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Theoretical Study of the Thermochemistry of Molecules in the Si−O−H System

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A self-consistent set of thermochemical parameters for 47 molecules in the Si−O−H system are obtained from a combination of *ab initio* electronic structure calculations and empirical corrections. Both stable and radical species are included in the study. Good agreement between the calculations and experimental data for the heat of formation of SiO is found, while the prediction for SiO_2 suggests that accepted literature values for the heat of formation of this molecule are too low, in agreement with a recently reported experimental measurement. Results for other species in this system are also compared with the literature and are found to be in acceptable agreement. Polynomial fits of the predicted thermodynamic data over the 300−4000 K temperature range are included in the supporting information.

I. Introduction

Reactions of compounds containing the elements silicon, oxygen, and hydrogen play an important role in a wide variety of industrially relevant processes. These include formation of silicon oxide thin films for microelectronic devices, optical films for glass, protective coatings for metals, and production of ceramic powders[1] and ultrapure silicon dioxide for communications-grade optical fiber using flames.[2] Silane combustion is also of interest from the point of view of safety (silane is pyrophoric) and because use of silane as an ignition promoter in supersonic jet engines has been considered.[3−5] The rapid evolution of technology in recent years has demanded equally rapid improvements in the methods and equipment used by these processes, requiring a much better understanding of the underlying chemistry and physics. Numerical models that include detailed reaction chemistry are valuable tools for process development, optimization, and scale up but require thermochemical data that are not available in many cases, including the Si−O−H system. Reports of experimental measurements of thermochemical quantities for these species are rare.[6−8] There have been numerous theoretical treatments of various silicon oxides,[9] but only a few have yielded thermochemical data suitable for use in modeling studies.[10−12] Darling and Schlegel applied the G-2 method to obtain heats of formation for the SiH_nO and SiH_nO_2 series.[10] However, the computationally intensive nature of the G-2 calculation limited their study to compounds containing no more than one silicon atom. Lucas et al. also performed G-2 calculations for the $SiOH_n$ ($n = 0-4$) and $SiOH_n^+$ ($n = 0-5$) series but did not report heats of formation at 298 K.[12] Finally, Zachariah and Tsang published a study of the kinetics of high-temperature $Si_xH_yO_z$ reactions in which they used the BAC-MP4 method (employed in the present study) to predict heats of formation for some Si−O−H species.[11]

In a series of papers over the last decade, we have established the use of *ab initio* calculations coupled with empirical bond additivity corrections as an effective method for estimating thermochemical quantities for compounds containing first- and second-row elements. This method, known as the BAC-MP4 method (for bond-additivity corrected-fourth-order Møller−Plesset perturbation theory), has been applied by us to first-row compounds[13] and the Si−H,[14−16] Si−H−Cl,[15] Si−F−H,[16] Si−N−F−H,[17] Si−C−H,[18] Si−C−Cl−H,[19] and Si−O−C−H[20] systems. In this work, we extend the BAC-MP4 method to a number of compounds in the Si−O−H system, including peroxy species that are thought to be important in the oxidation of silane.[5] With the exception of a few cyclic compounds reported by Zachariah and Tsang, we report predicted heats of formation for all neutral compounds included in the earlier theoretical studies[10−12] and discuss their significance relative to earlier works. To maximize the usefulness of these data, we include polynomial fits that describe the temperature dependence of the heat capacity, enthalpy, and entropy for all compounds in the study. These results provide a self-consistent set of thermochemical parameters for these species that will be useful for future studies of the reaction chemistry of this system.

II. Theoretical Methods

We have previously described the theoretical methods in detail,[13,16] so only a short description is presented here. Electronic structure calculations were performed using Gaussian 92[13,16,21] and earlier versions of these quantum chemistry codes. Equilibrium geometries and harmonic vibrational frequencies were obtained at the HF/6-31G* level of theory. Restricted Hartree−Fock theory (RHF)[22] was applied for the closed shell molecules and unrestricted Hartree−Fock theory (UHF)[23] was applied for the open-shell molecules, using the 6-31G* basis set.[24,25] Vibrational frequencies calculated at this level of theory are known to be systematically larger than experimental values;[26] thus, each calculated frequency was scaled by dividing it by 1.12.

