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Binding Interaction of the Trimethylsilyl Cation with Oxygen and Nitrogen Bases in the Gas Phase. Acetopheones, Benzaldehydes, Pyridines, Anilines, and *N*,*N*-Dimethylanilines

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The gas-phase basicities toward the trimethylsilyl cation, GB(Me_3Si^+), were determined for a series of acetophenones, benzaldehydes, pyridines, anilines, and *N*,*N*-dimethylanilines by measuring the equilibrium constants of trimethylsilyl cation transfer reactions. GB(Me_3Si^+) increases in the order aniline < benzaldehyde < acetophenone < *N*,*N*-dimethylaniline < pyridine, while GB(H^+) increases as benzaldehyde < acetophenone < aniline < pyridine < *N*,*N*-dimethylaniline. The effects of ring substituents on the GB(Me_3Si^+) of the respective bases are, however, linearly correlated with the corresponding proton basicities with a slope of 0.8 to 1.0, showing family-dependent linear relationships. Furthermore, an analysis of the substituent effects on the GB(Me_3Si^+) of acetophenone and benzaldehyde showed that the ρ values are close to those for the proton basicities, though the resonance demand of Me_3Si^+ adduct ions is slightly reduced compared with that for the protonated ones. DFT calculations at the B3LYP/6-31+G(d) level of theory reproduced such a trend in substituent effects as well as the family-dependent linear correlations between the H^+ and Me_3Si^+ basicities. Both the experimental and theoretical results lead to the conclusion that the binding interactions of Me_3Si^+ with O and N atoms of organic bases have a pronounced covalent character to a similar degree as that of a proton.

Although organosilicon chemistry has made significant progress over the last 50 years, progress in isolating and characterizing the three-coordinate cationic species, R_3Si^+, in the condensed phase has been made recently.[1—3] This might be due to the kinetic instability of silyl cations in solution. Their high electrophilicity allow them to interact with a wide variety of both π- and σ-electron donors, such as solvents and counter ions.[3] Silyl cations are, however, thermodynamically stable compared to R_3C^+ in the gas phase, as shown from the mass spectrometry of organosilicon compounds.[4] The gas-phase basicity (GB) toward R_3Si^+, obtained by measuring the R_3Si^+ transfer equilibrium (1), is a good model for understanding the intrinsic nature of the binding interactions between silyl cations and electron pair donors.[5—10]

$$\mathrm{B} + \mathrm{R_3Si^+{-}B_0} \rightleftharpoons \mathrm{R_3Si^+{-}B} + \mathrm{B_0} \qquad (1)$$

Wojtyniak and Stone[6] found that there is a linear relationship between the Me_3Si^+ basicities (GB(Me_3Si^+)) and the H^+ basicities (GB(H^+)) for oxygen bases such as alcohols, esters, and ketones, and noted that the Me_3Si^+ basicity has a lower response to changes in the structure of the base than does the H^+ basicity. From this result the Si–O bond in the Me_3Si^+ adduct ion with an oxygen base was inferred to have a relatively significant electrostatic character, as compared to the H–O bond in protonated ions. Similar results were also observed for alkylamine bases.[10] On the other hand, in a preliminary study we analyzed the effect of ring-substituents on the Me_3Si^+ basicity of acetophenones,[11a] where the environment at the binding site remains constant and the variation comes from the substituent in the benzene ring. It was found that there exists an excellent linear relationship between GB(Me_3Si^+) and GB(H^+) with a slope of 0.96 for *meta* substituents. Furthermore, an analysis of the substituent effect by means of the Yukawa–Tsuno (Y–T) equation (Eq. 2) gave a ρ of −8.08 and an r^+ of 0.70,

$$\log K/K_0 = \rho(\sigma^\circ + r^+\Delta\overline{\sigma}_R^+), \qquad (2)$$

where σ° and $\Delta\overline{\sigma}_R^+$ are the normal substituent constant and the resonance substituent constant, and r^+ is the resonance demand parameter representing the degree of the π-delocalization of the positive charge into the aryl π-system. An r^+ of 0.70 for the Me_3Si^+ basicity of acetophenone revealed that the positive charge formed on the benzylic carbon by the binding of Me_3Si^+ with the oxygen of the carbonyl group is significantly delocalized into the aryl π-system, although the degree of π-delocalization is somewhat smaller than that of the protonated conjugate acid ($r^+ = 0.80$).[11] These results led to a suggestion that the Si–O bond in the adduct ion, $Me_3Si^+{-}O{=}C\langle$, has a significant covalent character similar to that of the H–O bond in the protonated ion, $H^+{-}O{=}C\langle$.

In this study, we extended the scale of the Me_3Si^+ basicities to not only oxygen bases, but also to nitrogen bases, such as pyridines, anilines, and *N*,*N*-dimethylanilines. This allowed us to elucidate the intrinsic nature of the binding interaction between Me_3Si^+ and bases and to make a comparison with the protonation interactions. In addition, density functional theory (DFT) calculations were conducted on these Me_3Si^+-transfer reactions to compare with the experimental thermodynamic stabilities of the Me_3Si^+ adduct ions determined in the gas phase and to elucidate the structural features of their adduct ions.

