from Aldrich. Benzyl fluoride was obtained from Pfaltz and Bauer. Partially deuteriated 2-fluorobenzyl alcohol and partially deuteriated 2-aminobenzyl alcohol were synthesized by H/D exchange with D_2O. All samples were used as obtained without additional purification.

Benzenemethan-d_2-ol (Benzyl-α,α-d_2 Alcohol) (6). Preparation of this material was performed following the literature report[52] by reducing methyl benzoate with lithium aluminum deuteride in ether to give 6 in 55% yield: ^{1}H NMR ($CDCl_3$) δ 2.85 (br s, 1 H), 7.2–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 64.27 (quintet, J = 21.76 Hz), 127.08, 127.52, 128.40, 140.73.

2-Fluorobenzyl-α,α-d_2 Alcohol (15). The procedure used to prepare **6** was followed using ethyl 2-fluorobenzoate to give **15** (42%) as a colorless oil, bp 40 °C (0.02 mmHg): ^{1}H NMR ($CDCl_3$) δ 4.15 (br s, 1 H), 7.02 (t, 1 H, J = 7.1 Hz), 7.17 (t, 1 H, J = 7.6 Hz), 7.26–7.29 (m, 1 H), 7.31–7.32 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 57.83 (doublet of quintet, J = 22.2, 4.3 Hz), 114.89 (d, J = 0.27 Hz), 122.88, 129.00, 123.97, 160.25, 160.25 (d, J = 3.26 Hz). HRMS: calcd for $C_7H_5D_2FO$, m/z 128.0605; found, m/z 128.0606.

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[52] Hanzlik, R. P.; Schaefer, A. R.; Moon, J. B.; Judson, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 4926.

Effect of Substituents on the Gas-Phase Acidity of Silanols

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Abstract: Eighteen siloxide ions have been prepared by the gas-phase reactions of various silanes with hydroxide. These siloxide ions have then been selected by using tandem flowing afterglow–selected ion flow tube (FA-SIFT) techniques and used to determine the gas-phase acidities (ΔG°_{acid}) of the corresponding silanols. Such determinations for the simple silanols studied herein are impossible in solution because of facile condensation reactions. A variety of substituents on silicon have been studied, including alkyl, hydrogen, phenyl, methoxy, fluoro, and chloro substituents. Alkyl groups decrease silanol acidity, in contrast to alkyl group effects in alcohols. Phenyl, methoxy, fluoro, and chloro substituents all lead to increased acidity for silanols. The gas-phase acidity of trichlorosilanol is comparable to that of HBr and HNO_3. Polarizabilities and inductive effects are used to explain the substituent effects in these silanols. In addition, the heat of formation of trifluorosilanol has been estimated.

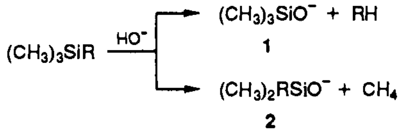
Introduction

The acidities of variously substituted silanols have been studied in solution in some detail, demonstrating (1) that silanols are considerably more acidic than their carbon analogues, (2) that they extensively hydrogen-bond, and (3) that aryl groups increase acidity, while steric hindrance has no effect.[1] Silicon substitution increases not only the acidity of an adjacent O–H but also that of the N–H, P–H, and S–H groups of amines, phosphines, and sulfides.[1] A major limitation of solution studies, however, is that simple substituent effects cannot be probed because unhindered silanols condense so rapidly to disiloxanes (eq 1).[2] Thus, despite their fundamental importance, simple substitution effects on silanol acidity have not been studied.

$$R_3SiOH + R_3SiOH \rightarrow R_3SiOSiR_3 + H_2O \qquad (1)$$

Pioneering work by Brauman and Blair has demonstrated that the order of gas-phase acidities can be quite different from that in solution.[3,4] The normal solution ordering for alcohols in protic solvents is $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$; in the gas phase, however, this order is reversed. Similarly, the acidity ordering for methyl-substituted amines in solution is different from that in the gas phase.[5] It has been suggested that in the gas phase negative charge is stabilized by dispersion (polarizability) effects to a greater extent than it is destabilized by inductive effects.[4] The reverse solution ordering then results from a combination of solvent effects. Polarizability effects are the most important determinant of the gas-phase acidities of amines[5] and alkanes[6] as well.

Because of our interests in gas-phase acidities[6-8] and in organosilicon chemistry,[9] questions about the gas-phase acidities of silanols naturally arise. Since unhindered silanols cannot be prepared in solution, gas-phase studies represent the only potential for acidity studies of silanols. The requirement of making a series of silanols is unnecessary in the gas phase, since we can easily prepare a series of siloxide ions (eq 2)[6] and study their protonation



$$(CH_3)_3SiR \xrightarrow{HO^-} \begin{cases} (CH_3)_3SiO^- + RH & \mathbf{1} \\ (CH_3)_2RSiO^- + CH_4 & \mathbf{2} \end{cases} \qquad (2)$$

by reference acids[10] using techniques we have applied widely.[9,11-13]

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[1] Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Functional Groups: The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 810–38.

