3$ and THF-d^8, it is clear that the reactions of incompletely condensed silsesquioxanes with TMSCl (in the absence of base) are inherently slow and relatively nonselective, especially at high conversions.

In the presence of bases (e.g., Et_3N or pyridine) the reactions of **1–4** with TMSCl occur rapidly upon mixing, as evidenced by the precipitation of amine hydrochloride ($Et_3N{\cdot}HCl$ or pyridine hydrochloride). Base catalysis of nucleophilic substitution reactions at silicon is well-documented,[16] so the rate enhancements alone are uneventful. What is noteworthy, however, is that the rate enhancements are accompanied in some instances by dramatic increases in selectivity. For example, the reaction of **1** with 0.80 equiv of TMSCl in 0.5 M Et_3N/THF[17] leads to a nearly quantitative yield of **2a** (based on TMSCl), indicating that the reactivity of **1** toward TMSCl in Et_3N/THF is approximately 3 orders of magnitude greater than the reactivity of **2a** (entry 6).[18] The selectivity for monosilylation of **1** is also very high in 0.5 M Et_3N/Et_2O (entry 8), but is somewhat lower in 0.5 M $Et_3N/CHCl_3$ and 0.5 M Et_3N/C_6H_6 (entries 5 and 9), solvents with lower dielectric strengths. Quite curiously, the selectivity for monosilylation of **1** is lower in pure Et_3N (entry 3) than in 0.5 M solutions of Et_3N in an organic solvent. The reaction of **2a** with TMSCl in 0.5 M Et_3N/THF (entries 7 and 15) is significantly less selective, affording a very modest 2.6:1 selectivity for the formation of **3** vs **5**.

The selectivity of silylation reactions involving **1** and **2a** decreases when pyridine is substituted for Et_3N. For the reaction of **2a** with TMSCl in 0.5 M pyridine/THF[17] the selectivity is only marginally affected (entry 16 vs 15). For trisilanol **1**, however, the results are much more dramatic: the selectivity for monosilylation drops sharply from ≥99:1 in 0.5 M Et_3N/THF to only 6:1 in 0.5 M pyridine/THF (entries 6 and 11). Similar results are also observed when ether is the solvent (entries 8 and 12). As observed for Et_3N-catalyzed reactions, the selectivity for the monosilylation of **2a** (to **3**) is lower than that observed for the monosilylation of **1** (to **2**), but the difference is much less dramatic (entries 15 and 16 vs 6 and 11).

One possible explanation for the remarkable selectivity for Et_3N-catalyzed monosilylation of **1** is that greater steric crowding in **2a** slows its rate of silylation versus **1**. A series of competition experiments was therefore performed using disilanol **4a** as a sterically uncongested silanols to probe for steric effects on the silylation reactions of **1** and **2a**. Disilanol **4a** is a logical choice for comparison because of its structural and electronic similarities to **1–3**. In addition, molecular models of **4a**, as well as a single-crystal X-ray diffraction study of its bis-triphenyltin derivative,[9] do not reveal any structural characteristics to suggest that the silylation of **4a** would be hindered by steric congestion.[19]

Competitive silylation of a 1:0.5 mixture of trisilanol **1** and **4a** occurs almost exclusively (≥99:1) on **1** (entry 18), indicating that **1** is approximately 3 orders of magnitude more reactive than **4a**.

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(17) At 0.5 M, solutions of Et_3N and pyridine are nominally 5% (v/v) and 4% (v/v), respectively.

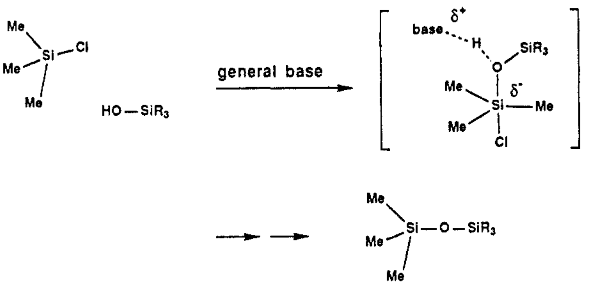
(18) Our limit of detection by ^1H NMR spectroscopy is approximately 1%. If silylation of **1** with 0.9 equiv of TMSCl gives only **2a**, the overall rate for the silylation of **1** near the end of the reaction must be at least 100 times the rate for silylation of **2a**. Since [**1**]:[**2a**] is approximately 10:90 near the end of the reaction, the bimolecular rate constant for silylation of **1** must be approximately 1000 times greater than the rate constant for silylation of **2a**.

