PERKIN 2

Gas-phase acidities of aryldimethylsilanes†

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Gas-phase acidities of aryldimethylsilanes have been determined by measuring equilibrium constants of proton-transfer reactions using a FT ion cyclotron resonance mass spectrometer. The acidity of dimethylphenylsilane was found to be 370.5 kcal mol^{-1}, *i.e.*, it is a stronger acid than dimethylsilane by 2.7 kcal mol^{-1}. The acid-enhancing effect of the phenyl group is significantly smaller than in the carbon analog. In addition, the acidities of aryldimethylsilanes were linearly correlated with the standard substituent constant ($\sigma°$), giving a ρ of 4.6, indicating that the thermodynamic stabilities of silyl anions are less sensitive to the polar effects of substituents than benzoate, phenoxide, anilide, and benzyl anions. More importantly, it was found that the *p*-nitro group, which has a large π-electron-accepting ability, also conforms to the $\sigma°$ correlation, suggesting that π-delocalization does not play a role in the stabilization of silyl anions; this is in contrast to the π-effects observed in carbon analogs. This is supported by theoretical stabilization energies and optimized geometrical features based on *ab initio* calculations.

Introduction

In this study, we have measured the equilibrium constants of proton-transfer reactions in the gas phase in order to determine a quantitative scale of thermodynamic stabilities of aryldimethylsilyl anions, which allows us to analyze in detail substituent effects on their stabilities.

Despite the extensive use of silyl anions as synthetic reagents to form silicon–carbon bonds,[1] as polymers, and as precursors in semiconductor manufacturing, the thermochemistry of silyl anions[2,3] has been studied much less than that of carbanions.[4] Silyl anions, like carbanions, are solvated in solution and they are associated with alkali metal cations. Gas-phase experiments, in the absence of solvent, allow the determination of the intrinsic properties of the anions through the measurement of their acidities, so that the relative stabilities of the anions can be compared. In the gas phase, silyl anions are much more stable than carbanions, *e.g.*, $\Delta G°_{acid}(CH_4) = 408.5$ kcal mol^{-1} (ref. 4) *vs.* $\Delta G°_{acid}(SiH_4) = 363.8$ kcal mol^{-1} (ref. 4) (1 cal = 4.184 J). This is related to correspondingly higher electron affinities [EA(SiH_3) = 32.4 kcal mol^{-1} (ref. 2 and 5) *vs.* EA(CH_3) = 1.8 kcal mol^{-1} (ref. 6)]. In addition, the acidity of silane was found to decrease by approximately 3–5 kcal mol^{-1} with successive methyl substitution,[2,7,8] in contrast to that for methane, where methyl substitution increases the acidity of methane, except for the first methyl substitution.[9] The substitution of a phenyl group was shown to have essentially no effect on the acidity of silanes,[2] suggesting that π-delocalization does not play a role in the stabilization of silyl anions. This is also in contrast to the observed π-effects in carbanions. We sought more detailed knowledge about the stabilization mechanism in silyl anions.

In this paper we report the gas-phase acidities for a series of ring-substituted dimethylphenylsilanes determined by measuring the equilibrium constants of the proton transfer reaction (1). The substituent effects on the stabilities of silyl anions are compared with those for carbanions. *Ab initio* calculations are also used to aid our understanding of the stabilization mechanisms for silyl anions.

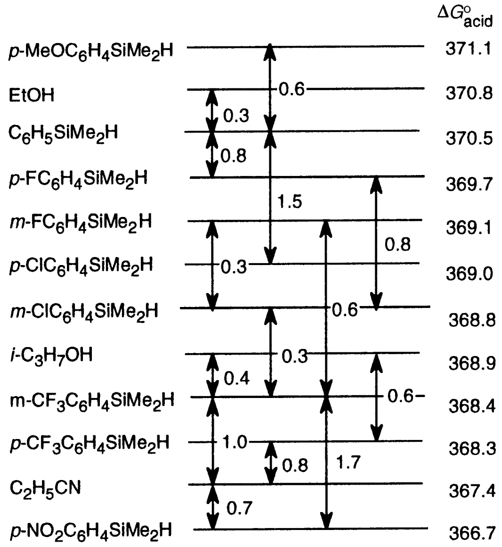
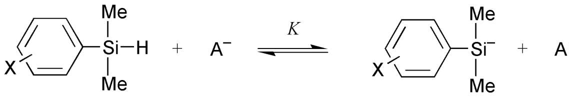


Fig. 1 Ladder for free energy changes at 323 K of proton transfer equilibria in kcal mol^{-1}.