[2] Birkofer, L.; Stuhl, O. In *The Chemistry of Functional Groups: The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 655–761.

[3] Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1968**, *90*, 6561–2.

[4] Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986–92.

[5] Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1971**, *93*, 3911–4.

[6] DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968–73.

[7] DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–3.

[8] Damrauer, R. In *Selective Hydrocarbon Activation: Principles and Problems*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1990; pp 535–56.

[9] DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127–33.

[10] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.

[11] Damrauer, R.; DePuy, C. H.; Barlow, S. E.; Gronert, S. *J. Am. Chem. Soc.* **1988**, *110*, 2005–6.

0002-7863/91/1513-4431$02.50/0

In this study, a number of differently substituted siloxide ions have been prepared by reaction 2. The reactivity of the resulting siloxides with reference acids gives the acidity of the corresponding silanols. The effects of substitution on silanol acidity can thus be probed.

This work has been carried out by using tandem flowing afterglow–selected ion flow tube (FA-SIFT) technology,[14] in which a siloxide ion is prepared in a flowing afterglow source, selected, injected into a second flow tube, and studied in the second flow tube by reaction with a number of reference acids. There are two important advantages of this gas–phase technology for the problem at hand: (1) there is no requirement that silanols be prepared and (2) an individual siloxide ion can be selected from a source reaction mixture of some complexity.

Experimental Section

All experiments were carried out at room temperature in a tandem flowing afterglow–selected ion flow tube (FA-SIFT), which has been described in detail previously.[14] A brief description of the technique follows. The FA-SIFT consists of four sections: a source (first) flow tube for ion preparation, an ion separation region, a second flow tube for studying the chemical reactions of the selected ions, and an ion detection region.

In the typical experiment to be reported in this paper, hydroxide ions are prepared in the first flow tube from oxide ions (O^-), which can be prepared by electron ionization of small amounts of N_2O (0.01 Torr) entrained in a rapidly flowing helium stream (0.4 Torr). The oxide ions are rapidly converted to hydroxide by hydrogen atom abstraction from methane (0.02 Torr) also entrained in the helium. The appropriate silane is added downstream through a movable inlet, where rapid reaction ensues, producing ionic products of which the major ones are siloxide ions. At the end of the first flow tube these ions are sampled through a nose-cone orifice into the ion separation region. The helium and other neutrals are removed by pumping while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole can be tuned to an appropriate m/z value, and the desired ion (for example, $[(CH_3)_3SiO]^-$) can be injected into the second flow tube, where it is entrained in helium (0.5 Torr). The reaction chemistry of the injected ion can then be probed by the addition of a variety of neutral acids to the second flow tube. At the end of the second flow tube, the ionic products are sampled through a nose-cone orifice, mass-analyzed, and detected by an electron multiplier. It is important to recognize that our assumption of the product ions is based on a recording of their m/z values and chemical intuition. Neutral products, in this study the silanols themselves, are not detected, but are assumed on the basis of mechanistic rationale.

Reaction of the selected siloxide ions with reference acids, in essence, characterizes the corresponding conjugate acid (silanol), giving a determination of the gas-phase acidity of that parent. For example, a typical siloxide ion is reacted with a series of reference acids to determine whether the siloxide abstracts a proton from the reference acid. Such determinations allow us to bracket an acidity between two reference acids, one from which the siloxide can abstract a proton and another from which it cannot. The reference acids are selected so that the narrowest possible acidity range is bracketed. Among the inherent difficulties of this approach are (1) that sometimes only a limited number of reference acids are available for the acidity region under study, (2) that some reference acids, particularly C–H and N–H acids, undergo slow proton transfer, and (3) that a reference acid whose acidity is close to that of the conjugate acid under study gives proton transfer which is a sensitive function of the amount of reference acid added. Recognizing these difficulties, we have reported acidities that use only alcohols as the unreactive component of the bracketing experiments, thus ensuring that slow proton-transfer reactions are not giving false negative results. All the reported brackets that are C–H and N–H acids are ones which do react by proton transfer. Such an approach is particularly conservative and can lead to wide bracket gaps for certain acids (see alkyl substitution section).

All reactions were studied at a flow of 250 STP $cm^3\ s^{-1}$. Gases were obtained from commercial sources and were of the following purities: He, 99.995%; N_2O, 99.99%; O_2, 99.95%; CH_4, 99.99%. Other reagents were obtained from commercial sources or prepared and were purified as necessary before use. The helium buffer gas was passed through a liquid-nitrogen-cooled molecular sieve trap before entering the flow tubes.