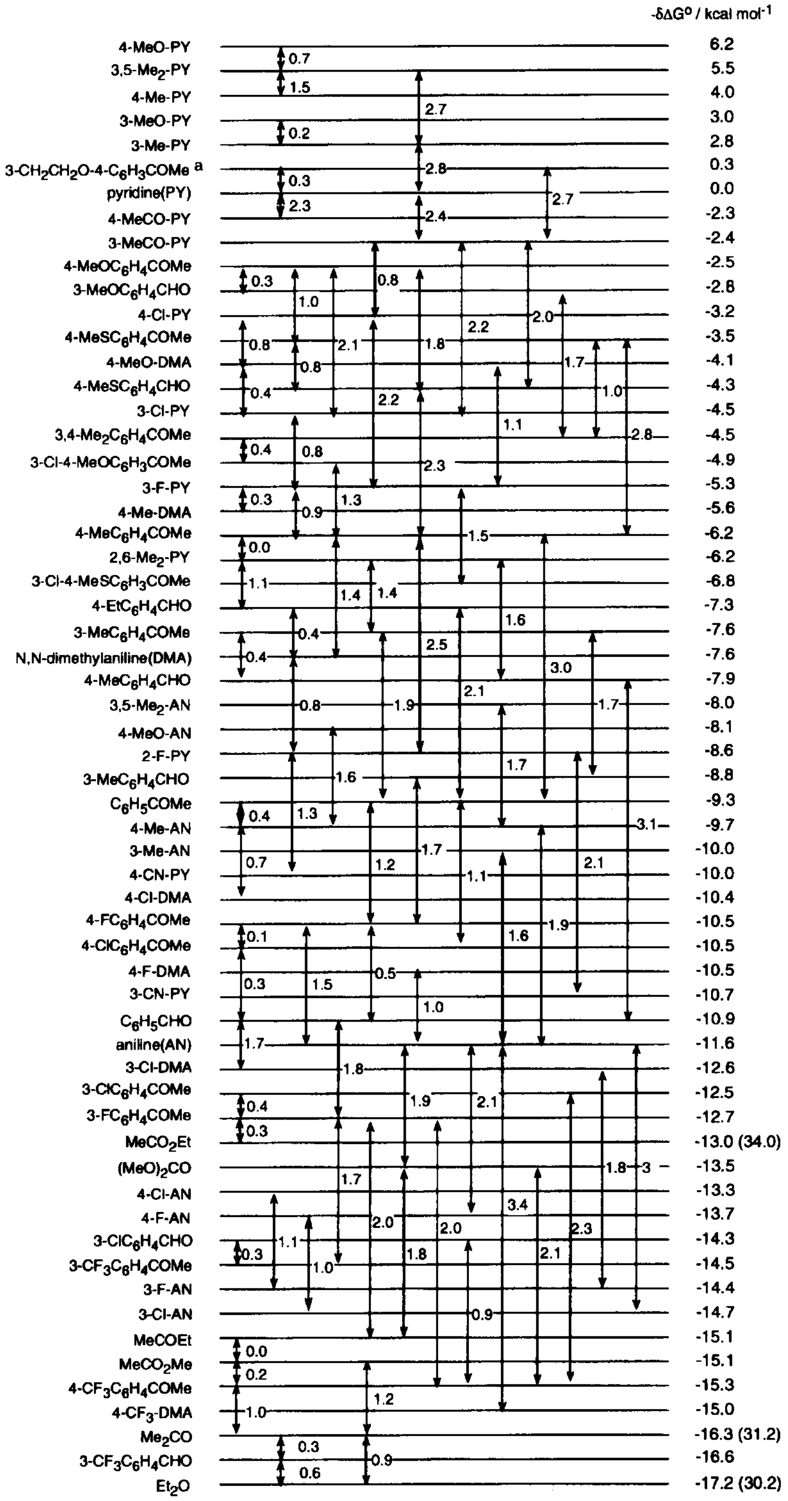


Fig. 1. Ladder of ΔG° values for Me_3Si^+ transfer equilibrium. Trimethylsilyl cation basicity increases from bottom to the top. Selected values are relative basicities to pyridine. PY: pyridine, AN: aniline, DMA: *N*,*N*-dimethylaniline. Values in parentheses are absolute basicities.[6]

Results and Discussion

The free-energy changes of Me_3Si^+ transfer equilibria in the gas phase are shown in Fig. 1. Comparisons of the overlapping and successive steps on the ladder show an internal consistency of about 0.3 kcal mol^{-1}. The selected relative Me_3Si^+ basicity values correspond to a negative free-energy change according to the following reaction:

$$B + C_5H_5N\text{–}SiMe_3^+ \rightleftharpoons B\text{–}SiMe_3^+ + C_5H_5N \qquad (3)$$

$$-\Delta G^\circ = \Delta GB(Me_3Si^+) \qquad (4)$$

The ladder includes substituted acetophenones studied previously in our laboratory.[11] The values of several acetophenone derivatives were revised in this study. Acetone, diethyl ether, and ethyl acetate of known absolute $GB(Me_3Si^+)$ values[6] are also included for calibrating the relative $GB(Me_3Si^+)$ values to an absolute scale. Differences in $GB(Me_3Si^+)$ among these three compounds are in complete agreement with the corresponding values from the literature.[7] The calibrated absolute scale $GB(Me_3Si^+)$ values are given in Table 1 together with the corresponding $GB(H^+)$ values.

The observed $GB(Me_3Si^+)$ increases in the order aniline (35.5) < benzaldehyde (36.2) < acetophenone (37.8) < *N*,*N*-dimethylaniline (39.5) < pyridine (47.1), while the $GB(H^+)$ increases as benzaldehyde (191.7) < acetophenone < (198.2) < aniline (203.3) < pyridine (214.7) < *N*,*N*-dimethylaniline (217.3). There are obvious disparities in the basicity order between the Me_3Si^+ and H^+ basicities. The $\Delta GB(Me_3Si^+)$ value of aniline relative to pyridine agrees with the corresponding $\Delta GB(H^+)$, but $\Delta GB(Me_3Si^+)$ of *N*,*N*-dimethylaniline is remarkably lower than the expected value from $\Delta GB(H^+)$. The $\Delta GB(Me_3Si^+)$ values of acetophenone and benzaldehyde are higher than those expected from their $\Delta GB(H^+)$. These results suggest that there are differences in the factors which determine $GB(Me_3Si^+)$ from those for $GB(H^+)$. However, $GB(Me_3Si^+)$ of substituted derivatives of the respective base series increases as the electron-releasing ability of the ring-substituent increases. This trend is consistent with the H^+ basicities of the corresponding derivatives. Indeed, a plot of $GB(Me_3Si^+)$ against the corresponding $GB(H^+)$ indicates that there are family-dependent linear relationships with similar slopes (0.8 to 1.0) for acetophenones, benzaldehyde, pyridines, anilines, and *N*,*N*-dimethylanilines series (Fig. 2). An exception is seen for 2,6-dimethylpyridine, which significantly deviates downward from the line given by other pyridines. It is informative to analyze the structural effects on $GB(Me_3Si^+)$ within the respective series to elucidate the nature of the binding interaction between Me_3Si^+ and neutral molecules.

Table 1. Gas-Phase Basicities toward Me_3Si^+ and H^+

	$GB(Me_3Si^+)$ [a]	$GB(H^+)$ [b]
Acetophenones		
—	37.8	198.2
4-OMe	44.6	206.2
4-SMe	43.6	204.9
3-Cl-4-OMe	42.2	203.5
3-Cl-4-SMe	40.3	202.6
4-Me	40.9	202.1
3,4-Me_2	42.6	203.2
3-Me	39.5	199.9
4-F	36.6	197.5
4-Cl	36.6	197.6
3-Cl	34.6	194.8
3-F	34.4	194.5
3-CF_3	32.6	192.9
4-CF_3	31.8	192.3
Benzaldehydes		
—	36.2	191.7
4-OMe	44.3	201.9
4-SMe	42.8	201.2
4-Et	39.8	196.4
4-Me	39.2	196.2
3-Me	38.3	194.7
3-Cl	32.8	188.7
3-CF_3	30.5	185.6
Pyridines		
—	47.1	214.7
4-OMe	53.3	220.0
3,5-Me_2	52.6	219.2
4-Me	51.1	217.9
3-OMe	50.1	217.9
3-Me	49.9	217.7
2,6-Me_2	40.9	222.5
4-$COCH_3$	44.8	210.9
3-$COCH_3$	44.7	210.9
4-Cl	43.9	211.3
3-Cl	42.6	208.6
3-F	41.8	207.8
2-F	38.5	204.5
3-CN	36.4	202.9
4-CN	37.1	204.6
Anilines		
—	35.5	203.3
4-OMe	39.0	207.3
3,5-Me_2	39.1	—
4-Me	37.4	206.7
3-Me	37.1	206.4
4-Cl	33.8	201.8
4-F	33.4	201.1
3-F	32.7	200.0
3-Cl	32.4	200.2
N,*N*-Dimethylanilines		
—	39.5	217.3
4-OMe	43.0	220.6
4-Me	41.5	219.3
4-Cl	36.7	214.7
4-F	36.6	215.2
3-Cl	34.5	213.7
4-CF_3	32.1	209.6

In kcal mol^{-1}. a) $GB(Me_3Si^+)$ are anchored by acetone (GB = 31.2 kcal mol^{-1}).[6] b) Taken from Refs. 12 and 15. All $GB(H^+)$ listed are calibrated using the values for respective unsubstituted members compiled in Ref. 16.