(1)

Results and discussion

The gas-phase acidities of aryldimethylsilanes were derived from the proton-transfer equilibrium constants. The scale of acidity of these silanes was determined as shown on the ladder of interconnected ΔG° values in Fig. 1. Because the gas-phase acidities, $\Delta G°_{acid}$, for reference acids involved in the

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† Electronic supplementary information (ESI) available: cartesian coordinates of aryldimethylsilyl anions optimized at RHF/6-31+G*. See http://www.rsc.org/suppdata/p2/b1/b100488n/

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equilibrium proton transfer reactions are known, the ΔG°_{acid} for aryldimethylsilanes can be calculated, as shown in eqn. (2).

$$\Delta G^\circ_{acid}(XC_6H_4Si(Me_2)H) = -RT\ln K + \Delta G^\circ_{acid}(AH) \quad (2)$$

Although the present measurements were carried out at 323 K, selected ΔG°_{acid} values may be regarded as mean values at 300 K, because the ΔG°_{acid} values of the reference acids were evaluated at 300 K.[4] In addition, since the entropy changes of the proton-transfer reaction are small in the gas phase,[10] it is reasonable to assume $\Delta G^\circ_{(323\ K)} \approx \Delta G^\circ_{(300\ K)}$.

From this ladder of free energy changes, the ΔG°_{acid} of unsubstituted dimethylphenylsilane is found to be 370.5 kcal mol^{-1} at 300 K. The ΔG°_{acid} values are available for relevant silane compounds in the literature.[4] Some of them were determined from the free energy changes between silanes and reference acids by measuring equilibrium constants and/or kinetic rate constants. Prior to a comparison of the present results with those for other relevant silanes, it is necessary to examine the acidity values in the literature, because these values may need to be corrected due to differences in the acidity scales of the reference acids used for measurements. Based on the latest database of gas-phase acidities complied by Bartmess,[4] the revised values are obtained as follows, 363.8, 369.6, 373.2, 361.0, and 366.5 kcal mol^{-1} for SiH_4, $MeSiH_3$, Me_2SiH_2, $PhSiH_3$, and $PhSiMeH_2$, respectively. The ΔG°_{acid} of 377 ± 2 kcal mol^{-1} for Me_3SiH in the literature was obtained by a bracketing experiment using furan (380.0 kcal mol^{-1}) and methanol (375.2 kcal mol^{-1}).[11] Since the proton transfer reaction with methanol was found to be complicated by competition with another reaction channel,[12] Brauman *et al.*[2] presumed the true Si–H acidity to be close to the acidity of methanol, based on the derived bond dissociation energy and consistency with measurements made by different methods, and gave the value as 375 ± 2 kcal mol^{-1}. To examine the reliability of these values we carried out *ab initio* calculations for these methyl-substituted silanes at the RHF/6-311++G** level of theory. Based on a linear correlation between calculated and observed acidities for SiH_4, $MeSiH_3$, and Me_2SiH_2, $\Delta G^\circ_{acid}(obsd) = 0.72\Delta G^\circ_{acid}(calcd) + 96.4$ ($R = 0.998$);[13] the value $\Delta G^\circ_{acid} = 376.3$ kcal mol^{-1} is obtained for Me_3SiH. Although this value is still within the stated error bar (± 2 kcal mol^{-1}), the correction is important as it allows us to compare acidities of relevant compounds in detail.