(19) For comparison, the competitive silylation of a 2:1 molar ratio of Ph_3SiOH and **4a** with a deficiency of TMSCl (0.42 equiv/Ph_3SiOH) in 0.5 M Et_3N/THF afforded a 55:45 mixture of products derived from silylation of Ph_3SiOH and **4a**, respectively.

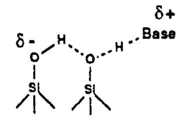
In contrast, reactions performed in 0.5 M pyridine/THF (entry 19) or in THF without any base (entry 17) exhibit only marginal selectivity. The competitive silylation of disilanol **2a** and **4a** in 0.5 M Et$_3$N/THF is relatively nonselective, showing only a slight preference for silylation of **2a** (entry 20). Poor kinetic selectivity is also observed for competitive silylation of **3** vs **4a** (entry 22).

Since detailed mechanisms for the silylation reactions described here are not known,[20] it is difficult to quantitatively access the magnitude and importance of steric effects. Nevertheless, our results—particularly the observation that the selectivity for monosilylation **1** decreases when the base is changed from Et$_3$N to pyridine—are not consistent with any notion that the enhanced reactivity of **1** toward TMSCl is a consequence of greater steric crowding in other silsesquioxanes (i.e., **2a**, **3**, **4a**). Instead, our results indicate that differential steric effects are relatively unimportant and suggest that the Et$_3$N-catalyzed silylation of **1** is actually uniquely accelerated.

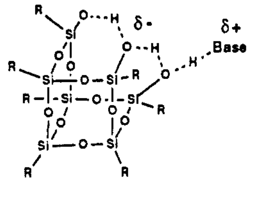
The origin of the enhanced reactivity of **1** toward TMSCl/Et$_0$N is not entirely clear. Although Et$_3$N (pK_a 10.72 for Et$_3$NH$^+$)[21] is a stronger base than pyridine (pK_a 5.17 for C$_5$H$_5$NH$^+$)[21] and would be expected to be a better catalyst for general-base catalysis,[22] our experimental results require that the Et$_3$N-catalyzed silylation of **1** be approximately 3 orders of magnitude more facile than the silylation of **2a**, **3**, or **4**.[18] A preferential rate enhancement of this magnitude cannot be rationalized by using a common general-base-catalyzed process with chemically similar intermediates.



While it is tempting to invoke simple hydrogen-bonded transition states to explain our results, the poor selectivity for monosilylation of **2a** (entry 15) and dramatic drop in selectivity when pyridine is substituted for Et$_3$N are inconsistent with the simple hydrogen-bonded vicinal pair (e.g., **6**), which is traditionally proposed.[23a,b]



6



7

An interesting mechanistic alternative is that hydrogen bonding between three juxtaposed siloxy groups is responsible for the enhanced reactivity of **1**. The effects of hydrogen bonding on the pK_as of polyhydroxylic compounds are well-documented[24] and in the case depicted by **7** would be expected to lower the pK_a of **1** by 4–6 pK_a units relative to **3** or **4**. Since the pK_as of simple silanols are approximately 14,[25] the pK_a of **1** would be expected to be 8–10, which would be comparable to the pK_a of Et$_3$NH$^+$. Under these circumstances, large deviations from general base catalysis (i.e., rate enhancements) could occur due to the onset of much more facile specific-base-catalyzed processes.[22]