Substituent Effects. Acetophenones and Benzaldehydes. Figures 3 and 4 show plots of the $GB(Me_3Si^+)$ values versus the corresponding $GB(H^+)$ values for the acetophenone and benzaldehyde series, respectively. As previously reported,[11] for the acetophenone series, a straight line can be obtained for *meta* substituents and *p*-CF_3, which have no conjugate interaction with the positive charge de-

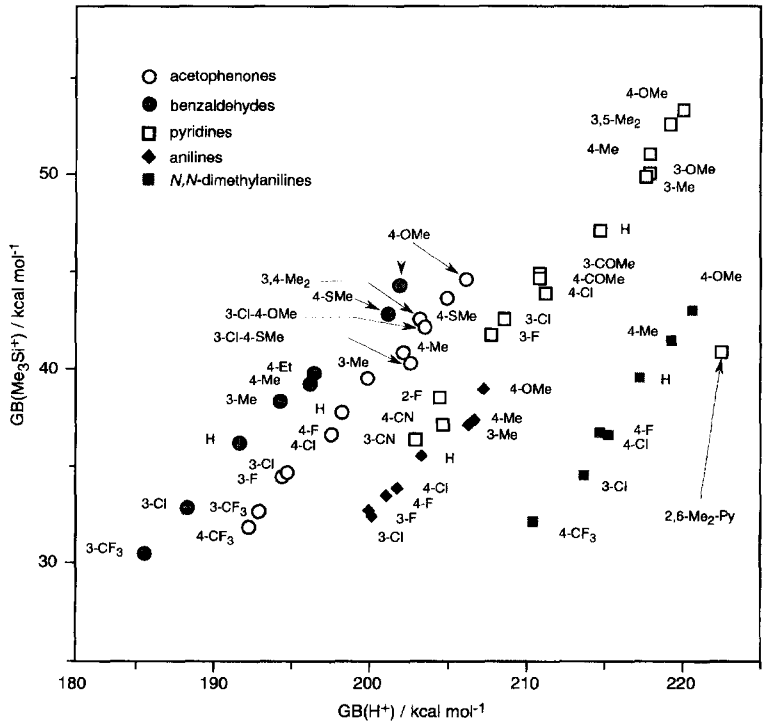


Fig. 2. Plot of $GB(Me_3Si^+)$ vs. $GB(H^+)$.

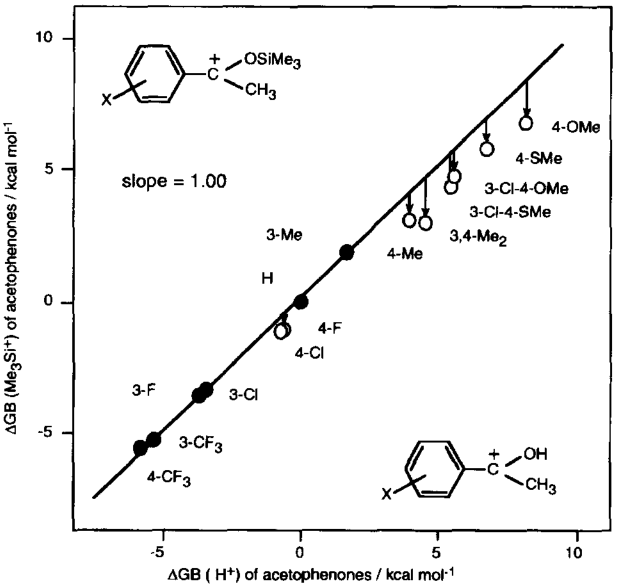


Fig. 3. Comparison between $\Delta GB(Me_3Si^+)$ and $\Delta GB(H^+)$ for acetophenones.

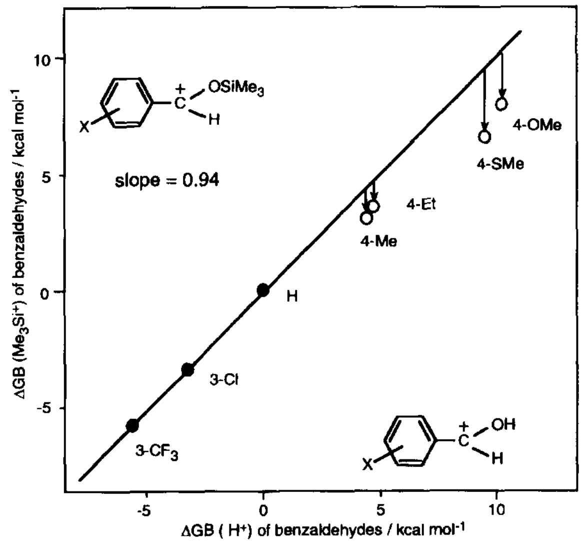


Fig. 4. Comparison between $\Delta GB(Me_3Si^+)$ and $\Delta GB(H^+)$ for benzaldehydes.

veloped at the carbonyl carbon atom. With respect to this line, the strong *para* π-donating substituents show slightly negative deviations and the magnitude of deviations seems to be proportional to the π-donating ability of the respective substituents, i.e., a stronger π-donor shows a greater deviation. This suggests that the resonance-stabilization effect is reduced in the Me_3Si^+ adduct ion compared with that of the corresponding protonated ion. The application of the Y–T equation (Eq. 2) to the present data gives a ρ of -8.1 and an r^+ of 0.75 with satisfactory precision (correlation coefficient = 0.994 and standard deviation = ± 0.5 kcal mol^{-1}, Fig. 5),

$$\log K/K_0 = -1000\Delta GB(Me_3Si^+)/2.303RT \qquad (5)$$
$$= -8.1(\sigma^\circ + 0.75\Delta\bar{\sigma}_R^+).$$

The r^+ value of 0.75 is smaller than that for proton basicity ($r^+ = 0.82$),[12] clearly indicating that the π-delocalization of positive charge into the aryl π-system is reduced in the Me_3Si^+ adduct ion. On the contrary, the ρ value of -8.1 is close to that for $\Delta GB(H^+)$ ($\rho = -8.8$),[12] indicating the similar susceptibility of the substituent effect in these two systems.

The plot for the benzaldehyde series given in Fig. 4 demon-

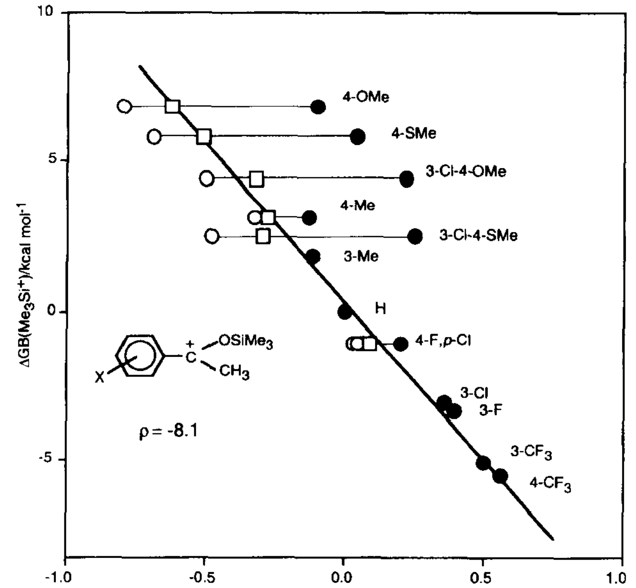


Fig. 5. The Y–T plot for $\Delta GB(Me_3Si^+)$ of acetophenones. Closed circles; σ°, open circles; σ^+, squares; $\overline{\sigma}$ at $r^+ = 0.75$.

strates more clearly the negative deviations of *para* π-donor substituents when a straight line is drawn through nonconjugate substituents (H, *m*-F, and *m*-CF_3), suggesting that the Y–T analysis can be also applied to the substituent effect on the stability of the Me_3Si^+ adduct ions of benzaldehydes. Although the data do not cover a sufficiently wide variation of substituents for a detailed analysis of the substituent effect, the Y–T analysis gives a ρ value of −8.2 and an r^+ of 0.84 with satisfactory precision (correlation coefficient = 0.997 and SD = ±0.4 kcal mol^{-1}, Fig. 6). An r^+ value of 0.84 is also smaller than the corresponding value for the proton basicity ($r^+ = 1.06$).[12] It is evident that the negative deviations of the *para* π-donors observed in Figs. 3 and 4 can be attributed to reduced π-delocalization of the positive charge into the aryl π-system of the adduct ions.