From these revised acidity values, the acidities of phenylsilanes are found to decrease approximately by 3 to 5 kcal mol^{-1} with successive methyl substitution; $PhSiH_3 > PhSiMeH_2 > PhSiMe_2H$. This is consistent with the trend for methyl-substituted silanes. Indeed, the effect of methyl substitution on the acidity of phenylsilane ($PhSiH_3$) is correlated linearly with the corresponding effect on the acidity of silane (SiH_4) with a slope of unity [eqn. (3)].

$$\Delta G^\circ_{acid}(PhSiMe_nH_{(3-n)}) = 9.5 + 0.98\,\Delta G^\circ_{acid}(Me_nSiH_{(4-n)}) \quad R = 0.972 \quad (3)$$

In addition, it is found that the phenyl stabilization of silyl anions is, remarkably, smaller than that for carbanions, *e.g.*, the effect of phenyl substitution on the stability of carbanions is −34.8 kcal mol^{-1} for CH_3^- and −38.5 kcal mol^{-1} for Me_2CH^-, while that for silyl anions is −3 to −4 kcal mol^{-1}. Thus, it is evident that phenyl substitution has essentially a much smaller effect on the acidity of silanes, as noted previously by Brauman *et al.*[2]

Fig. 2 shows a plot of the relative acidities of aryldimethylsilanes against those of the corresponding benzoic acids as a standard substituent effect in the gas phase (Table 1).[14,15] There is a simple linear relationship between these two quantities. The slope of 0.33 indicates that the response of the stability of the silyl anion to the substituent is significantly smaller than that in the carboxylate anion. This is in contrast to the effect for benzyl anions, phenoxides, and anilides. For example, the corresponding plot for acidities of toluenes is shown in Fig. 3.[16] There is a linear relationship for *meta* substituents and *para* substituents having no π-interaction with the negative charge at the benzylic carbon atom. The slope of 1.35 in this plot is four times larger than that shown in Fig. 2, indicating that the magnitude of the substituent effect for the silyl anions is intrinsically smaller than

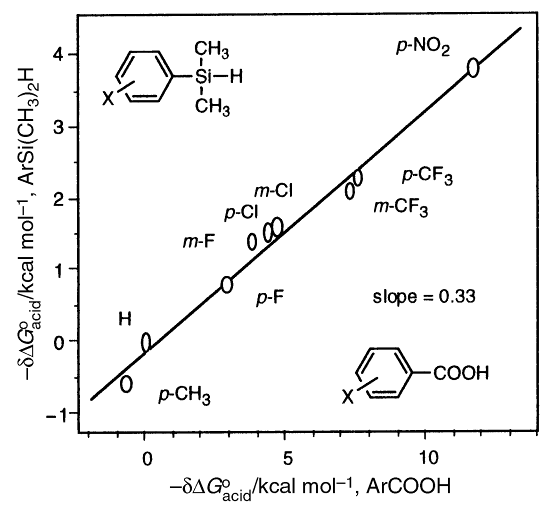


Fig. 2 Plot of $-\delta\Delta G^\circ_{acid}$ between aryldimethylsilanes and benzoic acids.

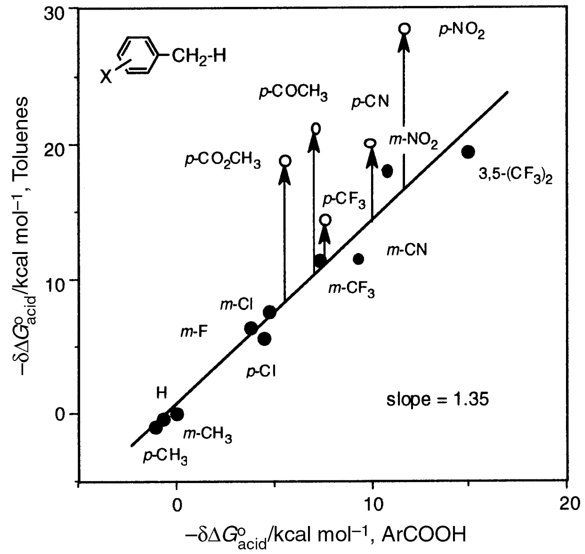


Fig. 3 Plot of $-\delta\Delta G^\circ_{acid}$ between substituted toluenes and benzoic acids.