Results and Discussion

Acidity studies have played a central role in the development of our understanding of the effects of substituents on thermodynamic and kinetic properties in chemistry.[15] Until recently, acidity studies were carried out in solution, giving rise to the orthodoxy that solution results were a reflection of intrinsic substituent effects. Thus, the acidity ordering of simple carboxylic acids in solution, $CH_3CO_2H > CH_3CH_2CO_2H > (CH_3)_2CHCO_2H > (CH_3)_3CO_2H$, became one of the classical examples of the importance of inductive methyl release in determining solution acidities.[15] A similar effect for alcohols, namely $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$, was treated in the same orthodox manner until Brauman and Blair reported that the alcohol acidity order was reversed in the gas phase.[3,4] They pointed out that solvent must play a very important role in the alcohol acidity ordering, suggesting that the solvent's ability to differentially solvate the corresponding alkoxide ions largely determines alcohol acidities in protic solvents. Brauman and Blair postulated that two completing effects operate in the gas phase: (1) a dispersion or polarizability effect in which methyl substitution stabilizes negative charge and (2) an inductive effect in which methyl substitution destabilizes negative charge. For alcohols and acids in the gas phase, the polarizability stabilization controls acidity. A number of subsequent gas-phase studies by Brauman and coworkers[4,5] and others[16] have established the fundamental nature of these original ideas. The orthodoxy is now that intrinsic substituent effects are better reflected in gas-phase than in solution studies and that polarizability effects will dominate in alkyl substitution.

Our interest in gas-phase acidities has been focused in two areas: (1) the acidity of weakly acidic alkanes[6-8] and (2) the acidity of silicon-containing molecules.[9-13] In our alkane acidity studies, we have determined a number of new gas-phase acidities using methodology based on the competitive cleavage of substituted silanes by hydroxide (eq 2). Linear plots from eq 2 of log (**1**/**2**) versus the known acidities of methane, benzene, and ethylene established a free energy relationship, which, after some refinement, allowed us to determine the kinetic acidity of a number of alkanes.[6-8] Thus, the **1**/**2** ratio was measured for a variety of R groups and used to determine the acidity of the corresponding RH. Among the effects we have studied were those of α- and β-methyl substitution. In the α series, $CH_3\text{–}H$, $CH_3CH_2\text{–}H$, $(CH_3)_2CH\text{–}H$, and $(CH_3)_3C\text{–}H$, ΔH°_{acid} values of 416.6, 420.1, 419.4, and 413.1 kcal/mol, respectively, show that α-methyl substitution generally increases acidity.[6] However, interpretation is not altogether clear, since the first methyl substitution is acid weakening while all others are acid strengthening. We have suggested that the acid-weakening inductive effect is quickly saturated by acid-strengthening polarizability effects in $CH_3CH_2\text{–}H$, $(CH_3)_2CH\text{–}H$, and $(CH_3)_3C\text{–}H$. In the β series, $CH_3CH_2\text{–}H$, $CH_3CH_2CH_2\text{–}H$, $(CH_3)_2CHCH_2\text{–}H$, and $(CH_3)_3CCH_2\text{–}H$, where the acidic hydrogen is always primary, methyl substitution effects are more regular, with ΔH°_{acid} values of 420.1, 415.6, 412.9, and 408.9 kcal/mol resulting. In this series, polarizability dominates with the β-methyl-substituted alkanes becoming more acidic with every β-methyl substitution.[6] We have also examined the effects of ring size and unsaturation on hydrocarbon acidity.

There have been a number of determinations of the acidity of silicon-containing compounds with emphasis on how silicon in various bonding situations affects acidity. In addition, examinations of the effect of substitution on silicon have been carried out. Work in these areas has concentrated on sila-substituted analogues of isobutene,[17] dimethylcarbene,[18] formaldehyde,[12]

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(12) Gronert, S.; O'Hair, R. A. J.; Prodnuk, S.; Sülzle, D.; Damrauer, R.; DePuy, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 997–1003.

(13) Damrauer, R.; Krempp, M. *Organometallics* **1990**, *9*, 999–1004.

(14) Van Doren, J. M.; Barlow, S. E.; Depuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom, Ion Processes* **1987**, *81*, 85–100.

(15) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987.

(16) Boand, G.; Houriet, R.; Gäumann, T. *J. Am. Chem. Soc.* **1983**, *105*, 2203–6.

(17) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* **1986**, *5*, 2050–4.

(18) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* **1986**, *5*, 2054–7.

acetone,[13,19,20] acetaldehyde,[13] and methyl formate[13] and on studies of methyl substitution effects in methylsilanes.[21] In the methylsilane studies, we reported the gas-phase C–H and Si–H acidities (where appropriate) of silane, methylsilane, dimethylsilane, trimethylsilane, and tetramethylsilane. When competition between C–H and Si–H abstraction was possible, we discovered that proton abstraction occurred preferentially from C–H, giving the carbanion, which is less thermodynamically stable than the corresponding silyl anion. This study provided the first examples of a kinetically controlled proton abstraction in the gas phase; others have since been reported.[22] Subsequent to our flowing afterglow methylsilane studies, Brauman and co-workers reported Si–H acidities of several of the methylsilanes we had measured, with reasonable agreement between us.[23] Among the more interesting findings of both of these studies are the small effect of methyl substitution on Si–H and C–H acidity and the tremendous stabilization of both silyl anions and α-silyl carbanions.

