Equilibrium Structure, Spectroscopic Constants, and Gas-Phase Basicity of the Silaformyl Anion, $HSiO^-$

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The equilibrium structure and anharmonic force field of the silaformyl anion, $HSiO^-$, have been determined from large-scale ab initio calculations using the coupled-cluster method, CCSD(T), with basis sets of double- through quintuple-ζ quality. The vibrational−rotational energy levels of the main isotopic species were calculated by both variational and perturbational approach. The accurate ground-state spectroscopic constants were then determined, which (we believe) can be useful in future detection of the silaformyl anion in the gas phase and/or inert-gas matrixes by means of the vibrational−rotational spectroscopy. In conjuction with the results of analogous calculations on silanone (H_2SiO) and hydroxysilylene (HSiOH), the gas-phase proton affinities of the $HSiO^-$ anion are predicted to be 349.6 and 348.2 ± 1 kcal/mol, respectively, at 0 K. Calculations were also performed for the $SiOH^-$ isomer, yielding the gas-phase proton affinity of this anion of 391.1 ± 1 kcal/mol at 0 K. Correcting these values for the thermal energy contributions, the basicities at 298 K, $\Delta G°$, of the $HSiO^-$ anion are predicted to be 343.1 and 341.7 ± 1 kcal/mol, respectively, while that of the $SiOH^-$anion is 384.8 ± 1 kcal. The former two values are substantially lower than the experimental basicity of the $HSiO^-$ anion reported in the literature.

1. Introduction

The silaformyl anion, $HSiO^-$, is a highly reactive species detected so far only in the gas phase by mass spectrometry.[1,2] Little is known about the chemistry of the silaformyl anion, and its gas-phase basicity, $\Delta G°$, was estimated experimentally by Gronert et al.[1] to be 356 ± 8 kcal/mol at room temperatue. The experimental studies were unable to determine the structure of the $[H_2,Si,O]$ neutral species formed upon protonation, although the theoretical studies, ref 2 and references therein, suggested two possibilities: silanone (H_2SiO) and hydroxysilylene (HSiOH). Moreover, the equilibrium structure and relative energy of the silaformyl anion and its isomer, $SiOH^-$, are known only from the theoretical studies.[1,2] The structure of both molecules was determined by Rusho et al.[2] using the second-order Møller−Plesset approach, MP2[3], with the split-valence polarized double-ζ basis set, 6-31++G(d,p).[4] The single-point calculations were then performed using the coupled-cluster method, CCSD(T),[5,6] including single and double excitations and a perturbational correction due to connected triple excitations, and the basis set of triple-ζ quality, 6-311++G(2df,2pd).[4] As a result, the gas-phase basicity of the silaformyl anion was calculated to be about 344 kcal/mol,[2] substantially lower than the experimental value.

State-of-the-art ab initio methods seem a valuable alternative for predicting fundamental properties of the silaformyl anion, including the thermodynamics and structures of the neutral products associated with protonation. In light of disagreement between the available experimental and theoretical values of the basicity, calculations near the one- and *N*-particle basis set limits are clearly required. The reliable prediction requires thus two primary ingredients, namely, accurate inclusion of the electron correlation effects and a large one-particle basis set. In most cases, the single-reference coupled-cluster approach, particularly the CCSD(T) method, is an excellent way to account for a very large fraction of the valence and core correlation energy.[7] As a one-particle basis set, a sequence of the systematically expandable correlation-consistent polarized basis sets, cc-pV*n*Z,[8] can be used. These basis sets approach uniformly the complete basis set (CBS) limit, and in conjuction with various extrapolation techniques[9−13] make it possible to predict properties of small molecules to remarkably high accuracy.

The present study was undertaken with the aim of predicting the fundamental properties of the silaformyl anion with accuracy approaching that of the experimental studies. The results reported in this paper may be helpful for detecting the $HSiO^-$ molecule by means of the other experimental techniques, especially the high-resolution vibrational−rotational spectroscopy. The results may also serve as high-level benchmark data for the evaluation of density functional theory (DFT) for molecules containing the Si−O linkage.