Table 1 Relative gas-phase acidities of aryldimethylsilanes and benzoic acids

	$-\delta\Delta G^\circ$/kcal mol^{-1}		
Substituent	$XC_6H_4SiMe_2H$	XC_6H_4COOH[a]	σ°/gas[b]
p-NO_2	3.8	11.7	0.80
p-CF_3	2.3	7.6	0.56
m-CF_3	2.1	7.3	0.50
m-F	1.4	3.8	0.39
m-Cl	1.6	4.7	0.36
p-Cl	1.5	4.4	0.32[c]
p-F	0.8	2.9	0.20
H	0.0	0.0	0.00
p-MeO	−0.6	−0.7	−0.10

1 cal = 4.184 J. [a] Taken from ref. 15. [b] Standard substituent constants in the gas phase, ref. 17. [c] Revised value for the substituent effect in the anionic system.

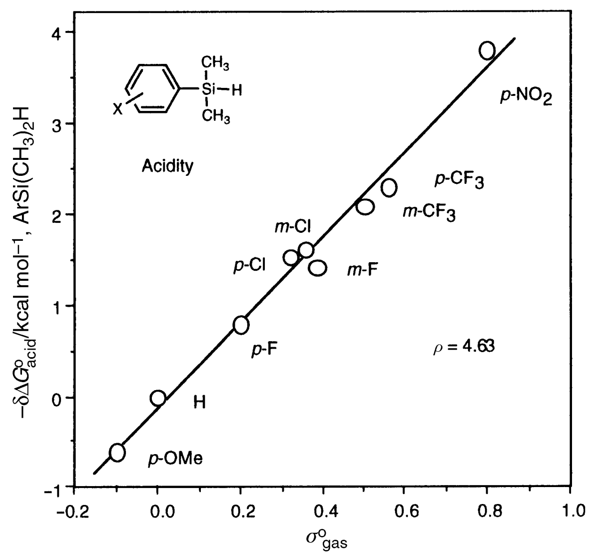
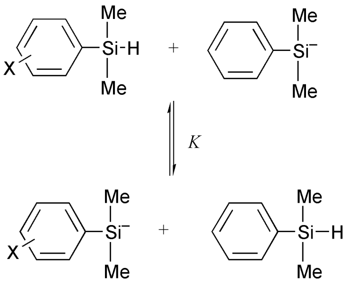


Fig. 4 Plot of $-\delta\Delta G^{\circ}_{acid}$ of aryldimethylsilanes against σ°_{gas}.

that for the benzylic carbanions. Moreover, it is found from Fig. 3 that strong π-acceptors show large positive deviations with respect to the line based on non-conjugative substituents. These deviations can easily be interpreted by the enhanced resonance effect of the substituent to stabilize the benzyl anions, *i.e.*, the negative charge is significantly delocalized into the aryl moiety.[15] In contrast, Fig. 2 does not show any appreciable deviation of the *para* nitro group, leading to the conclusion that the negative charge at the silicon atom upon deprotonation is not delocalized into the aromatic moiety at all. In fact, the substituent effect on the acidity of dimethylphenylsilane is linearly correlated with σ°,[17] which involves no resonance effect contribution (see Fig. 4), giving a ρ of 4.6. This conclusion is also consistent with studies both of NMR chemical shifts in various phenylsilyl anions[18] and of the absorption spectra of phenylsilyllithium salts in THF.[19]

The anion stabilization for these compounds can also be calculated using *ab initio* theory. We have performed calculations using 6-31+G* and 6-311++G** basis sets and used isodesmic reaction (4) to estimate stabilization energies.



(4)

The results are summarized in Table 2. From these calculations, the stabilization of the *para* nitro group at the 6-31+G* level is 13.5 kcal mol^{-1} and at the 6-311++G** level is 13.2 kcal mol^{-1}; there is no significant difference between the two basis sets. To improve the calculated energies, single point MP2 calculations were also carried out with 6-31+G* and 6-311++G** basis sets using optimized structures at RHF/6-31+G* and RHF/6-311++G**, respectively. The MP2 results give essentially similar stabilization effects, though the stabilization effect of the *para* nitro group is slightly smaller than that obtained by RHF calculations. Comparison of the calculated stabilization effects with the experimental values reveals that the calculated values are approximately three times larger than the observed effects. Despite this discrepancy between calculated and experimental stabilization energies, it is found that there is a good linear relationship between both sets of values as shown in Fig. 5. The *para* nitro group having a strong π-accepting ability also conforms to this linear relationship, indicating that the absence of a resonance effect by the *para* nitro group in the dimethylphenylsilyl anion is not incidental but essential.