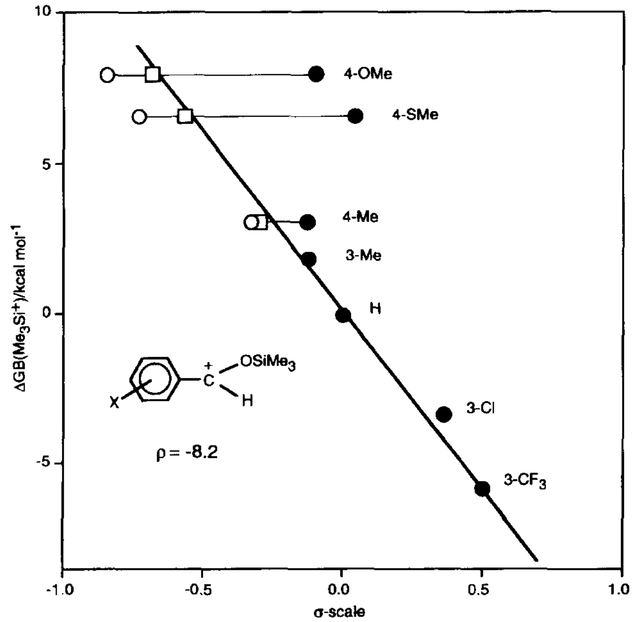
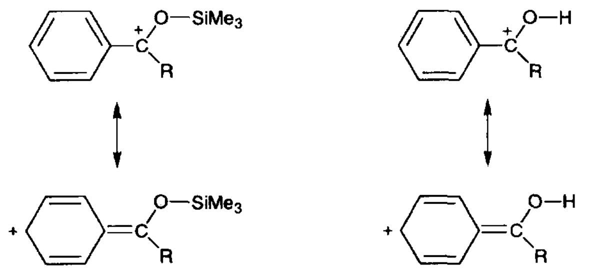


Fig. 6. The Y–T plot for $\Delta GB(Me_3Si^+)$ of benzaldehyde. Closed circles; σ°, open circles; σ^+, squares; $\overline{\sigma}$ at $r^+ = 0.84$.

In our previous studies on the proton basicities of benzoyl compounds,[12] it was found that the r^+ value for the system, of which the conjugate acid ion is stabilized by the electron-releasing group attached at central carbon atom, tends to be smaller than that for a system destabilized by the electron-attracting group, i.e., 0.23 for *N*,*N*-dimethylbenzamides[13] and 1.20 for α,α,α-trifluoroacetophenones.[14] Accordingly, the r^+ value for Me_3Si^+ basicities smaller than the corresponding H^+ basicities suggests that the $OSiMe_3$ group in the limiting structure of the adduct ion can stabilize the positive charge at the benzylic carbon more effectively than the OH group(Scheme 1). A larger electron-releasing ability of the $OSiMe_3$ group is not unexpected, because Si is less electronegative than H.

Pyridines, Anilines, and *N*,*N*-Dimethylanilines. The relative Me_3Si^+ basicities of pyridines are plotted against the corresponding values of the H^+ basicities in Fig. 7. In contrast to the acetophenone and benzaldehyde series the systematic deviations of *para* π-donors are not observed, but a good linear relationship between the Me_3Si^+ and H^+ basicities is obtained with a slope of unity, excluding 2,6-dimethylpyridine:



Scheme 1.

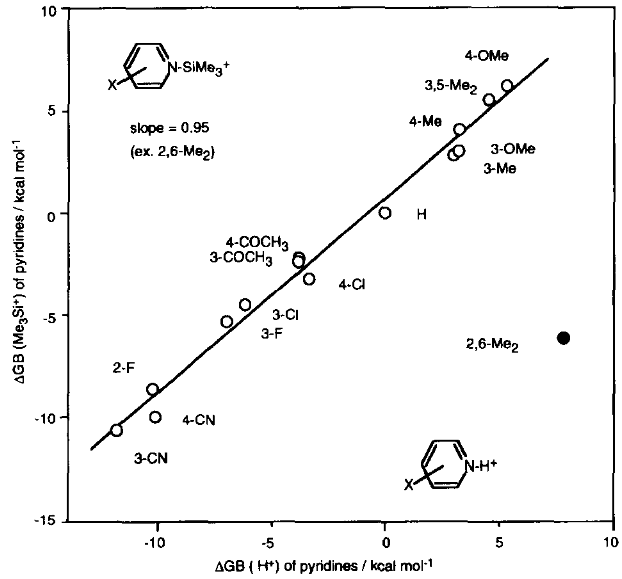


Fig. 7. Comparison between $\Delta GB(Me_3Si^+)$ and $\Delta GB(H^+)$ for pyridines.

$$\Delta\mathrm{GB(Me_3Si^+)} = 0.95\Delta\mathrm{GB(H^+)} + 0.7 \quad (R = 0.993). \tag{6}$$

This is not surprising. Even though resonance stabilization in the Me_3Si^+ adduct ion of pyridine by the π-donating substituent at position 4 is reduced compared with that for protonation in the same degree as that observed for the acetophenone and benzaldehyde systems, such a change in stabilization by the π-donor substituent at position 4 does not seem to be detectable, because the resonance effect of the π-donor substituent at position 4 gives a relatively small contribution to the stability of the pyridinium ion in solution and in the gas-phase compared to conjugate acids of acetophenones and benzladehydes.[15] Indeed, the comparison of $GB(Me_3Si^+)$ between 4-substituted and 3-substituted pyridines plotted in Fig. 8 shows a feature characteristic of the substituent effect on the $GB(H^+)$ of pyridine. That is, the electron-donating group at position 4 stabilizes the positive charge at the nitrogen atom in the adduct ion by resonance effect. For the adduct ions of anilines and *N*,*N*-dimethylanilines there should be a linear relationship between $GB(Me_3Si^+)$ and $GB(H^+)$, because the positive charge at the nitrogen atom cannot delocalize into the π-system of the benzene ring, i.e., no resonance stabilization by a π-donating substituent. In fact, good linear relationships are observed for both the aniline and *N*,*N*-dimethylaniline series, although the number of substituents is limited:

Anilines :

$$\Delta\mathrm{GB(Me_3Si^+)} = 0.80\Delta\mathrm{GB(H^+)} - 0.4 \quad (R = 0.986), \tag{7}$$

N,*N*-Dimethylanilines :

$$\Delta\mathrm{GB(Me_3Si^+)} = 1.10\Delta\mathrm{GB(H^+)} - 0.2 \quad (R = 0.994). \tag{8}$$

Accordingly, the magnitude of the slopes of the linear correlations for these series is simply regarded as being a measure of the sensitivity of the binding energy to changes in the structure of the base for Me_3Si^+ relative to H^+. Such a slope was often used as a criterion to estimate the extent of ionic character relative to the covalent one in the binding interaction of a Lewis cation with bases.[17] When the bond between a Lewis cation and a base is ionic, the increase in the size of Lewis cation would result in a smaller ion-dipole and ion-induced dipole contributions to the binding energies, because of the longer distance between the Lewis cation and the ligand in the complex. This would lower the response of the binding energy to any structural change of the bases. If the structural change causes not only a change in the polarity of the base molecule, but also a steric environmental change at the binding site, it would be difficult to use a slope as a criterion for characterizing the binding interaction. However, because the effect of substituents remote from the binding site does not involve such steric factors, it reflects purely the nature of the binding interaction. Although Me_3Si^+ is much larger in size than a proton, the slopes between the Me_3Si^+ and H^+ basicities are very close to unity for all series. This strongly suggests that the N–Si and O–Si bonds in the $SiMe_3{}^+$ adduct ions have a significant covalent character similar to that of the binding with H^+.