2. Method of Calculation

The electronic structure of the $HSiO^-$ and $SiOH^-$ molecules was determined using the CCSD(T) method and the correlation-consistent valence basis sets of double- through quintuple-ζ quality, cc-pVDZ through cc-pV5Z[8,14]. The largest basis set, cc-pV5Z, consists of a $(20s12p4d3f2g1h)/[7s6p4d3f2g1h]$ set for silicon, a $(14s8p4d3f2g1h)/[6s5p4d3f2g1h]$ set for oxygen, and a $(8s4p3d2f1g)/[5s4p3d2f1g]$ set for hydrogen. Only the spherical harmonic components of polarization *d* through *h* functions were used. In the correlation treatment involving only the valence electrons, the 1*s*-like orbital of the oxygen atom and the 1*s*-, 2*sp*-like orbitals of the silicon atom were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent core-valence basis sets, cc-pCV*n*Z.[15,16]

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TABLE 1: The Molecular Parameters of the Silaformyl Anion, Determined Using the CCSD(T) Method and Various cc-pV*n*Z and aug-ccpV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
cc-pV*n*Z				
r(HSi) (Å)	1.6471	1.6318	1.6165	1.6132
r(SiO) (Å)	1.6118	1.5786	1.5729	1.5691
∠(HSiO) (deg)	106.46	106.27	105.98	106.00
Energy + 364 (hartree)	−0.657802	−0.792680	−0.836519	−0.851987
aug-cc-pV*n*Z				
r(HSi) (Å)	1.6299	1.6163	1.6102	
r(SiO) (Å)	1.6265	1.5848	1.5750	
∠(HSiO) (deg)	105.25	105.76	105.87	
Energy + 364 (hartree)	−0.714411	−0.814895	−0.845510	

TABLE 2: The Molecular Parameters of the $SiOH^-$ Isomer, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
r(SiO) (Å)	1.8109	1.7646	1.7429	1.7367
r(OH) (Å)	0.9653	0.9568	0.9554	0.9553
∠(SiOH) (deg)	102.28	104.20	105.70	106.37
Energy + 364 (hartree)	−0.593823	−0.727396	−0.775472	−0.789937

TABLE 3: The Core-Related Corrections ($A - V$)[a] to the Molecular Parameters of the Silaformyl Anion and Its Isomer, Determined Using the CCSD(T) Method and Various cc-pCV*n*Z Basis Sets

	cc-pCVTZ	cc-pCVQZ
$HSiO^-$		
r(HSi) (Å)	−0.0021	−0.0027
r(SiO) (Å)	−0.0027	−0.0043
∠(HSiO) (deg)	−0.03	−0.03
Energy (hartree)	−0.342452	−0.379009
$SiOH^-$		
r(SiO) (Å)	−0.0033	−0.0050
r(OH) (Å)	−0.0008	−0.0009
∠(SiOH) (deg)	−0.01	−0.01
Energy (hartree)	−0.342231	−0.378618

[a] A difference between the value determined correlating all the electrons, except the 1*s* electrons of the silicon atom, (A) and the value determined correlating only the valence electrons (V).

The basis sets of triple- and quadruple-ζ quality were employed. The cc-pCV*n*Z basis set is obtained by augmenting the standard cc-pV*n*Z basis set with a set of tight functions. The largest basis set applied in this work, cc-pCVQZ, is obtained by augmenting the cc-pVQZ basis set with a (3*s*3*p*3*d*2*f*1*g*) set for silicon[16] and with a (3*s*3*p*2*d*1*f*) set for oxygen.[15] This basis set consists thus of a (19*s*14*p*6*d*4*f*2*g*)/[9*s*8*p*6*d*4*f*2*g*] set for silicon, a (15*s*9*p*5*d*3*f*1*g*)/[8*s*7*p*5*d*3*f*1*g*] set for oxygen, and a (6*s*3*p*2*d*1*f*)/[4*s*3*p*2*d*1*f*] set for hydrogen. In the correlation treatment involving the core and valence electrons, only the 1*s*-like orbital of the silicon atom was excluded from the active space.