Although it is highly unlikely that discrete ions or solvent-separated ion pairs would form in THF by deprotonation of **1** with Et$_3$N, the unique hydrogen-bonding capability of **1** might manifest itself by stabilizing a contact ion pair with a relatively large degree of proton transfer to the amine (e.g., **7**). If β in the Brønsted equation[26] for general-base catalysis is viewed as the degree of proton transfer in or prior to the transition state, the Et$_3$N-catalyzed silylation of **1** would then be expected to exhibit large rate enhancements relative to reactions with less acidic silanols (e.g., **2a**, **3**, and **4**) or less basic amines (i.e., pyridine). The poorer selectivities observed for reactions using weakly basic pyridine, pure Et$_3$N, or cosolvents such as benzene or CHCl$_3$ are consistent with this explanation: ion pairing would be less likely with weaker bases and in noncoordinating solvents with lower dielectric constants (ϵ for Et$_3$N, pyridine, THF, CHCl$_3$, and C$_6$H$_6$ are 2.42, 12.3, 7.58, 4.81, and 2.28, respectively).[27,28]

Although additional work is necessary to determine the actual origin of the enhanced reactivity of **1** toward TMSCl/Et$_3$N, several interesting observations clearly emerge from our data. Firstly, silylation in the absence of amine bases is sluggish, and there is very little difference in kinetic selectivity for either isolated silanols or intramolecularly hydrogen-bonded silanols. All types of siloxy groups have comparably low reactivity toward TMSCl. Secondly, the presence of amine bases greatly increases the rates of silylation, but the relative reactivities of isolated siloxy groups and hydrogen-bonded disiloxy groups are only marginally effected. As is the case for reactions that are not catalyzed by amines, isolated siloxy groups and hydrogen-bonded disiloxy groups have comparable reactivities. Finally, there is a pronounced kinetic preference for amine-catalyzed monosilylation of **1**, a silanol possessing as many as three mutually hydrogen-bonded siloxy groups. This preference is relatively modest with weakly basic pyridine, but is quite dramatic with more strongly basic Et$_3$N: under the appropriate circumstances (0.5 M Et$_3$N/THF, 25 °C), trisilanol **1** is approximately 3 orders of magnitude more reactive toward TMSCl than its monosilylated derivative **2a**.

The implications of our work for silica surface chemistry are clear: the silica surface sites which may be most reactive toward amine-catalyzed silylation are those possessing at least three

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(20) See ref 16 for detailed discussions concerning the mechanisms of silylation reactions.

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(25) The pK_a of **4a** was determined to be 14.0 ± 0.7 in THF and 50% THF/DMF by treating **4a** with sodium 9-(methoxycarbonyl)fluorenide and measuring the equilibrium concentrations of the fluorenide anion and its conjugate acid (pK_a 11.0) by UV–vis and ^{1}H NMR spectroscopy.

(26) The Brønsted expression for general-base catalysis is[22] $\log (k_B/q) = \log G_B + \beta[\mathrm{p}K_a + \log (p/q)]$, where k_B is the rate constant for the reaction, pK_a is the pK_a for the conjugate acid of the base doing the catalysis, G_B is a constant characteristic of the reaction, p is the number of equivalent protons which can be transferred from the acid, q is the number of sites on the base than can accept the protons, and β is a measure of the sensitivity of the reaction to the strength of the base.

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(28) A reviewer has suggested that reactions of **1** in 0.5 M Et$_3$N/pyridine might exhibit high selectivities for monosilylation. Although an intriguing possibility, it can be demonstrated both computationally and experimentally that the large excess of pyridine actually produces low selectivities. Based on entries 6 and 15 from Table I, the relative rate constants for silylation of **1**, **2a**, and **3** are 200:2.6.1. Assuming that the rate constant for pyridine-catalyzed silylation of **3** is 80% of that observed for Et$_3$N-catalyzed reactions, the relative rate constants for silylation of **1**, **2a**, and **3** are 12:2:0.8 in pure pyridine (entry 4). For a hypothetical reaction performed with 50 mg of **1** and 0.8 equiv of TMSCl in 1 mL of 0.5 M Et$_3$N/pyridine, iterative calculations of instantaneous concentrations estimate that the ratios of **2a**:**3**:**5** after all TMSCl is consumed will be 90:9.7:0.2. The product ratios determined experimentally were 79:10:11.

mutually hydrogen-bonded hydroxy groups, not those with isolated siloxy groups[7c,29] or geminally[7g] or vicinally[23] hydrogen-bonded disiloxy groups. If these sites represent a significant proportion of surface sites with hydrogen-bonded siloxy groups, extensive surface modification should occur via multiply hydrogen-bonded sites. Our work has specifically addressed silylation with TMSCl, but similar selectivities should be observed with other electrophilic reagents (e.g., dichloro- or trichlorsilanes, alkoxysilanes, phosphorus or sulfur halides, metal halides). Surface sites possessing three (or more) adjacent siloxy groups may therefore play an important role in the chemistry of silica and silica-supported catalysts.