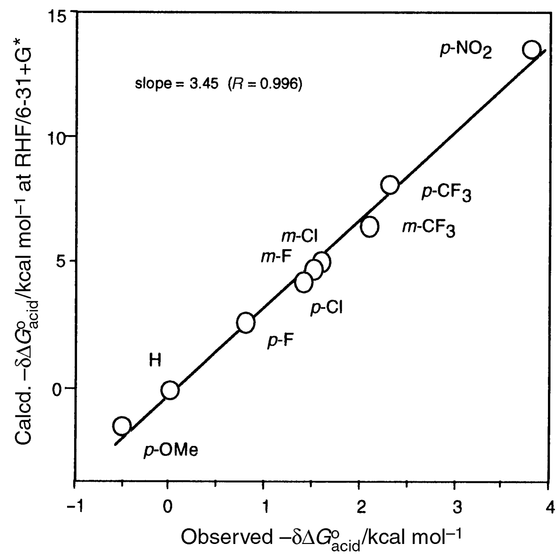


Fig. 5 Plot of calculated $-\delta\Delta G^{\circ}_{acid}$ *vs.* observed $-\delta\Delta G^{\circ}_{acid}$ for aryldimethylsilanes.

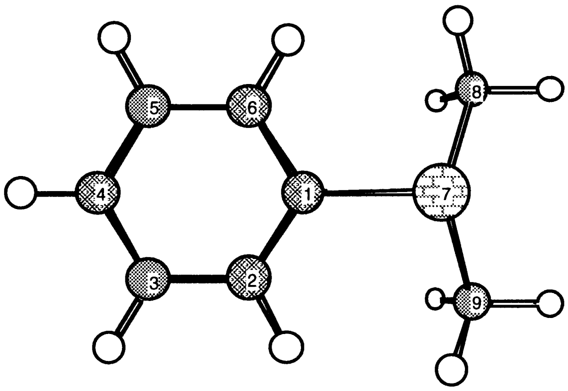


Fig. 6 Numbering of atoms for dimethylphenylsilane.

The optimized geometries of neutrals and anions aid our understanding of the mechanism of the stabilization. Selected bond lengths and angles are summarized in Table 3. The numbering of atoms is shown in Fig. 6. In order to examine the dependency of calculated structures on the level of theory used, we optimized the structures at MP2/6-31+G* for *para* nitro, *meta* fluoro, and unsubstituted derivatives. These results are also given in Table 3. There is no difference in bond lengths and angles between these two methods for the neutral silanes and the silyl anions except for the C1–Si bond length of the silyl anions. Although the MP2 method tends to give shorter C1–Si bond lengths than the RHF calculation, examination of the C1–Si bond lengths shows a trend that bond lengths increase upon deprotonation. If π-delocalization of the negative charge at Si into the aromatic moiety exists, resonance theory tells us that the C1–Si bond should shorten upon deprotonation. The present results show this is not the case, supporting strongly the absence of π-delocalization in silyl anions. Another geometrical feature may be explored by bond angles at Si atom. All silyl anions calculated in this study are found to be pyramidal at silicon, in contrast with the corresponding carbanions, which are planar. The ∠C1–Si–C8, ∠C1–Si–C9, and ∠C8–Si–C9 decrease substantially upon deprotonation, from approximately 110–111 to 98–100°. The small central angles at silicon, as well as the long C1–Si bond lengths, upon deprotonation may be

Table 2 Calculated relative acidities of aryldimethylsilanes, $-\delta\Delta G^\circ_{\text{acid}}$[a]