The CCSD(T) calculations were performed using the MOLPRO-2000 package of ab initio programs.[17,18]

Vibrational−rotational energy levels of the silaformyl anion were determined by both variational and perturbational approach.

Within the variational approach, the energy levels were calculated using the six-dimensional vibration−rotation Hamiltonian of a triatomic molecule developed by Carter and Handy.[19−21] The Hamiltonian consists of an exact representation of the kinetic energy operator and of a representation of the potential energy operator in terms of valence curvilinear coordinates. The initial basis set consisted of Morse oscillator functions for the stretching coordinates and of associated Legendre functions for the bending coordinate. Expansion functions were formed as products of contracted combinations of the initial basis set functions, and the matrix elements were evaluated by numerical quadrature. For each value of the rotational quantum number *J*, the secular matrix was constructed using the vibrational expansion functions and the rotational symmetric-top functions, and then diagonalized to obtain the vibrational−rotational energy levels and wave functions. The size of the vibrational basis set was chosen to ensure convergence in the energy to within $\approx 10^{-6}$ cm^{-1} for the low-lying vibrational−rotational energy levels. The calculations were performed using the RVIB3 program.[20]

Within the perturbational approach, the energy levels and spectroscopic constants were determined using the standard perturbational formulas for vibrational−rotational energy levels,[22] and this was done employing the SPECTRO program.[23]

3. Results and Discussion

The calculated equilibrium structural parameters and total energy of the silaformyl anion are given in Table 1. The calculated values tend to approach well-defined asymptotic limits with enlargement of the one-particle basis set. To estimate the CBS limit for a molecular parameter, the exponential/Gaussian extrapolation formula[10] was applied. This extrapolation scheme makes use of a simple relation between a molecular property and a cardinal number *n* assigned to the cc-pV*n*Z basis set. The other, analogous extrapolation algorithms[9,11−13] were also applied, and the spread in the determined CBS limit values was used as an estimate for extrapolation accuracy. The total energy lowering from the cc-pV5Z to cc-pV6Z basis set is computed in this way to be ≈6 mhartrees, while that to the infinite basis set is estimated to be ≈9 mhartrees.

To investigate the effects of diffuse functions, which might be substantial for an anion, additional calculations were performed with the augmented correlation-consistent basis sets, aug-cc-pV*n*Z, of double- through quadruple-ζ quality.[24] The calculated equilibrium structural parameters and total energy of the silaformyl anion are also listed in Table 1. For the aug-cc-pVDZ basis set, inclusion of the diffuse functions affects significantly indeed values of all the structural parameters. However, for the basis set of quadruple-ζ quality, aug-cc-pVQZ, these changes are by 1 order of magnitude smaller and amount to 0.006 and 0.002 Å for the HSi and SiO bond lengths, respectively, and to 0.1° for the angle HSiO. The total energies of the silaformyl anion computed with the cc-pVQZ and aug-cc-pVQZ basis sets differ by merely 9.0 mhartrees.

The calculated equilibrium structural parameters and total energy of the $SiOH^-$ isomer of the silaformyl anion are given in Table 2. For all the one-particle basis sets employed, the $SiOH^-$ isomer was found to be ≈ 40 kcal/mol less stable than the silaformyl anion. It is interesting to note that the 1,2-hydrogen migration leads to substantial lengthening of the SiO bond, which is by nearly 0.2 Å longer for the $SiOH^-$ structure than for the $HSiO^-$ one.

The core-related effects were computed as differences between the molecular parameters determined in calculations correlating only the valence electrons and those when all the electrons were correlated, both calculations performed using the core-valence basis sets. The calculated corrections to the molecular parameters of the silaformyl anion and its isomer are listed in Table 3.[25] As for the molecular equilibrium parameters, the corrections tend to approach asymptotic limits. Inclusion of the core-related correlation effects changes significantly only the bond lengths, whereas the angles HSiO and SiOH remain almost unaffected. The core−core and core−valence correlation energies are computed for both molecules to be essentially the same.