In all of these studies, silicon either bears a hydrogen or is α to a carbon bearing a hydrogen. In such situations, acidity (either Si–H or C–H) is increased by the presence of silicon over the corresponding carbon analogue. Thus, tetramethylsilane is more acidic than neopentane by some 20 kcal/mol,[21,24] trimethylsilane is more acidic than 2-methylpropane by about 30 kcal/mol,[21,23] 1,1-dimethylsilene is more acidic than isobutene by about 10 kcal/mol,[17] and silaacetone is more acidic than acetone by 5 kcal/mol.[13] Some interesting ambiguities arise in some of our acidity studies because the anions that we have prepared could be protonated at more than one site. This is illustrated by $[SiCH]^-$, whose conjugate acid could be either $HSi{\equiv}CH$, $H_2Si{=}C$, or $Si{=}CH_2$,[11] and by $[HSiO]^-$, whose parent could be HSiHO or HSiOH.[12] Computational studies give insight on such questions; for the cases at hand, the parent compounds are $Si{=}CH_2$ and HSiHO, respectively.[11,12]

The work reported here seeks to make comparisons between silanols and alcohols, their carbon analogues. All such comparisons are for β substitution and are, thus, expected to be more regular than other substituent effects. Three questions will be considered: (1) what is the effect of alkyl substitution on silicon, (2) what are the effects of other substitutions on silicon, and (3) how can we explain these effects, particularly in terms of what already is known about alcohol acidities and the acidity of silicon-containing compounds?

Table I presents the gas-phase acidities of 18 silanols that were all measured by bracketing their corresponding siloxides with reference acids (only the acidity of triethylsilanol was previously reported).[10,25] Table I also lists the bracketing acids for each of the siloxides studied. *It is very important to understand that an acid with increased acidity means a stronger acid and that increased acidity corresponds to a smaller numeric value for* ΔG°_{acid}.

General Comments on the Gas-Phase Acidities of Silanols. The most striking feature in Table I is the enhanced acidity of silanols over alcohols (compare ΔG°_{acid} values for SiH_3OH and CH_3OH of 352 and 374 kcal/mol, respectively). These results were anticipated and are a manifestation of the large electronegativity difference between silicon and carbon (1.9 and 2.6 on the Allred–Rochow scale).[1] The more positive character of silicon gives a greater stabilization of the anionic oxygen than provided by carbon. Related electronegativity effects have been observed. For example, AsH_3 is more acidic than PH_3, which itself is more acidic than NH_3. Similarly, HF is more acidic than H_2O, which itself is more acidic than NH_3, and NH_3 is more acidic than CH_4.[10,26]

Table I. ΔG°_{acid} Values for Substituted Silanols

silanol	ΔG°_{acid},[a,b] kcal/mol	brackets[c] (+)	brackets[c] (−)
SiH_3OH[d]	352	CH_3NO_2	CF_3CH_2OH
CH_3SiH_2OH[e]	353	pyrrole	CF_3CH_2OH
$(CH_3)_2SiHOH$[f]	353	pyrrole	CF_3CH_2OH
$(CH_3)_3SiOH$[g]	353	pyrrole	CF_3CH_2OH
$CH_3CH_2(CH_3)_2SiOH$[h]	353	pyrrole	CF_3CH_2OH
$(CH_3CH_2)_2(CH_3)SiOH$[i]	353	pyrrole	CF_3CH_2OH
$(CH_3CH_2)_3SiOH$[j]	353	pyrrole	CF_3CH_2OH
$C_6H_5SiH_2OH$[k]	348	*t*-BuSH	CH_3SH
$C_6H_5(CH_3)_2SiOH$[l]	353	pyrrole	CF_3CH_2OH
$C_6H_5(CH_3)(H)SiOH$[m]	350	CH_3NO_2	CH_3SH
$CH_3O(CH_3)_2SiOH$[n]	353	pyrrole	CF_3CH_2OH
$(CH_3O)_2(CH_3)SiOH$[o]	348	*t*-BuSH	CH_3SH
$(CH_3O)_3SiOH$[p]	348	*t*-BuSH	CH_3SH
$(CH_3O)_2SiHOH$[q]	348	*t*-BuSH	CH_3SH
$F(CH_3)_2SiOH$[r]	348	*t*-BuSH	CH_3SH
$F_2(CH_3)SiOH$[s]	340	HCO_2H	CH_3CO_2H
F_3SiOH[t]	333	HCl	HCO_2H
Cl_3SiOH[u]	317	CF_3CO_2H	HNO_3