To determine atomization enthalpies and thus heats of formation, the effects of electron correlation are included by performing single-point calculations, using Møller−Plesset

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TABLE 1: BAC Parameters for the BAC-MP4 (SDTQ) and BAC-MP2 Levels of Theory

bond	A_{ij} (MP4)[a]	A_{ij} (MP2)[a]	α_{ij}(MP4)[b]	α_{ij}(MP2)[b]
Si−H	92.79	126.63	2.0	2.0
Si−O	7038.5	3289.3	3.978	3.857
O−H	72.45	64.37	2.0	2.0
O−O	169.78	16.84	2.0	1.0

atom	B_k(MP4)	B_k(MP2)
Si	0.2	0.3
O	0.225	0.38
H	0.0	0.0

[a] In kcal mol^{-1}. [b] In Å^{-1}.

perturbation theory and the HF/6-31G* geometries. MP4-(SDTQ)/6-31G** calculations (fourth-order perturbation theory using the 6-31G** basis set with single, double, triple, and quadruple substitutions) were performed to obtain electronic energies. This level of theory has been used in most of the previous work; the errors remaining in the total energies are sufficiently systematic that empirical bond additivity corrections can provide enthalpies accurate to a few kcal mol^{-1}. The form of the BAC parameters α_{ij}, A_{ij}, and B_{ij} used to calculate the corrections for individual molecules is given in eqs 1−4 for a molecule of the form $X_k-X_i-X_j$:

$$E_{\mathrm{BAC}}(X_i-X_j) = f_{ij}g_{kij} \tag{1}$$

where

$$f_{ij} = A_{ij}\exp(-\alpha_{ij}R_{ij}) \tag{2}$$

$$g_{kij} = (1 - h_{ik}h_{ij}) \tag{3}$$

$$h_{ik} = B_k \exp\{-\alpha_{ik}(R_{ik} - 1.4\ \text{Å})\} \tag{4}$$

A_{ij} and α_{ij} are empirically derived parameters that depend on the X_i-X_j bond type and R_{ij} is the bond distance (angstroms). The factor B_k in eq 4 depends on the identity of atom k.

Table 1 lists the values for A_{ij}, α_{ij}, and B_k used in this work. For O−H bonds, A and α were chosen to give a good overall fit to a set of reference compounds whose heats of formation are well-established in the literature.[13] A and α for O−O bonds are based on H_2O_2 for single bonds and O_2 for double bonds.[13] For Si−H bonds, silane was used as a reference compound to determine A, while the α value was determined by analogy with related classes of compounds.[16] For Si−O bonds, a good reference compound for determining BAC parameters does not exist. As discussed in section III and in our previous paper on the Si−O−C−H system,[20] almost no thermochemical data are available for species in the Si−O−H system. Although experimental data have been reported for SiO[6,7] and SiO_2,[6,8] the bonding in these species is not representative of most of the species in this study and, thus, these molecules are not useful for establishing BACs. Thus, in the absence of computationally accessible species with well-accepted heats of formation, we chose to use the G-2 values calculated by Darling and Schlegel[10] for $SiH_2(OH)_2$ and $H_2Si{=}O$ as references to establish the corrections for Si−O single and double bonds. This choice resulted in predicted heats of formation for compounds in the Si−O−C−H system in good agreement with previously reported values.[20] Values for B_H and B_O were determined previously.[13] As in our earlier studies,[16] the B_{Si} values are based on trends in other atoms, but the results are not very sensitive to the value of this parameter.

Table 2 lists calculated bond lengths for each species in this study, as well as the MP4(SDTQ) BACs corresponding to each bond and any spin corrections.[16] The sum of these bond additivity corrections is combined with the MP4(SDTQ) electronic energy and the unscaled zero-point energy to obtain the heat of formation at 0 K ($\Delta H°_f(0)$). Entropies, heat capacities, enthalpies, and free energies as a function of temperature were calculated using the heats of formation at 0 K, equations derived from statistical mechanics, and the calculated geometries and scaled frequencies. For consistency with our earlier reports,[7,14−18,20] the unscaled frequencies are used for determining $\Delta H°_f(0)$, while the scaled frequencies are used to calculate thermochemistry at higher temperatures. Minor differences that would result from using the scaled frequencies to calculate $\Delta H°_f(0)$ are incorporated into the BACs.