The best estimate of the molecular parameters of the silaformyl anion and its isomer at the CCSD(T) level of theory can be determined by adding the changes in the parameters due to the core-related correlation effects to the CBS limits determined with the valence cc-pV*n*Z basis sets. The equilibrium structural parameters of the silaformyl anion are calculated in this way to be r_e(HSi) = 1.609 Å, r_e(SiO) = 1.563 Å, and $\angle_e$(HSiO) = 106.0°. Likewise, the equilibrium structural parameters of the $SiOH^-$ isomer are r_e(SiO) = 1.728 Å, r_e(OH) = 0.954 Å, and $\angle_e$(SiOH) = 106.7°. Considering convergence of the computed values with the basis-set size, we estimate uncertainties in the structural parameters to be about ±0.001 Å for the bond lengths and ±0.1° for the valence angles.

To characterize further the silaformyl anion, the potential energy surface was determined by computing the total energy at 152 points in the vicinity of the equilibrium configuration. The energies were determined at the CCSD(T)/cc-pV5Z level of theory to accuracy better than 10^{-8} hartrees and they range to about 9000 cm^{-1} above the minimum.

The potential energy surface was then approximated by a three-dimensional expansion along the internal valence coordinates. The internal coordinates for the stretching modes were chosen as Simons-Parr-Finlan coordinates,[26] $q = (r - r_e)/r$, where r and r_e are instantaneous and equilibrium bond lengths, respectively. For the HSiO bending mode, a curvilinear displacement coordinate was used,[27] defined by $q = (\angle - \angle_e)$(HSiO). The coordinates for the SiO and HSi stretching modes are referred to hereafter as q_1 and q_2, respectively, while that for the HSiO bending mode as q_3.

The potential energy surface of the silaformyl anion was approximated by a Taylor expansion:

$$V(q_1, q_2, q_3) = \frac{1}{2}\sum_{ij} f_{ij}s_is_j + \frac{1}{6}\sum_{ijk} f_{ijk}s_is_js_k + \frac{1}{24}\sum_{ijkl} f_{ijkl}s_is_js_ks_l + \cdots \quad (1)$$

where $\{s_i\}$ are the coordinates q_1, q_2, and q_3. The expansion coefficients f were determined from a least-squares fit of eq 1 to the computed total energies. In the fit to all 152 data, 52 expansion coefficients appeared to be statistically significant. The coefficients include all the force constants up to the quintic order. The optimized values of the force constants are listed in Table 4. The root-mean-square deviation of the fit was about 7 μhartrees (1.5 cm^{-1}). The anharmonic force field thus determined was used in the variational approach.

Within the perturbational approach, the displacement coordinates were chosen for all the vibrational modes of the silaformyl anion. In the fit, 54 expansion coefficients appeared to be statistically significant. The coefficients include all the force constants up to the quintic order, as well as some force constants at the sextic order. The root-mean-square deviation of the fit was about 10 μhartrees (2.2 cm^{-1}). As is customary, the anharmonic force field was truncated at the quartic order in the subsequent calculation.

The calculated potential energy surfaces were modified by replacing the equilibrium structural parameters with the "best" estimates discussed above. The modified anharmonic force fields were then used to determine the vibrational−rotational energy levels.

The calculated fundamental energy levels and vibrational spectroscopic constants of the main $HSiO^-$ isotopomer are given in Table 5. Within the variational approach, the harmonic wavenumbers and anharmonic constants were calculated from the frequencies of the fundamental, first overtone, and combination transitions. All of the normal vibrations appeared to be characteristic, and the ν_1, ν_2, and ν_3 modes correspond to the HSi stretching, SiO stretching, and HSiO bending modes, respectively. The Fermi resonance of the type $2\omega_i \sim \omega_j$ occurs for the ν_3 and ν_1 modes. The corresponding anharmonic terms, with near-zero denominators, were removed from the perturbational formulas and the resonance interactions were treated explicitly by diagonalizing an appriopriate energy-level matrix. The off-diagonal element of the energy matrix, W, was predicted to be 16.8 cm^{-1}.