[a] The free energy change, ΔG°_{acid}, is commonly referred to as the acidity. [b] The acidity values reported are determined in relative terms and their ordering with the bracketing reference acids is known precisely. In absolute terms, the acidities depend on how accurately the acidities of the reference acids are known. This, of course, varies with the experimental method used in their determination. As a result, it is difficult to provide error limits on the accuracy of the data that are universally accepted. We estimate that a ±4 kcal/mol absolute error limit is consistent with our methodology and the reference acids used by us. [c] A (+) in the bracket column signifies that the reference acid reacts with the corresponding siloxide, giving the silanol and the M − 1 of the reference acid; a (−) signifies that the acid listed does not react with the siloxide. [d] Corresponding siloxide prepared from hydroxide and SiH_4. [e] Corresponding siloxide prepared from hydroxide and CH_3SiH_3. [f] Corresponding siloxide prepared from hydroxide and $(CH_3)_2SiH_2$. [g] Corresponding siloxide prepared from hydroxide and $(CH_3)_3SiH$. [h] Corresponding siloxide prepared from hydroxide and $(CH_3)_3SiCH_2CH_3$. [i] Corresponding siloxide prepared from hydroxide and $(CH_3)_2Si(CH_2CH_3)_2$. [j] Corresponding siloxide prepared from hydroxide and $(CH_3CH_2)_3SiH$. [k] Corresponding siloxide prepared from hydroxide and $C_6H_5SiH_3$. [l] Corresponding siloxide prepared from hydroxide and $C_6H_5(CH_3)_2SiH$. [m] Corresponding siloxide prepared from hydroxide and $C_6H_5(CH_3)SiH_2$. [n] Corresponding siloxide prepared from hydroxide and $(CH_3)_2Si(OCH_3)_2$. [o] Corresponding siloxide prepared from hydroxide and $(CH_3)_2Si(OCH_3)_2$. [p] Corresponding siloxide prepared from hydroxide and $(CH_3O)_4Si$. [q] Corresponding siloxide prepared from hydroxide and $(CH_3O)_3SiH$. [r] Corresponding siloxide prepared from hydroxide and $(CH_3)_3SiF$. [s] Corresponding siloxide prepared from hydroxide and $(CH_3)_2SiF_2$. [t] Corresponding siloxide prepared from hydroxide and CH_3SiF_3. [u] Corresponding siloxide prepared from hydroxide and $SiCl_4$.

In a recent computational study, Sauer and Ahlrichs predicted a gas-phase anion proton affinity (ΔH°_{acid}) of 359.3 kcal/mol for SiH_3OH.[27] After a suitable entropy correction (about 6–8 kcal/mol), this result is in excellent agreement with our experimental value.

Alkyl Substitution. In addition to the large acidifying effect of silicon just discussed, we see from Table I that β-alkyl substitution leads to slight decreases in silanol acidity in stark contrast to the effects of β-methyl substitution in alcohols.[3,4] Thus, β-methyl or -ethyl substitution leads to a slight decrease in acidity: SiH_3OH has a ΔG°_{acid} value of 352 kcal/mol while CH_3SiH_2OH, $(CH_3)_2SiHOH$, $(CH_3)_3SiOH$, $CH_3CH_2(CH_3)_2SiOH$, $(CH_3CH_2)_2(CH_3)SiOH$, and $(CH_3CH_2)_3SiOH$ all have ΔG°_{acid} values of 353 kcal/mol. Although the magnitude of this effect is very small, it is real. We will see subsequently that other β-methyl substitution effects in silanols are larger. We have been very conservative in our reporting of brackets for these compounds and, thus, have only reported bracketing acids known to react rapidly (see Experimental Section for more detail). As a result, all of

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(19) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863–4.

(20) Tumas, W.; Salomon, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2541–6.

(21) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637–40.

(22) Grabowski, J. J.; Cheng, X. *J. Am. Chem. Soc.* **1989**, *111*, 3106–8.

(23) Wetzel, D. M.; Salomon, K. E.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 3835–41.

(24) Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333–6.

(25) Thomas, D.; Bartmess, J. E. Unpublished results; see ref 10.

(26) Bartmess, J. E.; McIver, R. T. J. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.

(27) Sauer, J.; Ahlrichs, R. *J. Chem. Phys.* **1990**, *93*, 2575–83.

the methyl- and ethyl-substituted silanols have been assigned the same acidity.

Since the opposing effects of polarizability and induction are commonly accepted factors governing alkyl substituent effects, changes in their magnitude can reverse an alkyl substitution trend. We have seen that polarizability effects outweigh inductive effects in the alcohol series. With methyl- and ethyl-substituted silanols, the opposite is possible, since polarizability effects[15,28] have an r^{-4} distance dependence while inductive effects[15,28] vary as r^{-2}. It seems reasonable to suggest that in silanols, where the Si–C and Si–O bond distances are both about 0.2 Å longer than the corresponding C–C and C–O bonds,[29] the acid-weakening inductive effect becomes more important than the polarizability effect because it operates with relatively greater effect with distance.