There are two major sources of uncertainty in the calculated heats of formation: uncertainties resulting from the applicability of the theoretical methods to a given molecule and systematic uncertainties resulting from lack of good reference compounds for the BACs. The magnitude of the first is estimated using an *ad hoc* method developed previously that uses the results from lower-level calculations[16] and is reported in Table 4. The second source of uncertainty, lack of good reference compounds, can add a few kcal mol^{-1} to the uncertainty estimates discussed above and will scale with the number of bonds in the molecule. The use of different reference values would shift our calculated heats of formation as a group, with the consequence that calculated bond dissociation enthalpies and reaction enthalpies are affected less than the heats of formation. Overall, we believe that the uncertainties in the BAC-MP4 heats of formation lie in the 3−7 kcal mol^{-1} range.

Two conventions were followed in determining nomenclature for the various compounds. Groups enclosed in parentheses are bound to the neighboring atoms through the heavy atom of the group. Groups following the group in parentheses are bound to the heavy atom (usually silicon) immediately prior to the group in parentheses. For example, in the compound $HSi(OH)_2O$, the two OH groups are bound to silicon through their oxygen atom and the oxygen atom is bound to silicon. Several peroxy species were included in the study; the peroxy moiety is indicated by "OO". Cyclic compounds are denoted by the use of the word "cyclic." Heavy atoms at the left and right ends of the molecular formulas for these compounds are joined to complete the cyclic structure. For example, in the compound listed as "$-O(SiH_2)O(SiH_2)-$," the structure of the ring is −O−Si−O−Si−, where the hyphens on either end indicate that the O and Si atoms are joined. Double bonds are indicated by an equal sign, as in the case $(HO)_2Si{=}O$.

III. Results and Discussion

The results of applying the BAC-MP4 method to species in the Si−O−H system are given in Tables 3−6. As in previous papers in this series, the focus is on thermochemical parameters, rather than on the *ab initio* calculations themselves. Consequently, more detailed information from the calculations, including geometries from the Hartree−Fock calculations, total energies obtained from perturbation theory, and vibrational frequencies, are reserved for the supporting information (described in the Appendix).

Table 3 lists $\Delta H°_f(0)$ at various levels of theory for the compounds included in the study and is given to provide a measure of the accuracy of the calculations. In virtually all cases, $\Delta H°_f(0)$ converges to an approximately constant value, indicating that errors in the calculation are likely to be small. It is also worth noting that substantial differences exist between the (uncorrected) MP4 and BAC-MP4 values, highlighting the need to couple empirical corrections, such as the BAC method

TABLE 2: Bond Additivity Corrections for the MP4(SDTQ) Level of Theory (kcal mol^{-1})