The largest difference between the variational and perturbational approach occurs for the HSi stretching mode. This is likely

TABLE 4: The Calculated Anharmonic Force Field (in aJ)[a] of the Silaformyl Anion

f_{11}	16.8239	f_{11111}	127.3
f_{22}	3.5947	f_{22222}	153.0
f_{33}	0.8895	f_{33333}	−1.4
f_{12}	0.6411	f_{12222}	−52.3
f_{13}	0.3123	f_{13333}	−3.0
f_{23}	−0.0530	f_{23333}	−1.5
f_{111}	−54.382	f_{11112}	−54.3
f_{222}	−8.501	f_{11113}	−25.4
f_{333}	−0.680	f_{22223}	12.4
f_{122}	1.500	f_{11222}	8.8
f_{133}	−0.901	f_{11333}	3.2
f_{233}	−0.562	f_{22333}	1.1
f_{112}	−0.048	f_{11122}	−0.8
f_{113}	0.205	f_{11133}	−3.6
f_{223}	−0.302	f_{22233}	−4.5
f_{123}	−0.875	f_{12333}	−2.3
f_{1111}	−46.97	f_{12223}	10.2
f_{2222}	−18.47	f_{11123}	20.2
f_{3333}	0.76	f_{12233}	4.5
f_{1222}	0.30	f_{11233}	0.6
f_{1333}	1.51	f_{11223}	−0.5
f_{2333}	0.32		
f_{1112}	−6.20		
f_{1113}	−3.67		
f_{2223}	−0.66		
f_{1122}	3.04		
f_{1133}	−2.94		
f_{2233}	−2.88		
f_{1233}	1.74		
f_{1223}	−1.42		
f_{1123}	0.92		

[a] The coordinates q_1 and q_2 are dimensionless, the coordinate q_3 is given in radians.

TABLE 5: The Fundamental (ν) and Harmonic (ω) Wavenumbers, and Anharmonic Constants (x, in cm^{-1}) of the Silaformyl Anion

	variational[a]	perturbational[b]
ν_1	1448.6	1439.6
ν_2	1052.9	1048.8
ν_3	790.7	791.1
ω_1	1551.2	1558.9
ω_2	1064.1	1059.2
ω_3	813.4	813.6
x_{11}	−43.3	−51.4
x_{22}	−5.9	−5.9
x_{33}^*	−1.9	−1.4
x_{12}	3.6	4.5
x_{13}^*	−35.6	−37.5
x_{23}	−2.4	−2.1

[a] Determined using the anharmonic force field given in Table 4. [b] Determined as described in text. The anharmonic constants for which the Fermi resonance has been taken into account are marked with an asterisk.

TABLE 6: The Ground-State Rotational and Quartic Centrifugal Distortion Constants (in MHz) of the Silaformyl Anion

	variational[a]	perturbational
A	221351	221198
B	19425.5	19423.0
C	17790.0	17792.4
Δ_J	0.026	0.026
Δ_{JK}	0.887	0.863
Δ_K	27.102	25.229
δ_J	0.002	0.002
δ_K	0.609	0.516

[a] Determined from the $J = 0 - 5$ rotational energy levels calculated variationally.

TABLE 7: The Rotation-Vibration Interaction Constants (in MHz) of the Silaformyl Anion, Determined by the Perturbational Approach

	$i = 1$	$i = 2$	$i = 3$
α_i^A	9533	109	−4041
α_i^B	−22	148	−54
α_i^C	24	112	87

the result of approximations inherent to the second-order perturbational method applied and large anharmonicity of the ν_1 mode.