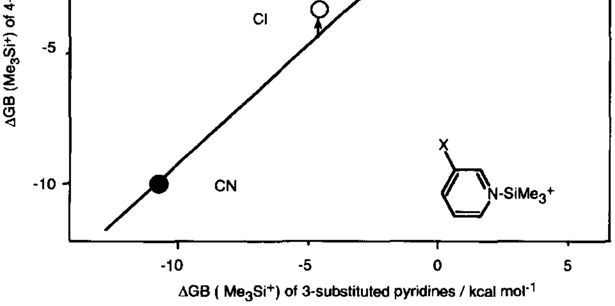


Fig. 8. Plot of $\Delta GB(Me_3Si^+)$ of 4-substituted pyridines against the corresponding values of 3-substituted derivatives.

Theoretical Calculations. Theoretical DFT calculations were carried out for the Me_3Si^+-adduct ions and the corresponding neutral bases. The structures were optimized at the B3LYP/6-31+G* level of theory. These geometries were identified by means of a full analysis of the vibrational modes at those stationary points. For a comparison, the corresponding protonated ions were also calculated at the same level of theory. The results are summarized in Tables 2, 3, and 4.

Energies. The energies of formation of the Me_3Si^+ adduct ions (9), which correspond to the experimental GB-(Me_3Si^+), were obtained using the calculated energies of the respective species. The results are summarized in Table 5 together with the corresponding energy changes for the H^+ transfer reaction:

$$\mathrm{B + SiMe_3^+ \rightleftharpoons B\text{–}SiMe_3^+}, \tag{9}$$

$$\mathrm{B + H^+ \rightleftharpoons B\text{–}H^+}. \tag{10}$$

The calculated $GB(H^+)$ values agree with the experimental ones within 2 kcal mol^{-1}, except for 4-trifluoromethyl-*N*,*N*-dimethylaniline. There is indeed a good linear relationship ($R = 0.995$) with a slope of 1.03, indicating that the theoretical calculation at the present level of theory can reproduce the $GB(H^+)$ values,

$$\mathrm{GB(H^+)_{calcd}} = 1.03\mathrm{GB(H^+)} - 6.7. \tag{11}$$

Similarly, it is found that the calculated Me_3Si^+ basicities of acetophenones, benzaldehydes, and anilines agree with the experimental values within 2 kcal mol^{-1}. The corresponding differences for pyridines, except for 2,6-dimethylpyridine, are slightly larger. On the contrary, the calculated Me_3Si^+ basicities of all the *N*,*N*-dimethylanilines are significantly smaller than the experimental values by 10 kcal mol^{-1}, i.e.,

Table 2. Total Energies, Zero-Point Energies, and Thermal Corrections to Free Energies of Neutral Molecules at B3LYP/6-31+G*

Base	*E*	ZPE	TCF
XC_6H_4COMe			
H	−384.91195	0.13814	0.10540
4-NH_2	−440.27288	0.15462	0.12034
4-OMe	−499.44060	0.17073	0.13442
4-Me	−424.23122	0.16554	0.12967
3-F	−484.15309	0.12977	0.09561
3-CF_3	−721.97050	0.14245	0.10286
4-CF_3	−721.97047	0.14249	0.10304
XC_6H_4CHO			
H	−345.58879	0.10995	0.07938
4-OMe	−460.11804	0.14268	0.10864
4-CF_3	−682.64651	0.11425	0.07566
XC_5H_4N			
H	−248.29580	0.08887	0.06146
4-OMe	−362.82564	0.12179	0.09081
4-CF_3	−585.35335	0.09332	0.05838
2,6-Me_2	−326.93925	0.14371	0.11080
$XC_6H_4NH_2$			
H	−287.61612	0.11709	0.08790
4-OMe	−402.13953	0.14962	0.11663
4-CF_3	−624.67924	0.12154	0.08478
$XC_6H_4NMe_2$			
H	−366.22882	0.17389	0.14046
4-OMe	−480.75213	0.20645	0.16978
4-CF_3	−703.29270	0.17821	0.14009

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Table 3. Total Energies, Zero-Point Energies, and Thermal Corrections to Free Energies of Adduct Ions with H^+ at B3LYP/6-31+G*

Adduct ions	*E*	ZPE	TCF
$XC_6H_4CMeOH^+$			
H	−385.24946	0.15072	0.11857
4-NH_2	−440.63451	0.16809	0.13344
4-OMe	−499.79248	0.18357	0.14647
4-Me	−424.57504	0.17808	0.14088
3-F	−484.48313	0.14247	0.10791
3-CF_3	−722.29715	0.15521	0.11555
4-CF_3	−722.29561	0.15499	0.11607
$XC_6H_4CHOH^+$			
H	−345.91824	0.12337	0.09275
4-OMe	−460.46383	0.15624	0.12218
4-CF_3	−682.96306	0.12756	0.08872
$XC_5H_4NH^+$			
H	−248.66081	0.10306	0.07555
4-OMe	−363.20287	0.13584	0.10478
4-CF_3	−585.70294	0.10740	0.07276
2,6-Me_2	−327.31732	0.15775	0.12429
$XC_6H_4NH_3^+$			
H	−287.96256	0.13164	0.10263
4-OMe	−402.49393	0.16441	0.13065
4-CF_3	−625.01062	0.13623	0.09898
$XC_6H_4NMe_2H^+$			
H	−366.59686	0.18879	0.15541
4-OMe	−481.12740	0.22148	0.18454
4-CF_3	−703.64593	0.19314	0.15543

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an underestimation of the binding energy between the N and Si atoms. A similar underestimation is observed for 2,6-dimethylpyridine. A common feature for *N*,*N*-dimethylanilines and 2,6-dimethylpyridine seems to be crowdness at the binding site with Me_3Si^+, suggesting that the binding energies obtained at the present level of theory are sensitive to the steric environment at the binding site. However, when a correlation is limited to the *N*,*N*-dimethylaniline series, there is a good linear relationship with a slope of 1.10, though there are only three points. Such a good linear relationships is observed for respective series. Indeed, there exists an excellent linear relationship ($R = 0.996$) for $\Delta GB(Me_3Si^+)$ of acetophenones,

$$\Delta GB(Me_3Si^+)_{calcd} = 1.02\Delta GB(Me_3Si^+)_{obsd} + 0.9. \qquad (12)$$

The existence of family-dependent linear relationships indicates that the present calculations can be used to analyze the substituent effect on the Me_3Si^+ basicity as well as the H^+ basicity, even though the calculation does not reproduce the absolute $GB(Me_3Si^+)$ values for *N*,*N*-dimethylanilines and 2,6-dimethylpyridine.