species	spin or UHF correction[a]	Si−O bond length[b] (no.)[c]	BAC	Si−H bond length (no.)	BAC	O−H bond length (no.)	BAC	O−O bond length (no.)	BAC	Si−Si bond length (no.)	BAC
$Si(OH)_4$		1.629 (4)	10.54			0.947 (4)	10.90				
$HSi(OH)_3$		1.631	10.54	1.462	4.99	0.947 (3)	10.90				
		1.632	10.49								
		1.641	10.15								
$H_2Si(OH)_2$		1.642 (2)	10.18	1.468 (2)	4.92	0.947 (2)	10.90				
H_3SiOH		1.647	10.03	1.469	4.92	0.946	10.92				
				1.478 (2)	4.83						
$Si(OH)_3$	0.17 s	1.647	9.92			0.947	10.90				
		1.637	10.28			0.949	10.85				
		1.639	10.21			0.948	10.89				
$HSi(OH)_2$	0.20 s	1.640	10.28	1.478	4.83	0.947	10.90				
		1.650	9.86			0.946	10.92				
H_2SiOH	0.14 s	1.652	9.86	1.473	4.87	0.946	10.92				
				1.482	4.78						
$Si(OH)_2$		1.638	10.34			0.951	10.82				
		1.656	9.64			0.948	10.89				
HSiOH (trans)	0.45 u	1.651	9.91	1.509	4.54	0.948	10.88				
SiOH	0.56 s	1.649	9.96			0.949	10.86				
$Si(OH)_3O$	0.53 s	1.669	9.02			0.947 (3)	10.90				
		1.618	10.99								
		1.622	10.84								
		1.625	10.70								
$HSi(OH)_2O$	0.54 s	1.627 (2)	10.72	1.453	5.08	0.947 (2)	10.91				
		1.681	8.65								
$H_2Si(OH)O$	0.60 s	1.677	8.87	1.471	4.90	0.947	10.90				
		1.633	10.56	1.462	4.99						
H_3SiO	0.61 s	1.683	8.71	1.471 (3)	4.89						
$(HO)_2Si{=}O$		1.490	18.17			0.949	10.86				
		1.614	11.19			0.948	10.87				
		1.602	11.70								
$H(HO)Si{=}O$		1.494	18.21	1.456	5.05	0.950	10.84				
		1.612	11.39								
H_2SiO		1.498	18.19	1.469 (2)	4.91						
$HOSiO_2$	0.65 s	1.649	9.76			0.948	10.88				
		1.486	18.53								
		1.598	11.89								
$HOSi{=}O$	0.59 s	1.621	11.00			0.952	10.80				
		1.503	17.59								
$HSi{=}O$	0.84 s	1.501	17.99	1.505	4.57						
SiO		1.487	19.00								
$HSi({=}O)O$	0.67 s	1.490	18.55	1.459	5.02						
		1.648	9.89								
SiO_2		1.482 (2)	18.83								
$H_3SiOSiH_3$		1.626 (2)	10.84	1.473 (2)	4.88						
				1.474 (4)	4.86						
H_3SiOOH		1.677	8.77	1.470	4.90	0.950	10.85	1.409	9.99		
				1.472	4.89						
				1.469	4.92						
H_3SiOO	0.84 s	1.702	7.95	1.467	4.94			1.325	11.80		
				1.468 (2)	4.93						
H_2SiOOH	0.14 s	1.682	8.63	1.475 (2)	4.86	0.949	10.85	1.407	10.02		
HSiOOH	0.15 u	1.673	8.94	1.508	4.54	0.949	10.85	1.406	10.06		
HSiOO	0.88 u	1.680	8.67	1.510	4.53			1.342	11.40		
SiOOH	0.87 u	1.664	9.24			0.950	10.84	1.416	9.84		
−O(SiH)O−(cyclic)	0.36 u	1.638 (2)	10.20	1.482	4.79			1.517	7.94		
$-O(SiH_2)O(SiH_2)-$(cyclic)		1.671 (4)	9.04	1.466 (4)	4.94					2.393	5.18
−O(SiH)O−(cyclic)	0.03 u	1.632 (2)	10.42	1.460 (2)	5.01			1.521	7.88		
−SiOSiO−(cyclic)		1.683 (4)	8.61							2.469	4.23
$-(SiH_2)OSiO-$(cyclic)		1.667 (2)	9.17	1.466 (2)	4.94					2.430	4.69
		1.686 (2)	8.52								

[a] u: UHF-unstable corrections; s: spin-contamination corrections. [b] In angstroms. [c] Number of bonds.

or isodesmic reactions, with this level of theory. The literature values listed in Table 3 are discussed in Section IIIB.

Calculated heats of formation at 298 K ($\Delta H^\circ_f(298)$) are shown in Table 4 with error estimates calculated using the *ad hoc* approach mentioned earlier. This table also includes available measured and calculated values from the literature (comparison of these with our BAC-MP4 results is discussed below). Additional heats of formation needed to calculate bond dissociation energies (BDEs; Table 6) and to illustrate trends are included for reference in Table 4. Table 5 lists ΔS°(298 K) and values of ΔG°_f at various temperatures.