Table 6 lists the calculated ground-state rotational and quartic centrifugal distortion constants of the main $HSiO^-$ isotopomer. The calculated rotation−vibration interaction constants α are given in Table 7. Within the variational approach, the vibrational−rotational energy levels were calculated for $J = 0-5$. The spectroscopic constants were then determined by fitting the rotational energy levels of the ground vibrational state using the Watson's Hamiltonian in the A represention.[28] The silaformyl anion was found to be a nearly prolate asymmetric top with the Ray's asymmetry parameter $\kappa = -0.985$. To assess sensitivity of the predicted rotational constants to changes in the structural parameters, the constants were calculated for the equilibrium structural parameters being varied within the above-discussed estimated error bars. Varying the HSi bond length by ±0.001 Å results in a large change of the constant A of ∓270 MHz, while the constants B and C change by merely ∓1and ∓2 MHz, respectively. Similarly, varying the valence angle HSiO by ±0.1° results in changes of the constants A, B, and C of ±280, ∓5, and ∓2 MHz, respectively. Varying the SiO bond length by ±0.001 Å influences all the constants A, B, and C to a similar extent, of ∓8, ∓24, and ∓21 MHz, respectively.

Although there are no high-resolution experimental data for the silaformyl anion, it is interesting to compare the predicted spectroscopic constants with those determined by Izuha et al.[29] from the microwave spectrum of the silaformyl radical, $HSiO^\bullet$. For the $^2A'$ ground electronic state, the rotational constants A, B, and C were found to be 312110, 19887.01, and 18605.42 MHz, respectively. The quartic centrifugal distortion constants were determined to be: $\Delta_N = 0.02475$, $\Delta_{NK} = 1.3019$, $\Delta_K = 150$, $\delta_N = 0.0022$, and $\delta_K = 1.28$ MHz.

Proton transfer to the silaformyl anion can be characterized by the basicity of the anion or the acidity of a conjugated acid. The basicity is defined as the negative of the Gibbs free energy change, ΔG, of the protonation reaction $HSiO^- + H^+ \rightarrow [H_2,Si,O]$, where $[H_2,Si,O]$ denotes a conjugated acid. Alternatively, the acidity is defined as the Gibbs free energy change of the (reverse) deprotonation reaction. Both basicity and acidity values are obviously identical. As shown in the previous studies,[1,2] the conjugated acid of the silaformyl anion can be either silanone, H_2SiO, or the cis and trans isomers of hydroxysilylene, HSiOH. Among the species with the composition $[H_2,Si,O]$, the molecules mentioned were found theoretically to be the most stable ones, with the total electronic energies computed to be nearly the same (to within about 3 kcal/mol), ref 2 and references therein.

TABLE 8: Differences between the Total Electronic Energies (in kcal/mol) of the Silaformyl Anion and Its Parent Acids, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
H_2SiO	366.8	361.7	358.4	357.4
cis-HSiOH	372.4	365.0	360.1	358.1
trans-HSiOH	372.8	365.2	360.3	358.3

The gas-phase acidity is dominated by the deprotonation energy, ΔE, which is defined as the difference in total electronic energies of the anion $HSiO^-$ and the parent acid $[H_2,Si,O]$ (at their respective equilibrium conformations). The total electronic energies for the equilibrium conformations of the H_2SiO, *cis*- and *trans*-HSiOH molecules were determined previously[30,31] using the CCSD(T) method with the cc-pVDZ through cc-pV5Z basis sets. Thus, the computed total energies of the three possible parent acids[30,31] and those of the silaformyl anion, Table 1, were used to calculate the deprotonation energies, and the results are given in Table 8. As for the total energies, the calculated values tend to approach well-defined asymptotic limits with enlargement of the one-particle basis set. By using the cc-pVTZ, cc-pVQZ, and cc-pV5Z data and extrapolation algorithms mentioned above,[9−13] the estimates for the deprotonation energies at the infinite one-particle basis set we found to be 356.5 ± 0.3 kcal/mol for the H_2SiO molecule, and 356.2 and 356.4 ± 0.5 kcal/mol for the *cis*- and *trans*-HSiOH molecules, respectively.

The CBS limit values of the deprotonation energies were corrected for the effects of core−electron correlation and of the zero-point vibrations of the silaformyl anion and its parent acids.

The core−core and core−valence correlation energies of all the species involved are computed at the CCSD(T)/cc-pCVQZ level of theory to be essentially the same. The corresponding differences are therefore small and amount to merely −0.2 kcal/mol for the H_2SiO parent acid, and to 0.1 kcal/mol for the *cis*- and *trans*-HSiOH parent acids.