Substituent	RHF/6-31+G*[b]	MP2/6-31+G*[bc]	RHF/6-311++G**[d]	MP2/6-311++G**[de]
p-NO_2	13.5	12.7	13.2	11.9
p-CF_3	8.1	8.5	7.9	7.9
m-CF_3	6.4	7.0	6.3	6.5
m-Cl	5.1	4.7	5.0	4.4
p-Cl	4.8	4.2	4.7	3.9
m-F	4.2	3.9	4.1	3.5
p-F	2.7	3.0	2.6	2.4
H	0.0	0.0	0.0	0.0
m-Me	−0.5	−0.7	−0.5	−0.5
p-Me	−1.3	−1.0	−1.3	−0.9
p-MeO	−1.5	−1.0	−1.5	−1.1

All values in kcal mol^{-1} at 298.15 K. [a] Free energy changes for isodesmic reaction (4). [b] Structures are optimized at RHF/6-31+G*. [c] Thermal correction to free energy obtained at RHF/6-31+G* is used. [d] Structures are optimized at RHF/6-311++G**. [e] Thermal correction to free energy obtained at RHF/6-311++G** is used.

Table 3 Selected geometries of dimethylphenylsilyl anions and the corresponding silanes optimized at RHF/6-31+G*

	Bond length/Å			Angle/°		
Silyl anions	C1–Si	Si–C8	Si–C9	∠C1–Si–C8	∠C1–Si–C9	∠C8–Si–C9
p-NO_2	1.957	1.956	1.956	99.8	99.8	98.9
	[1.903]	[1.944]	[1.944]	[100.9]	[100.9]	[100.2]
	(1.955)	(1.951)	(1.952)	(100.0)	(99.9)	(99.0)
p-CF_3	1.967	1.960	1.957	100.0	98.7	98.4
m-CF_3	1.972	1.956	1.961	100.3	98.0	98.4
m-Cl	1.972	1.961	1.957	100.3	98.3	98.4
p-Cl	1.970	1.961	1.958	100.2	98.4	98.3
m-F	1.969	1.961	1.957	100.2	98.5	98.3
	[1.941]	[1.952]	[1.951]	[98.8]	[98.3]	[98.0]
	(1.967)	(1.956)	(1.953)	(100.4)	(98.6)	(98.6)
p-F	1.972	1.962	1.958	100.4	98.3	98.2
H	1.968	1.959	1.962	100.5	98.7	98.2
	[1.942]	[1.954]	[1.954]	[98.7]	[98.7]	[97.9]
	(1.966)	(1.954)	(1.957)	(100.6)	(98.7)	(98.5)
m-Me	1.967	1.962	1.959	100.6	98.7	98.2
p-Me	1.968	1.963	1.959	100.5	98.6	98.2
p-MeO	1.969	1.963	1.959	100.6	98.5	98.2
	Bond length/Å			Angle/°		
Silanes	C1–Si	Si–C8	Si–C9	∠C1–Si–C8	∠C1–Si–C9	∠C8–Si–C9
p-NO_2	1.902	1.887	1.887	110.2	110.2	110.8
	[1.890]	[1.882]	[1.882]	[109.6]	[109.6]	[110.7]
	(1.900)	(1.882)	(1.882)	(110.0)	(110.0)	(110.8)
p-CF_3	1.898	1.888	1.888	110.5	110.5	110.4
m-CF_3	1.896	1.888	1.888	110.6	110.6	110.4
m-Cl	1.896	1.888	1.888	110.6	110.6	110.3
p-Cl	1.894	1.889	1.889	110.7	110.7	110.2
m-F	1.896	1.888	1.888	110.6	110.6	110.3
	[1.887]	[1.883]	[1.883]	[109.8]	[109.8]	[110.5]
	(1.895)	(1.883)	(1.883)	(110.5)	(110.5)	(110.3)
p-F	1.891	1.889	1.889	110.9	110.9	110.0
H	1.892	1.890	1.890	110.9	110.9	109.9
	[1.884]	[1.885]	[1.885]	[110.0]	[110.0]	[110.2]
	(1.890)	(1.884)	(1.884)	(110.8)	(110.8)	(110.0)
m-Me	1.891	1.890	1.890	110.0	110.9	109.9
p-Me	1.889	1.890	1.890	111.0	111.0	109.8
p-MeO	1.885	1.891	1.891	111.2	111.2	109.6