In another interesting example of a reverse methyl substitution trend, McMahon, Kebarle, and co-workers[30] demonstrated that various halo-substituted carboxylic acids and alcohols decreased in acidity with methyl-for-hydrogen substitution. Thus, $CH_3CHClCO_2H$ and $CH_3CHBrCO_2H$ are about 1 kcal/mol less acidic than $ClCH_2CO_2H$ and $BrCH_2CO_2H$, respectively. Here, in contrast to the case of silanols, the effect is due to a γ substitution. They suggested that the polarizability effect is attenuated because the ionic charge, which is to be stabilized, is distributed over more than one center. Since the charge is reduced by being spread out, the potential function describing the dispersion interaction is correspondingly smaller (note that this interaction varies as the square of the charge).

Other Substituent Effects. We have measured a number of other silanol acidities to further probe the effect of β substitution patterns on silicon. Polar substituents in the gas phase generally enhance acidity and parallel solution effects. Because solvents tend to damp substituent effects with interactions of their own, the gas-phase effects are larger than those in solution. A number of linear free energy correlations between gas-phase acidities and various types of σ constants have been reported.[28]

There have, however, been no systematic studies of β substitution of alcohols other than the alkyl substitution effects to which we have already referred. Thus, corresponding comparisons with our silanol data cannot be made, with one exception. Benzyl alcohol and $C_6H_5SiH_2OH$ have $\Delta G°_{acid}$ values of 363 and 348 kcal/mol compared to 374 kcal/mol for methanol and 352 kcal/mol for SiH_3OH. Since the phenyl substituent cannot interact by resonance for either benzyl alcohol or $C_6H_5SiH_2OH$, its polarizability and inductive effects are the more critical features to explore. Both of these compounds should increase acidity with phenyl substitution, since phenyl is characterized as a substituent with a large polarizability and a weak inductive electron-withdrawing effect.[15,31] That the acid-increasing effect of phenyl substitution is larger for the alcohols than for the silanols is consistent with an explanation in which the polarizability effect of phenyl is attenuated in the silanol. Thus, the distance dependence of the larger polarizability effect for phenyl is more critical with the silanol than with the alcohol and, as a result, though the silanol is more acidic with phenyl substitution, the difference relative to the alcohols is greatly attenuated.

The acidity-decreasing effect with increasing β-methyl substitution is particularly clear for $C_6H_5SiH_2OH$, $C_6H_5(CH_3)(H)SiOH$, and $C_6H_5(CH_3)_2SiOH$ (348, 350, and 353 kcal/mol, respectively). Thus, the replacement of a hydrogen by methyl decreases the silanol acidity 2–3 kcal/mol per substitution. In the methyl-substituted alcohol series, each methyl substitution increases acidity by about 1–3 kcal/mol [CH_3OH, CH_3CH_2OH, $(CH_3)_2CHOH$, and $(CH_3)_3COH$ have $\Delta G°_{acid}$ values of 374, 371, 369, and 368, respectively].

A comparison of silanol acidities in which three substituents have replaced the three hydrogens of SiH_3OH (352 kcal/mol) can also be made. We have seen that methyl and ethyl substitutions lead to only slight acid weakening: $(CH_3)_3SiOH$, 353 kcal/mol; $(CH_3CH_2)_3SiOH$, 353 kcal/mol. As we might expect, polar substituents contribute to an increased acidity through their polarizability and inductive effects. Thus, $(CH_3O)_3SiOH$, F_3SiOH, and Cl_3SiOH have $\Delta G°_{acid}$ values of 348, 333, and 317 kcal/mol, respectively. It is perhaps surprising that three methoxy substitutions have so little effect on silanol acidity; however, the methoxy substituent is known to exhibit both electron-donating and -withdrawing tendencies.[15] These countertendencies appear well balanced in $(CH_3O)_3SiOH$. The extremely high acidity of Cl_3SiOH places it among the strongest gas-phase acids, comparable in acidity to HNO_3 and HBr (both 318 kcal/mol). The greater acidity of Cl_3SiOH versus F_3SiOH is at first surprising, but such effects are not without precedent in the gas phase. The observation that $HCCl_3$ is more acidic than HCF_3 (346 and 369 kcal/mol) can be attributed to polarizability effects, with the larger halogen of greater polarizability having a greater acidifying effect than the smaller, more electronegative fluorine.[32] In the silanol cases at hand, with the Si–Cl bond length greater than the Si–F bond length by about 0.4 Å,[29] we might expect that the inductive effect of fluorine would overwhelm the polarizability effect of chlorine. The observed order, however, indicates that the polarizability ordering ($Cl > C \gg H > F$)[33] is the critical factor controlling acidity over the distances in question.