For the sake of consistency with other theoretical studies, the zero-point vibrational effects were accounted for within the harmonic oscillator approximation. The harmonic force field and frequencies for all the species involved were computed at the CCSD(T)/cc-pVQZ level of theory. For the silaformyl anion, the harmonic zero-point energy (ZPE) was determined in this way to be 1713 cm^{-1}, as compared with the anharmonic ZPE of 1694 cm^{-1} calculated variationally with the force field of Table 4. For silanone, the harmonic ZPE was computed to be 4066 cm^{-1}, as compared with the anharmonic ZPE of 4036 and 4033 cm^{-1} calculated by the variational[30] and perturbational[32] approach, respectively. For the H_2SiO parent acid, the correction for the zero-point vibrations amounts thus to −6.7 kcal/mol within both harmonic and anharmonic oscillator approximation. The harmonic ZPE's for the cis and trans isomers of hydroxysilylene were computed to be 4543 and 4616 cm^{-1}, respectively. Using the anharmonic force field computed at the CCSD(T)/*spdf* level of theory and the perturbational approach, the ZPE's of the two isomers were determined by Martin[32] to be, respectively, 4450 and 4529 cm^{-1}. For the *cis*- and *trans*-HSiOH parent acids, the corrections for the harmonic zero-point vibrations are thus −8.1 and −8.3 kcal/mol, respectively. Including vibrational anharmonicity, these corrections amount to −7.9 and −8.1 kcal/mol, respectively.

TABLE 9: The Calculated Deprotonation Energies ΔE, Enthalpies ΔH^0, and Acidities ΔG^0 (in kcal/mol) of Parent Acids of the Silaformyl Anion

	ΔE^a	$\Delta H^{0\,b}$	$\Delta G^{0\,b}$
H_2SiO	349.6	351.0	343.1
cis-HSiOH	348.2	349.5	341.7
trans-HSiOH	348.2	349.5	341.7

[a] The estimated complete-basis-set limit at the CCSD(T) level of theory, including differences in the core−electron correlation and zero-point harmonic vibrational energies. [b] At 298.15 K, determined using the harmonic vibrational frequencies.

Our best estimates for the deprotonation energies at 0 K, ΔE, of the H_2SiO, *cis*-HSiOH, and *trans*-HSiOH parent acids are given in Table 9. Considering convergence of the computed values with the basis-set size, uncertainties inherent to the extrapolation algorithms, and some neglected effects (higher-order electron correlation, spin−orbit, relativistic, vibrational anharmonicity), the uncertainty in the calculated ΔE values we estimate to be ±1 kcal/mol.

To calculate the gas-phase acidities at 298 K, the ΔE values were corrected for thermal excitation of vibrational, rotational, and translational degrees of freedom and for the entropy changes.[4] The corrections were determined using the computed harmonic vibrational frequencies. The calculated deprotonation enthalpies, $\Delta H°$, and gas-phase acidities, $\Delta G°$, are listed in Table 9. The Si−H acidity of silanone and the O−H acidity of hydroxysilylene are predicted to be nearly the same (to within the estimated error bars), differing by only 1.4 kcal/mol.

Analogous calculations were performed for the $SiOH^-$ isomer. Using the results of Table 2, the differences between the total electronic energies of this anion and its conjugated acid—hydroxysilylene—were calculated to be 413.0, 406.1, 398.6, and 397.2 kcal/mol for the cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis set, respectively. The values quoted refer to the *trans*-HSiOH molecule, those for the *cis*-HSiOH molecule are smaller by 0.2 kcal/mol (compare Table 9). Similarly as for the silaformyl anion, the deprotonation energy at the infinite one-particle basis set we estimated to be 395.9 and 396.1 ± 0.5 kcal/mol for the *cis*- and *trans*-HSiOH molecules, respectively. The harmonic ZPE of the $SiOH^-$ isomer was computed to be 2739 cm^{-1}. Including the corrections for the effects of core−electron correlation (Table 3) and of the zero-point vibrations, our best estimate for the deprotonation energy at 0 K, ΔE, of hydroxysilylene is 391.1 ± 1 kcal/mol. The deprotonation enthalpy at 298 K, $\Delta H°$, was calculated then to be 392.5 kcal/mol, and the Si−H acidity of hydroxysilylene, $\Delta G°$, we predict to be 384.8 ± 1 kcal/mol.