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Supplementary Material Available: X-ray crystal data for **2b** including experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (12 pages); listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Iron-Induced Activation of Hydrogen Peroxide for the Direct Ketonization of Methylenic Carbon [$c\text{-}C_6H_{12} \rightarrow c\text{-}C_6H_{10}(O)$] and the Dioxygenation of Acetylenes and Arylolefins

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Abstract: In pyridine/acetic acid solvent bis(picolinato)iron(II) [$Fe(PA)_2$], (2,6-dicarboxylatopyridine)iron(II) [Fe(DPA)], and their μ-oxo dimers [$(PA)_2FeOFe(PA)_2$ and (DPA)FeOFe(DPA)] catalyze hydrogen peroxide for the selective ketonization of methylenic carbons ($>CH_2 \rightarrow >C{=}O$) and the dioxygenation of acetylenes to α-diketones and arylolefins to aldehydes. Cyclohexane is transformed with 72% efficiency ($c\text{-}C_6H_{12}$ oxidized per two HOOH) to give 95% cyclohexanone and 5% cyclohexanol, ethyl benzene with 51% efficiency to give acetophenone as the only detectable product, and *n*-hexane with 52% efficiency to give 53% 3-hexanone, 46% 2-hexanone, and <2% 1-hexanol. Suspensions of $KO_2(s)$ or $(Me_4N)O_2(s)$ in a pyridine/acetic acid solvent system are catalyzed by several iron complexes [$(py)_4FeCl_2$, $(py)_4Fe(OAc)_2$, $FeCl_3{\cdot}6H_2O$, $(MeCN)_4Fe(ClO_4)_2$, $(Ph_3PO)_4Fe(ClO_4)_2$, $Fe(PA)_2$, and $(PA)_2FeOFe(PA)_2$] to give HOOH and transform methylenic carbons to ketones, and to dioxygenate acetylenes and arylolefins. Electrolytic reduction of dioxygen (O_2) in the same solvent/catalyst systems results in analogous substrate transformations. The $Fe(PA)_2$ complex is uniquely efficient and exhibits catalytic turnover for $KO_2(s)$ suspensions as well as for electro-reduced O_2. All systems appear to produce a common reactive intermediate **3** $[(PA)_2\overbrace{FeOOFe}^{O}(PA)_2]$ via in situ formation of HOOH and $(PA)_2FeOFe(PA)_2$ (**1**).

During the past 6 years several reports[1-5] have described the selective transformation of methylenic groups ($>CH_2$) to ketones via four heterogeneous iron–dioxygen systems: (a) iron powder/sodium sulfide/O_2, (b) $Fe_3O(OAc)_6{\cdot}3.5py$/zinc dust/O_2, (c) $(py)_4FeCl_2/KO_2(s)$, and (d) $(py)_4FeCl_2/(O_2 + e^- \rightarrow O_2^{\bullet-})$ in 4:1 pyridine/acetic acid. These systems are postulated to contain σ-bonded iron–carbon intermediates[6] with superoxide ion ($O_2^{\bullet-}$) as the active form of reduced oxygen, which oxidizes the iron catalyst within the catalytic cycle. Pyridine is believed to be essential to the system as a trap for hydroxyl radical and thereby prevent Fenton chemistry. Acetic acid serves as a proton source to transform superoxide ion to hydroperoxyl radical ($HOO^\bullet$).

This background prompted us to undertake a detailed study to characterize and to optimize the iron/reduced dioxygen/(py/HOAc) systems.[1-5] In particular the investigations have sought to elucidate (a) the optimum complex for the iron catalyst, (b) the most efficient form of superoxide [(homogeneous $(Me_4N)O_2$, $(Me_4N)O_2(s)$, $KO_2(s)$, $KO_2(s)$/pyridine slurry, or electro-reduced dioxygen], and (c) the optimum solvent composition for the selective transformation of methylenic carbons to ketones.

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