We have been able to examine the stepwise substitution of methyl in the series $(CH_3)_nF_{3-n}SiOH$. The first methyl substitution [F_3SiOH to $F_2(CH_3)SiOH$] decreases the acidity by 7 kcal/mol, with the second to $F(CH_3)_2SiOH$ decreasing acidity another 8 kcal/mol. A final methyl substitution to $(CH_3)_3SiOH$ decreases the acidity an additional 5 kcal/mol. Such large effects are also not without precedent. In fact, the $\Delta G°_{acid}$ value of $FCOCH_2\text{–}H$ is 356 kcal/mol; methyl substitution leads to a decreased value of 362 kcal/mol in $CH_3COCH_2\text{–}H$.[10] In a related α-substitution effect, ab initio computations predict that $FCH_2\text{–}H$ should be about 12 kcal/mol more acidic than ethane.[34] We have recently confirmed this experimentally and find that the difference is 11 kcal/mol.[35] There is a substantial difference between the C–H acids just discussed and the silanols in this study. In the carbon acids, we would expect larger substituent effects, since the corresponding carbanions (conjugate bases), because of their strong basicity, are expected to make greater demands on stabilizing substituents.[6] In the silanols this would be less important.

We have also examined the stepwise β-methyl substitution of $(CH_3O)_3SiOH$. Replacement of methoxy by hydrogen and of methoxy by methyl has no effect on the acidity [$(CH_3O)_3SiOH$, $(CH_3O)_2SiHOH$, and $(CH_3O)_2(CH_3)SiOH$ all have $\Delta G°_{acid}$ values of 348 kcal/mol]. Two β-methyl substitutions, however, once again show methyl's acid-weakening effect [$CH_3O(CH_3)_2SiOH$ has $\Delta G°_{acid}$ of 353 kcal/mol] although not as demonstrably as in the β-phenyl substitution series.

Finally, it is interesting to compare the effect of various substituents in $X(CH_3)_2SiOH$ by examining the results in Table I. When X = H, CH_3, C_6H_5, and OCH_3, the acidity is 353 kcal/mol. Only the fluorine substituent exhibits a measurably different value (348 kcal/mol).

Thermochemistry. Larson and McMahon[36] have estimated the heats of formation of $F_2Si = O$ and $[F_3SiO]^-$. These data can be combined with our $\Delta G°_{acid}$ value for F_3SiOH to give a heat of formation of F_3SiOH of approximately −360 kcal/mol.

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[28] Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 248–350.

[29] Corey, J. Y. In *The Chemistry of Functional Groups: The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 1–56.

[30] Caldwell, G.; McMahon, T. B.; Kebarle, P.; Bartmess, J. E.; Kiplinger, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 80–2.

[31] Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047–52.

[32] Taft, R. W.; Abboud, J. L. M.; Anvia, F.; Berthelot, M.; Fujio, M.; Gal, J.-F.; Headley, A. D.; Henderson, W. G.; Koppel, I.; Quan, J. H.; Mishima, M.; Taagepera, M.; Ueji, S. *J. Am. Chem. Soc.* **1988**, *110*, 1797–800.

[33] Berry, R. S.; Rice, S. A.; Ross, R. *Physical Chemistry*; John Wiley & Sons: New York, 1980.

[34] Spitznagel, G. W.; Clark, T.; Chandrasekhar, F.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363–71.

[35] Gronert, S.; DePuy, C. H.; Damrauer, F. Unpublished work. Professor D. Geffken provided us with the sample of $(CH_3)_3SiCH_2F$ used in this determination.

[36] Larson, J. W.; McMahon, T. B. *Inorg. Chem.* **1987**, *26*, 4018–23.

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Conclusions

In reporting the gas-phase acidities of a variety of silanols, we have examined the effect of substituents on acidity. Alkyl substitution leads to decreased acidity, in contrast to alkyl substitution effects in alcohols. Polar substituents increase silanol acidity, with chlorine and fluorine having the greatest effect. The substituent effects are best understood in terms of polarizability and inductive contributions. With alkyl substitution, in which the polarizability and inductive effects are opposed, the polarization is attenuated relative to the inductive effect because of its more critical dependence on distance. With other substituents, these two effects tend to both lead to increases in acidity.

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Surface-Induced Heterocycle Formation: Sulfur Atom Abstraction during Cyclization

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Abstract: We have studied the mechanism of a novel cyclization reaction in which acetylene abstracts sulfur from the Pd(111) surface in the form of thiophene. The proposed mechanism is one in which adsorbed acetylene first dimerizes to form a C_4H_4 intermediate which is then capable of abstracting atomic sulfur to form thiophene. The appearance of thiophene in the gas phase is then rate limited by thiophene desorption kinetics. This sequential mechanism has also been proposed for acetylene cyclotrimerization to benzene on the clean Pd(111) surface. Thiophene formation from acetylene is sensitive to both the surface sulfur coverage and the temperature at which the sulfur overlayer is produced. The reaction of a C_4H_4 species produced from *cis*-3,4-dichlorocyclobutene exhibits exactly the same sensitivity to surface characteristics and hence is identified as the intermediate produced by acetylene dimerization. We discuss the potential of this chemistry as a process for the regeneration of catalytic surfaces deactivated by sulfur contamination.