Figure 9 shows a plot of the calculated Me_3Si^+ basicities, $GB(Me_3Si^+)$, against the corresponding H^+ basicities, $GB(H^+)$. It is evident that there are family-dependent linear relationships. Both the pyridine and aniline series fall on the same line. The correlation lines for the benzaldehyde and acetophenone series are placed above that for pyridines and

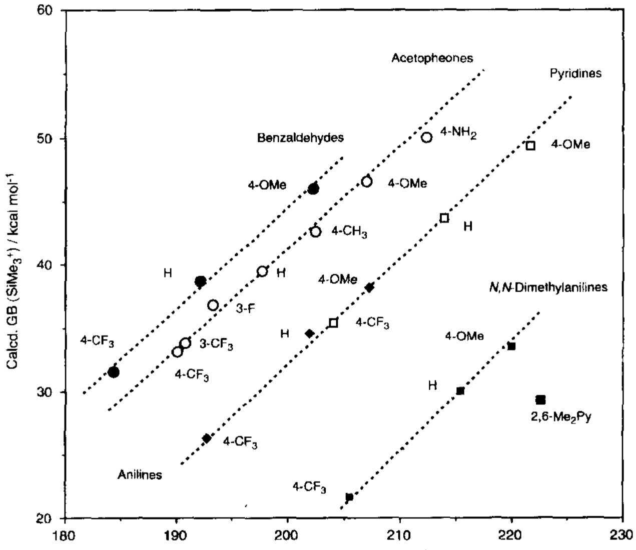


Fig. 9. Plot of the calculated $GB(Me_3Si^+)$ vs. the calculated $GB(H^+)$.

Table 4. Total Energies, Zero-Point Energies, and Thermal Corrections to Free Energies of Adduct Ions with Me_3Si^+ at B3LYP/6-31+G*

Adduct ions	*E*	ZPE	TCF
$XC_6H_4CMeOSiMe_3{}^+$			
H	−793.98621	0.25219	0.20748
4-NH_2	−849.36540	0.26955	0.22399
4-OMe	−908.52507	0.28499	0.23577
4-Me	−833.31006	0.27958	0.23151
3-F	−893.22139	0.24359	0.19590
3-CF_3	−1131.03598	0.25654	0.20542
4-CF_3	−1131.03463	0.25645	0.20522
$XC_6H_4CHOSiMe_3{}^+$			
H	−754.66274	0.22464	0.18259
4-OMe	−869.20360	0.25749	0.21193
4-CF_3	−1091.71014	0.22898	0.18047
$XC_5H_4NSiMe_3{}^+$			
H	−657.37860	0.20419	0.16564
4-OMe	−771.91793	0.23695	0.19530
4-CF_3	−994.42343	0.20841	0.16294
2,6-Me_2	−736.00457	0.26099	0.22050
$XC_6H_4NH_2SiMe_3{}^+$			
H	−696.68466	0.23312	0.19213
4-OMe	−811.21414	0.26566	0.22129
4-CF_3	−1033.73496	0.23741	0.18933
$XC_6H_4NMe_2SiMe_3{}^+$			
H	−775.29376	0.29071	0.24828
4-OMe	−889.82354	0.32286	0.27851
4-CF_3	−1112.34471	0.29454	0.24465
Me_3Si^+	−408.98570	0.10969	0.07661

In hartree.

Table 5. Calculated GB(H^+) and GB(Me_3Si^+) Values at B3LYP/6-31+G* [a)]

	GB(Me_3Si^+)	GB(H^+)
Acetophenones		
—	39.6	197.7
4-NH_2	50.1	212.4
4-OMe	46.5	207.0
4-Me	42.6	202.4
3-F	37.0	193.1
3-CF_3	33.8	190.7
4-CF_3	33.2	190.0
Benzaldehydes		
—	38.7	192.1
4-OMe	45.9	202.2
4-CF_3	31.6	184.5
Pyridines		
—	43.6	213.9
4-OMe	49.4	221.7
4-CF_3	35.4	204.1
2,6-Me_2	29.2	222.5
Anilines		
—	34.6	201.9
4-OMe	38.2	207.3
4-CF_3	26.4	192.8
N,*N*-Dimethylanilines		
—	30.1	215.3
4-OMe	33.6	219.9
4-CF_3	21.7	205.5

a) All values are in kcal mol^{-1} at 25 °C. Free energy for H^+ is −6.27 kcal mol^{-1} at 25 °C.

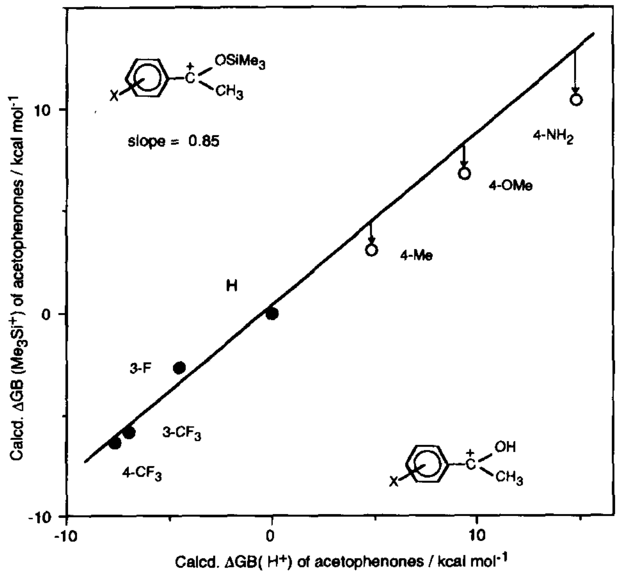


Fig. 10. Plot of the calculated ΔGB(Me_3Si^+) vs. the calculated ΔGB(H^+) for acetophenones.

anilines, and the *N*,*N*-dimethylaniline series is placed significantly below. Even though the correction due to an underestimation of the GB(Me_3Si^+) value (mentioned above) is applied to the *N*,*N*-dimethylanilines, a pattern of parallel lines depending on a family of bases agrees with the experimental observations in Fig. 2. This indicates that the family-dependent linear relationship is not a coincidence, but would be an essential matter.

For a more detailed comparison, the calculated Me_3Si^+ basicities are plotted against the corresponding H^+ basicities for the acetophenone series in Fig. 10. One can find that non-conjugative substituents give a straight line with a slope of 0.85 and *para* strong π-donor substituents show negative deviations. This trend is consistent with the experimental observations shown in Fig. 3, indicating that the theoretical calculations at the present level of theory properly describes the difference in charge-delocalization between the Me_3Si^+ and H^+ adduct ions. It is therefore interesting to examine the structural features of the Me_3Si^+ adduct ions.