A. Heats of Formation and Bond Dissociation Energies. The heats of formation for Si−O−H compounds display two trends that are also observed in compounds containing silicon bound to other ligands. First, ΔH°_f (298) for the saturated species in the series $Si(OH)_nH_{4-n}$ decreases approximately

TABLE 3: Calculated $\Delta H_f°(0\ K)$ for Si−O−H Compounds at Various Levels of Theory (kcal mol^{-1})

species	MP4	BAC-MP2	BAC-MP3	BAC-MP4 (SDQ)	BAC-MP4 (SDTQ)	(G2)[a]
$Si(OH)_4$	−231.2	−317.0	−319.8	−318.4	−317.0	
$HSi(OH)_3$	−162.2	−231.8	−232.2	−231.7	−231.1	
$H_2Si(OH)_2$	−93.6	−146.7	−145.7	−145.7	−145.7	
H_3SiOH	−27.3	−63.5	−62.7	−62.8	−62.8	−65.0
$Si(OH)_3$	−120.1	−185.3	−183.4	−183.3	−183.3	
$HSi(OH)_2$	−54.2	−102.9	−100.6	−100.9	−101.2	
H_2SiOH	8.4	−23.6	−21.7	−21.9	−22.2	−24.0
$Si(OH)_2$	−71.9	−112.9	−111.2	−112.3	−113.6	
HSiOH (trans)	6.6	−17.7	−16.9	−18.2	−19.2	−22.8
SiOH	23.1	1.9	3.9	2.7	1.7	0.1
$Si(OH)_3O$	−169.2	−242.6	−246.7	−245.4	−244.0	
$HSi(OH)_2O$	−101.0	−158.1	−159.2	−158.9	−158.6	
$H_2Si(OH)O$	−34.5	−75.0	−75.2	−75.2	−75.3	
H_3SiO	30.9	7.4	7.4	7.2	6.9	2.6
$(HO)_2Si{=}O$	−127.1	−189.1	−195.4	−192.6	−189.9	
$H(HO)Si{=}O$	−64.3	−109.7	−112.0	−110.8	−109.8	
$H_2Si{=}O$	5.9	−22.1	−22.1	−22.1	−22.1	−22.6
$HOSiO_2$	−64.0	−113.2	−120.2	−117.9	−115.8	
$HOSi{=}O$ (cis)	−33.8	−74.2	−73.0	−73.3	−73.8	
$HSi{=}O$	30.9	7.7	9.9	8.6	7.5	8.5
SiO	−8.0	−24.0	−23.7	−25.3	−27.0	−23.2
$HSi({=}O)O$	−0.9	−33.4	−36.5	−35.6	−35.0	
SiO_2	−29.5	−65.1	−69.0	−67.6	−67.2	
$H_3SiOSiH_3$	−23.7	−75.2	−76.0	−75.5	−74.6	
H_3SiOOH	9.0	−33.9	−33.6	−34.1	−35.3	
H_3SiOO	39.9	7.8	7.8	5.8	4.6	
H_2SiOOH	45.2	6.6	7.9	7.2	5.8	
HSiOOH	40.7	10.2	10.2	8.2	6.2	
HSiOO	80.6	61.2	59.8	56.9	55.1	
SiOOH	57.1	29.0	30.6	28.4	26.3	
−O(SiH)O− (cyclic)	51.7	18.9	24.1	21.2	18.2	
$-O(SiH_2)O(SiH_2)-$ (cyclic)	−90.2	−154.5	−147.9	−150.2	−151.3	
−O(SiH)O− (cyclic)	16.3	−21.1	−17.7	−20.0	−22.4	
−SiOSiO− (cyclic)	−53.0	−91.6	−81.9	−86.9	−91.6	
$-(SiH_2)OSiO-$ (cyclic)	−74.1	−125.5	−117.3	−121.0	−124.1	

[a] Lucas,D. J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1993**, *99*, 6697.

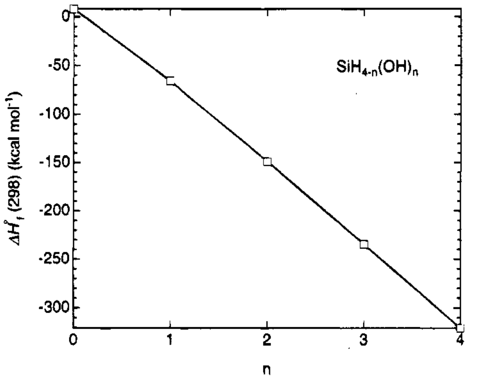

Figure 1. Calculated heats of formation for $SiH_{4-n}(OH)_n$ species as a function of n. As expected for closed-shell molecules, these species fall nearly on a straight line.