The Si−H acidities of silanone and hydroxysilylene were calculated by Rusho et al.[2] at the CCSD(T)/*spdf*//MP2/*spd* level of theory to be “near” 343 and 383 kcal/mol, respectively. And, the O−H acidity of hydroxysilylene was calculated to be “near” 344 kcal/mol. All these values are in (surprisingly) good agreement with the best estimates found in this study. The reason for this is likely a fortuitous cancellation of errors due to the use of inaccurate equilibrium structural parameters and to incomplete treatment of electron correlation. For example, the structural parameters of the silaformyl anion were computed at the MP2/6-31++G(d,p) level of theory to be[2] $r(\mathrm{HSi}) = 1.60$ Å, $r(\mathrm{SiO}) = 1.61$ Å, and $\angle(\mathrm{HSiO}) = 106°$. The calculated HSi and SiO bond lengths differ from those determined at the CCSD(T)/aug-cc-pVDZ level (Table 1) by about 0.03 and 0.02 Å, whereas the angle HSiO differs by 0.8°. Similar differences can be found for the structural parameters of the conjugated acids: H_2SiO and HSiOH. Using these structural parameters, differences between the total electronic energies for the pairs $H_2SiO/HSiO^-$ and $HSiOH/HSiO^-$ were computed at the CCSD(T)/6-311++G(2df,2pd) level of theory to be[2] 357 and 359 kcal/mol, respectively. As shown in Table 8, the differences are close to those determined here at the (far accurate) CCSD(T)/cc-pV5Z level. As concluded in ref 2, “the values near 344 kcal/mol most closely correspond to the experimental value of 356 ± 8 kcal/mol.” Since the theoretical methods applied in this study are more accurate, we believe that the “true” gas-phase basicity of the silaformyl anion must be somewhat lower than the experimental value.

To assess accuracy of the theoretical methods applied in this study, additional calculations were performed on silicon oxide, SiO. The spectroscopic constants of the molecule were determined previously by Martin[32] using the CCSD(T) method and correlation-consistent basis sets of double- to quintuple-ζ quality. Including the correction for core−electron correlation, the equilibrium SiO bond length was computed with the cc-pV5Z basis set to be[32] 1.5115 Å, as compared with the experimental value of 1.5097 Å.[33] For the main SiO isotopomer, the harmonic frequency ω_e and the anharmonic constant $\omega_e x_e$ were computed to be[32] 1245.6 and 5.9 cm^{-1}, respectively. The corresponding experimental values are[33] 1241.56 and 5.97 cm^{-1}, respectively.

Turning to the thermochemistry of the silaformyl anion,[1] the hydride affinity of silicon oxide can be calculated. The hydride affinity is defined as the negative of the enthalpy change, ΔH, of the reaction $SiO + H^- \rightarrow HSiO^-$. Using the cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets, differences between the total electronic energies of all the species involved were computed by the CCSD(T) approach to be 63.6, 63.4, and 59.7 kcal/mol, respectively. By applying the extrapolation algorithms mentioned above,[9−13] the best estimate for the difference at the infinite one-particle basis set we found to be 56.3 ± 1.0 kcal/mol. A difference between the harmonic ZPE’s of the $HSiO^-$ and SiO molecules was calculated to be −3.1 kcal/mol, yielding our best estimate for the hydride-transfer energy at 0 K, $\Delta E = 53.2 \pm 1$ kcal/mol. Including the calculated correction for thermal excitation, the hydride affinity of silicon oxide at 298 K, $\Delta H°$, we predict to be 54.3 ± 1 kcal/mol. The calculated value falls close to the error bars of the experimental value of 49 ± 5 kcal/mol.[1]

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