[a] Values in parentheses, [ ] and ( ), are obtained at MP2/6-31+G* and RHF/6-311++G**, respectively.

due to the repulsive interaction between the negative charge at the Si atom and the π-electrons of the benzene ring. These geometrical features of silyl anions are consistent with earlier theoretical studies of substituent effects on the stability of simple silyl anions ($XSiH_2^-$ where X = NH_2, OH, F, SiH_3, PH_2, SH, Cl having a lone pair of electrons),[20,21] *i.e.*, it has been shown that the X–Si and Si–H bond lengths increase upon deprotonation by 0.1 Å and that the central Si bond angle decreases by approximately 10°. In addition, even the potentially conjugated $N{\equiv}CSiH_2^-$, $HC({=}O)SiH_2^-$, and $HC{\equiv}CSiH_2^-$ anions were found to be pyramidal at silicon, indicating no significant charge delocalization.[22,23] Thus, the small central angles are characteristic of silyl anions. Such small angles, in general, are related to substantial p-character in the bonds, and the extra electron is therefore located in an orbital with substantial s-character.[7] An orbital with more s-character is expected to bind an electron more tightly than one with more p-character. Probably, this is the reason for the absence of π-delocalization of the negative charge, in contrast with what is observed in carbanions.

Conclusions

The substituent effect on the gas-phase acidity of dimethylphenylsilane is significantly smaller than that for carbon acids. Resonance stabilization does not play an important role for the stability of silyl anions. This is supported by geometrical features of silyl anions obtained by *ab initio* calculations, though the stabilization energies are not reproduced quantitatively by these calculations.

Experimental

Chemicals and syntheses

The silanes used in this study were available from our previous study[24] except for the *p*-nitro derivative. *p*-Nitrophenyldimethylsilane was prepared from *p*-nitrobenzoyl chloride and 1,1,2,2-tetramethyl-1,2-dichlorodisilane according to Rich's procedure.[25]

1,1,2,2-Tetramethyl-1,2-dichlorodisilane.[26] A mixture of hexamethyldisilane (15 g, 100 mmol) and concentrated sulfuric acid (100 g) was vigorously stirred at 23 °C for 2 days. The mixture was then cooled to 0 °C and powdered ammonium chloride (16 g, 300 mmol) was added over 30 min with stirring. The oil bath was then heated up to 150 °C and the distilled product was collected. The crude dichloride was redistilled at 138–142 °C to give 1,1,2,2-tetramethyl-1,2-dichlorodisilane (4.37 g, 23%).

***p*-Nitrophenyldimethylchlorosilane.** A mixture of *p*-nitrobenzoyl chloride (3.1 g, 17 mmol) and 1,1,2,2-tetramethyl-1,2-dichlorodisilane (4.0 g, 21 mmol) was heated at 140 °C under nitrogen. To the solution bis(benzonitrile)palladium chloride (6.4 mg, 1.7×10^{-2} mmol) and triphenylphosphine (8.8 mg, 3.4×10^{-2} mmol) were added, resulting in the evolution of carbon monoxide. The mixture was heated at 140 °C for 20 h. Distillation (117–120 °C/5 mmHg) of the mixture afforded 1.5 g (41%) of *p*-nitrophenyldimethylchlorosilane. δ_H(500 MHz; $CDCl_3$; Me_4Si) 0.74 (6H, s, $SiMe_2$), 7.81 (2H, d, $J = 8.5$ Hz, Ph), 8.24 (2H, d, $J = 8.5$ Hz, Ph).