1. Introduction

There are a number of important cyclization reactions such as ethylene epoxidation and alkane dehydrocyclization that are catalyzed by metallic surfaces.[1,2] One novel reaction that has received attention over the past 5 years is the cyclotrimerization of acetylene on palladium surfaces. The first observations of this reaction under ultra-high-vacuum (UHV) conditions were reported by three groups in 1983,[3-5] and since then it has received careful study by Patterson et al.[6,7] The same reaction has also been observed on single-crystal surfaces of palladium at high pressures,[8,9] on Ni(111) surfaces,[10,11] and on the Cu(110) surface.[12] This paper presents a study of an important variant on this reaction in which sulfur is abstracted from the palladium surface in the form of thiophene.[13] Its importance stems from the fact that sulfur abstraction is necessary for regeneration of sulfur-contaminated catalytic surfaces. Furthermore, the fact that sulfur rather than acetylene is the third component being incorporated into the ring allows easier mechanistic study of the reaction.

The cyclotrimerization of acetylene to benzene on the clean Pd(111) surface occurs following acetylene adsorption at low temperatures (<150 K). During a thermal desorption experiment benzene desorption is observed both at 250 K and then again at 500 K. Patterson et al. have performed a comprehensive mechanistic study of this reaction. Using mixtures of C_2H_2 and C_2D_2 they have shown that the reaction occurs without carbon–carbon or carbon–hydrogen bond breaking. Using *cis*-3,4-dichlorocyclobutene ($C_4H_4Cl_2$) as a precursor, they have produced a C_4H_4 intermediate on the Pd(111) surface which cyclizes with C_2D_2 to yield benzene-d_2, clearly indicating that the reaction can occur via a sequential mechanism involving initial dimerization followed by cyclization.[6,7] Furthermore, molecular beam kinetics studies of the cyclotrimerization reaction revealed a C_4 species desorbing into the gas phase,[3] and catalysis of this reaction at high pressures by supported Pd particles has been found to produce 1,3-butadiene.[14] Most recently, a reaction similar to the one studied in this work has been observed to produce furan by heterocyclization of acetylene with oxygen atoms.[15] Vibrational spectra of the C_4H_4 species generated during decomposition of $C_4H_4Cl_2$ have been obtained with use of HREELS.[16] Comparison with vibrational spectra of several inorganic complexes indicates that the C_4H_4 intermediate is a cyclic compound with its ring plane tilted away from the surface normal. Obvious candidates are a metallapentacycle or a palladium-substituted cyclobutene.

There are a number of inorganic and organometallic complexes that either catalyze cyclization reactions[17-20] or will react with other reagents to form cyclic species.[21,22] One of the best known

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[1] Sachtler, W. M. H.; Backx, C.; Van Santen, R. A. *Catal. Rev.-Sci. Eng.* **1981**, *23* (*1*), 127.

[2] Sharan, K. M. *Catal. Rev.-Sci. Eng.* **1984**, *26* (2), 141.

[3] Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Surf. Sci.* **1983**, *135*, 128.

[4] Gentle, T. M.; Meutterties, E. L. *J. Phys. Chem.* **1983**, *87*, 2469.

[5] Sesselmann, W.; Woratschek, B.; Ertl, G.; Kuppers, J.; Haberland, H. *Surf. Sci.* **1983**, *130*, 245.

[6] Patterson, C. H.; Lambert, R. M. *J. Phys. Chem.* **1986**, *92*, 1266.

[7] Patterson, C. H.; Lambert, R. M. *J. Am. Chem. Soc.* **1988**, *110* (*20*), 6871.

[8] Rucker, T. G.; Logan, M. A.; Gentle, T. M.; Meutterties, E. L.; Somorjai, G. A. *J. Phys. Chem.* **1986**, *90*, 2703.

[9] Logan, M. A.; Rucker, T. G.; Gentle, T. M.; Meutterties, E. L.; Somorjai, G. A.; *J. Phys. Chem.* **1986**, *90*, 2709.

[10] Bertolini, J. C.; Massardier, J.; Dalmai-Imelik, G. *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 1720.

[11] Yang, Q. Y.; Johnson, A. D.; Manyard, K. J.; Ceyer, S. T. *J. Am. Chem. Soc.* **1989**, *111* (*23*), 8748.

[12] Avery, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 6711.

[13] Gentle, T. M.; Walley, K. P.; Tsai, C. T.; Gellman, A. J. *Catal. Lett.* **1989**, *2*, 19.

[14] Ormerod, R. M.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1421.

[15] Ormerod, R. M.; Lambert, R. M. *Catal. Lett.* **1990**, *6*, 121.

[16] Patterson, C. H.; Mundenar, J. M.; Timbrell, P. Y.; Gellman, A. J.; Lambert, R. M. *Surf. Sci.* **1989**, *208*, 93.

[17] Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engel.* **1984**, *23*, 539.

[18] Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10* (*1*), 1.

[19] Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.

[20] Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 3800.

0002-7863/91/1513-4435$02.50/0