Geometries. The numbering of atoms and the structures of unsubstituted members of respective series are shown in Fig. 11. Table 6 to Table 9 summarize the selected bond lengths. In acetophenones and benzaldehydes, the C1–C7 bond and the C2–C3/C5–C6 bond shorten and the C=O lengthens when Me_3Si^+ binds to the O atom of the carbon-

Table 6. Selected Bond Lengths[a)] of Acetophenones and Their Adduct Ions Optimized at B3LYP/6-31+G*

	4-NH_2	4-OMe	4-Me	H	3-F	3-CF_3	4-CF_3
Neutrals							
C1–C2	1.408	1.410	1.407	1.406	1.405	1.405	1.406
C1–C6	1.406	1.400	1.403	1.405	1.404	1.402	1.402
C2–C3	1.386	1.385	1.390	1.393	1.394	1.398	1.390
C5–C6	1.390	1.397	1.396	1.397	1.388	1.392	1.390
C3–C4	1.411	1.407	1.407	1.400	1.400	1.403	1.402
C4–C5	1.408	1.402	1.400	1.397	1.389	1.393	1.390
C1–C7	1.488	1.492	1.498	1.500	1.504	1.504	1.505
C7–O8	1.228	1.226	1.225	1.224	1.223	1.222	1.223
H^+							
C1–C2	1.437	1.431	1.424	1.424	1.420	1.420	1.420
C1–C6	1.433	1.432	1.428	1.426	1.422	1.421	1.425
C2–C3	1.376	1.375	1.382	1.386	1.381	1.384	1.387
C5–C6	1.369	1.371	1.378	1.384	1.388	1.387	1.382
C3–C4	1.429	1.421	1.411	1.403	1.400	1.406	1.400
C4–C5	1.428	1.421	1.415	1.405	1.400	1.400	1.406
C1–C7	1.400	1.407	1.416	1.423	1.428	1.428	1.428
C7–O8	1.328	1.323	1.316	1.312	1.305	1.305	1.308
Me_3Si^+							
C1–C2	1.431	1.429	1.418	1.417	1.415	1.414	1.414
C1–C6	1.428	1.422	1.419	1.418	1.415	1.415	1.415
C2–C3	1.370	1.372	1.385	1.389	1.383	1.388	1.389
C5–C6	1.373	1.382	1.383	1.387	1.390	1.389	1.387
C3–C4	1.426	1.419	1.409	1.400	1.396	1.400	1.400
C4–C5	1.424	1.414	1.412	1.402	1.400	1.403	1.402
C1–C7	1.418	1.426	1.438	1.445	1.450	1.451	1.452
C7–O8	1.300	1.293	1.283	1.279	1.276	1.276	1.275

a) In Ångstroms.

Table 7. Selected Bond Lengths[a)] of Benzaldehydes and Their Adduct Ions Optimized at B3LYP/6-31+G*

	XC_6H_4CHO			$XC_6H_4CHOH^+$			$XC_6H_4CHOSiMe_3^+$		
	4-OMe	H	4-CF_3	4-OMe	H	4-CF_3	4-OMe	H	4-CF_3
C1–C2	1.410	1.403	1.405	1.430	1.427	1.423	1.422	1.419	1.415
C1–C6	1.400	1.405	1.400	1.435	1.426	1.426	1.428	1.420	1.418
C2–C3	1.384	1.396	1.389	1.375	1.381	1.387	1.380	1.388	1.390
C5–C6	1.396	1.392	1.396	1.367	1.385	1.380	1.371	1.385	1.383
C3–C4	1.410	1.402	1.404	1.421	1.409	1.400	1.417	1.402	1.400
C4–C5	1.403	1.398	1.397	1.428	1.404	1.410	1.424	1.407	1.408
C1–C7	1.473	1.481	1.485	1.388	1.400	1.404	1.405	1.420	1.426
C7–O8	1.221	1.219	1.217	1.312	1.300	1.297	1.283	1.275	1.268

a) In Ångstroms.

yl group. Such variations of the bond lengths are consistent with the general prediction of resonance theory for the charge-delocalized benzylic cation, i.e., the positive charge on the benzylic carbon formed by the binding of Me_3Si^+ with oxygen atom of the carbonyl group can be transferred into the benzene ring through a resonance interaction, giving a partial quinonoid structure of the benzene ring. The C–N bonds for aniline and *N,N*-dimethylaniline are prolonged to the same degree with those for protonation when Me_3Si^+ binds to the N atom (Table 10). This change is reasonably interpreted by the loss of the π-delocalization of lone-pair electrons on N into the benzene ring in the adduct ion.

The sum of angles at Si atom ($\sum\angle$CSiC) of the $SiMe_3^+$ adduct ions may be another geometrical feature reflecting the nature of the Si–O/Si–N bond. The sum of angles would be a measure of the ionic character of the Si-bond. The sum for all adduct ions falls in a range of 337° to 344°,[18] while the sum for Me_3Si^+ is 360°. A sum smaller than 360° indicates that the structure of the Si atom in the $SiMe_3^+$ adduct obviously has a significant tetrahedral character, rather than a trigonal planar one. The N–Si bond length in pyridine–$SiMe_3^+$ (1.919 Å) is longer than the ordinary single covalent bond N–Si (e.g., 1.719 Å for the N–Si bond in Me_2N–$SiMe_3$),[19] but is close to the value determined experimentally for [Me_3Si–pyr-

Table 8. Selected Bond Lengths[a)] of Pyridines and Their Adduct Ions Optimized at B3LYP/6-31+G*

	XC_5H_4N				$XC_5H_4NH^+$				$XC_5H_4NSiMe_3{}^+$			
	4-OMe	H	4-CF_3	2,6-Me_2	4-OMe	H	4-CF_3	2,6-Me_2	4-OMe	H	4-CF_3	2,6-Me_2
C1-C2	1.390	1.398	1.397	1.402	1.377	1.385	1.385	1.390	1.373	1.386	1.385	1.393
C4-C5	1.400	1.398	1.397	1.402	1.370	1.385	1.384	1.390	1.382	1.388	1.389	1.393
C2-C3	1.403	1.396	1.396	1.394	1.416	1.400	1.400	1.398	1.414	1.398	1.400	1.389
C3-C4	1.400	1.396	1.396	1.394	1.418	1.400	1.400	1.397	1.410	1.396	1.394	1.389
C1-N7	1.345	1.340	1.339	1.343	1.354	1.353	1.353	1.363	1.366	1.358	1.357	1.379
C5-N7	1.336	1.340	1.339	1.343	1.362	1.353	1.352	1.363	1.357	1.356	1.353	1.379

a) In Ångstroms.

Table 9. Selected Bond Lengths[a)] of Anilines and Their Adduct Ions Optimized at B3LYP/6-31+G*

	$XC_6H_4NH_2$			$XC_6H_4NH_3{}^+$			$XC_6H_4NH_2SiMe_3{}^+$		
	4-OMe	H	4-CF_3	4-OMe	H	4-CF_3	4-OMe	H	4-CF_3
C1–C2	1.407	1.406	1.408	1.388	1.391	1.388	1.398	1.394	1.393
C1–C6	1.400	1.406	1.408	1.397	1.390	1.393	1.391	1.394	1.393
C2–C3	1.391	1.395	1.390	1.397	1.398	1.398	1.388	1.397	1.395
C5–C6	1.400	1.395	1.390	1.386	1.398	1.393	1.398	1.397	1.395
C3–C4	1.402	1.398	1.400	1.406	1.398	1.395	1.409	1.397	1.398
C4–C5	1.407	1.398	1.400	1.412	1.398	1.400	1.405	1.397	1.398
C1–N7	1.396	1.402	1.391	1.495	1.500	1.498	1.484	1.483	1.408

a) In Ångstroms.