***p*-Nitrophenyldimethylsilane.** $LiAlH_4$ (0.27 g, 7.0 mmol in dry ether 100 mL) was added slowly to an ethereal solution of *p*-nitrophenyldimethylchlorosilane (1.5 g, 7.0 mmol) under a nitrogen atmosphere, then aq. HCl (10%, 30 mL) was added. The mixture was extracted with ether, washed with saturated aqueous NaCl solution, and dried over anhydrous magnesium sulfate. Removal of solvent afforded the crude product (0.9 g, 28%) and purification by silica gel column chromatography gave pure *p*-nitrophenyldimethylsilane (0.1 g), which was characterized by ^1H NMR and elemental analysis as follows. δ_H(500 MHz; $CDCl_3$; Me_4Si) 0.74 (6H, s, $SiMe_2$), 4.58 (1H, m, SiH), 7.71 (2H, d, $J = 8.5$ Hz, Ph), 8.18 (2H, d, $J = 8.5$ Hz, Ph). Anal. Calcd. for $C_8H_{11}O_2NSi$: H, 6.21; C, 53.30; N, 7.53. Found: H, 6.12; C, 53.01; N, 7.73%.

Gas-phase acidity measurements

The gas-phase acidity measurements were performed on an Extrel FTMS 2001 Fourier transform mass spectrometer. Most of the experimental techniques used for the measurements of the equilibrium constants of the reversible proton-transfer reaction (8) are the same as the general method described in the literature.[27] Only significant changes and additional procedures will be given here.

All equilibrium measurements were performed at 50 °C at a 3.0 T magnetic field strength using a cubic (2 × 2 × 2 in.) trapped analyzer cell. Typical operating pressures were 10^{-6}–10^{-7} Torr. The proton-transfer reactions were initiated by a pulsed electron beam (electron energy of 0.3–1.0 eV, uncorrected, with a pulse width of 5 ms) through the ICR cell. Methyl nitrite of *ca.* 1×10^{-7} Torr was used for the initiation of the chemical ionization of the acids studied, eqns. (5)–(7). Each

$$\text{MeONO} + e^- \rightleftharpoons \text{MeO}^- + \text{NO} \qquad (5)$$

$$\text{MeO}^- + A_oH \rightleftharpoons A_o^- + \text{MeOH} \qquad (6)$$

$$\text{MeO}^- + AH \rightleftharpoons A^- + \text{MeOH} \qquad (7)$$

$$A^- + A_oH \rightleftharpoons A_o^- + AH \qquad (8)$$

neutral sample was separately introduced into the ICR cell through a variable leak valve (ANELVA). The mass spectra and timeplots were acquired and processed in a FT mode. After a reaction period of 0.5 to 1 s, depending upon the pressure of the neutrals, equilibrium was attained and relative abundances of A^- and A_o^- were measured by signal intensities of ICR spectra. Each measurement was performed at several ratios of partial pressures and at different overall pressures. The pressures of the neutral reactants were measured by means of a Bayard–Alpert-type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.[28] Arithmetic mean values of K from eqn. (9) were used for the calculation of $\Delta G°$ at 343 K [eqn. (10)] with an average uncertainty of ± 0.2 kcal mol^{-1} in most cases.

$$K = [A_oH/AH][A^-/A_o^-] \qquad (9)$$

$$\Delta G° = RT \ln K \qquad (10)$$

The proton-transfer reactions were examined by ion-eject experiments using the SWIFT technique.[29] Each sample was subjected to several freeze–pump–thaw cycles on the ICR inlet vacuum system to remove entrapped impurities. The gas-phase acidity values for the reference compounds were taken from the literature.[4]

Calculations

Ab initio calculations were carried out using the Gaussian 98 program[30] suite. The geometries were fully optimized at the RHF/6-31+G* and RHF/6-311++G** levels of theory with normal convergence. Vibrational normal mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface and to calculate the thermal correction needed to obtain the Gibbs free energies. The zero point energies used for the thermal correction were unscaled. To improve the calculated energies, single point MP2 calculations were also carried out at the 6-31+G* and 6-311++G** basis sets using the frozen-core approximation. Thermal corrections to the Gibbs free energy evaluated at HF/6-31+G* and RHF/6-311++G** levels were also applied to total energy of single point MP2 calculations. For unsubstituted, *m*-fluoro and *p*-nitro derivatives, the geometries were optimized at the MP2/6-31+G* level to examine the dependency of calculated structures on the level of theory used.

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