Table 10. Selected Bond Lengths[a)] of *N*,*N*-Dimethylanilines and Their Adduct Ions Optimized at B3LYP/6-31+G*

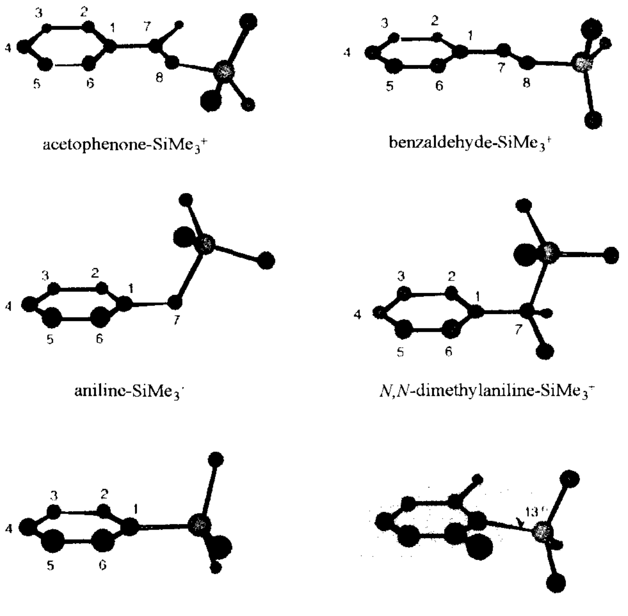
	$XC_6H_4NMe_2$			$XC_6H_4NMe_2H^+$			$XC_6H_4NMe_2SiMe_3{}^+$		
	4-OMe	H	4-CF_3	4-OMe	H	4-CF_3	4-OMe	H	4-CF_3
C1–C2	1.414	1.415	1.418	1.393	1.394	1.394	1.396	1.400	1.400
C1–C6	1.402	1.415	1.418	1.394	1.393	1.392	1.405	1.400	1.400
C2–C3	1.387	1.395	1.390	1.398	1.397	1.395	1.398	1.398	1.395
C5–C6	1.404	1.395	1.390	1.397	1.398	1.396	1.387	1.397	1.396
C3–C4	1.404	1.397	1.400	1.396	1.400	1.400	1.402	1.695	1.400
C4–C5	1.395	1.397	1.400	1.400	1.396	1.396	1.406	1.396	1.400
C1–N7	1.419	1.395	1.382	1.494	1.494	1.492	1.503	1.504	1.500

a) In Ångstroms.

idine]$^+$I$^-$ in a solid (1.858 Å),[20] in which the positive charge of the cation is regarded as being formally localized on the pyridine.

All of the structural features obtained by theoretical calculations are indicative of a pronounced covalent character of the base-Si bonds in the adduct ion with $SiMe_3{}^+$.

Family-Dependent Linear Relationship. The most significant difference between the Me_3Si^+ and H^+ basicities is that there exist parallel linear relationships, depending on a family of the bases. This means that the disparity observed for an unsubstituted member of the respective series consistently holds for all substituted derivatives. Similar family-dependent linear correlations were observed for a comparison of the Li^+ vs. H^+ gas-phase basicities.[21] In addition, slopes significantly smaller than unity (0.4 to 0.6) were obtained. The vertical gaps as well as the low response to the substituent change were attributed to the significant ionic character of the Li–O/Li–N bond in the Li^+ adduct ion. The gaps shown in Fig. 2, however, cannot be attributed to the change in the electrostatic interaction, because the binding interaction with Me_3Si^+ is mostly covalent, as discussed above. We can thus see a suggestive result in Figs. 2 and 9. The experimental and theoretical results indicate that the Me_3Si^+ basicity of 2,6-dimethylpyridine is ca. 15 kcal mol^{-1} lower than that expected from its H^+ basicity. This is reasonably attributed to the steric effect of two methyl groups at the 2- and 6-positions in the pyridine ring, which interferes with the approach of a large Me_3Si^+ cation to the basic nitrogen atom compared to the small proton. The optimized structures of the adduct ions indeed show that the N–Si bond length in the Me_3Si^+ adduct is longer in 2,6-dimethylpyridine (1.952 Å) than that in pyridine (1.919 Å), and that the Si atom of 2, 6-dimethylpyridine–$SiMe_3{}^+$ is out of the pyridine ring plane by 13° due to steric effects of two methyl groups, as shown Fig. 11. Similarly, the optimized geometry of *N*,*N*-dimethylaniline-Me_3Si^+ ion shows that the N–Si bond (1.974 Å) is longer than that of the corresponding adduct ion of aniline (1.959 Å), while the N–H bond length is even shorter in



acetophenone-SiMe$_3^+$ benzaldehyde-SiMe$_3^+$

aniline-SiMe$_3^+$ N,N-dimethylaniline-SiMe$_3^+$

pyridine-SiMe$_3^+$ 2,6-Me2-pyridine-SiMe$_3^+$

Fig. 11. Structures of Me_3Si^+ adduct ions optimized at B3LYP/6-31+G*. Hydrogens are not shown.

N,N-dimethylaniline–H$^+$ (1.026 Å) than that in aniline–H$^+$ (1.208 Å). From these results, we can infer that the lower GB(Me_3Si^+) values of N,N-dimethylanilines than those of anilines are mostly attributed to the sterically hindered binding site.

Conclusions

Both the experimental and theoretical results indicate that the binding interaction of Me_3Si^+ with oxygen and nitrogen atoms of organic bases has a significant covalent character in a similar degree to that in the O–H/N–H bond in a protonated species, regardless of their small binding energies compared to those with a proton. That is, the nature of the binding interaction between a Lewis cation and bases is a different matter from the magnitude of the binding energy. In addition, the steric environment at the binding site is an important factor to determine the magnitude of the binding energy. Nevertheless, the covalent character of the base-Si bond is less sensitive to it.

Experimental

ICR Measurements. Equilibrium-constant measurements were performed on an Extrel FTMS 2001 spectrometer equipped with a dual-cell system. Details of the experimental techniques used for measuring the equilibrium constants (K) for the Me_3Si^+ transfer reaction (13), where B refers to a given base and B_0 is a reference base, were similar to those used for the previously described proton-transfer measurements.[12] Only significant changes and/or additional procedures are given here.

$$B + B_0SiMe_3^+ \rightleftharpoons BSiMe_3^+ + B_0 \tag{13}$$

$$K = [B_0/B]\cdot[BSiMe_3^+/B_0SiMe_3^+] \tag{14}$$

$$\Delta G^\circ = -RT\ln K \tag{15}$$

All measurements were performed at 50 °C at a constant magnetic field strength of 3.0 T. 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.[22] The overall pressures of the reagents were maintained at 1 to 3×10^{-4} Pa by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the reaction cell in the vacuum chamber. Tetramethylsilane was introduced into an ionization cell at 5—10×10^{-4} Pa using a pulsed valve. Me_3Si^+ generated by an electron-impact ionization of tetramethylsilane was transferred to a reaction cell. After a reaction period of 1 to 3 s, depending upon the reactant, the equilibrium was attained and the relative abundance of $BSiMe_3^+$ and $B_0SiMe_3^+$ was measured based on the signal intensities of the ICR spectra. Each experiment was performed at several ratios of partial pressures and at different overall pressures. The arithmetic-mean values of K from Eq. 14 were used to calculate ΔG° at 343 K (Eq. 15) with an average uncertainty of ±0.3 kcal mol^{-1} in most of these cases. More than two reference compounds were used to insure the internal consistency of the data. The occurrence of the Me_3Si^+-transfer reaction was examined by an ion-eject experiment using the SWIFT technique.[23]

Chemicals. Most of the compounds used in this study were commercial samples. Others were available from our previous studies.[12] The materials were purified by distillation or recrystallization, and were degassed prior to use by several freeze-pump-thaw cycles on the sample-inlet system of the ICR.

DFT Calculations. DFT calculations were carried out using the Gaussian 98 program[24] suite. The geometries were fully optimized at the B3LYP/6-31+G* level of theory. The zero-point vibrational energies were calculated from the B3LYP/6-31+G* harmonic frequencies. The force-constant matrices obtained for the stationary points were confirmed to have the correct number of negative eigenvalues (zero for equilibrium structures).

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