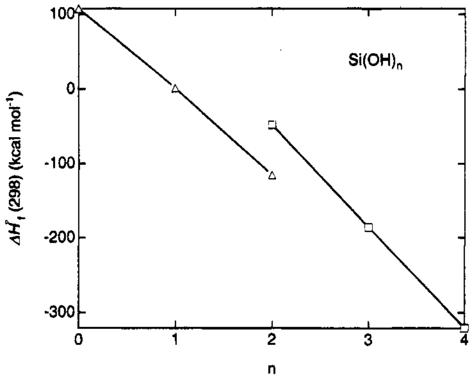

Figure 2. Calculated heats of formation for $Si(OH)_n$ species as a function of n. Triangles: species on this line (Si^3P, $SiOH(^2A'')$, and $Si(OH)_2$ (singlet), have an s^2p^2 electronic configuration at Si, causing their heats of formation to fall along a straight line. Squares: species on this line ($Si(OH)_2$ (triplet), $Si(OH)_3$, and $Si(OH)_4$) have an sp^3 electronic configuration at Si, causing their heats of formation to fall along a different line.

linearly with n. A linear regression gives a slope of −82.7 kcal mol^{-1} (Figure 1). The linearity is less perfect than observed in some other cases, with $\{\Delta H°_f(298)_{n=0} - \Delta H°_f(298)_{n=1}\} = 74$ kcal mol^{-1}, while for the succeeding three OH substitutions $\Delta(\Delta H°_f)$ remains relatively constant (83.2, 85.0, and 86.2 kcal mol^{-1}). In contrast, $\Delta(\Delta H°_f(298))$ varies by less than 1 kcal mol^{-1} in the series $Si(CH_3)_nH_{4-n}$. This suggests that the bonding in $Si(OH)_nH_{4-n}$ compounds is not completely localized. Alternatively, this nonlinearity could be the result of negative hyperconjugation (i.e., resonance between nonbonded substituents), which has been shown to be significant in silanols.[27] Thus, use of simple group additivity methods to calculate heats of formation for unknown species may produce significant errors.

A second trend observed in the Si−O−H system that is also seen in other silicon-containing compounds is the nonlinearity of the heats of formation in the $Si(OH)_n$ ($n = 0-4$) series (Figure 2). The two lines shown in Figure 2 result from the change in electronic configuration from s^2p^2 for $n \leq 2$, to sp^3 for $n > 2$. This change requires promotion of a 2s electron into the empty silicon 3p orbital, which for $n = 2$ is equivalent to the singlet−triplet splitting. Thus, $^3Si(OH)_2$ lies on roughly the same line as $Si(OH)_3$ and $Si(OH)_4$, while $^1Si(OH)_2$ lies on a different line with $Si(^3P)$ and ^2SiOH.

TABLE 4: $\Delta H_f°$(298 K) for the BAC-MP4(SDTQ) Level of Theory with Error Estimates and Literature Values for Si−O−H Compounds (kcal mol^{-1})

species	BAC−MP4	G2[a]	BAC−MP4[d]	other literature
$Si(OH)_4$	−320.8 ± 3.3			
$HSi(OH)_3$	−234.6 ± 1.6		−237.8	
$H_2Si(OH)_2$[m]	−149.0 ± 1.0	−149.0		
H_3SiOH	−65.8 ± 1.0	−67.5	−67.3	
$Si(OH)_3$	−185.8 ± 1.0			
$HSi(OH)_2$	−103.5 ± 1.2	−104.2		
H_2SiOH	−24.2 ± 1.2	−25.6	−26.1	
$Si(OH)_2$	−115.4 ± 2.9	−117.5	−117.7	
HSiOH (trans)	−20.5 ± 2.6	−23.7	−21.8	
SiOH	1.4 ± 3.2	0.1	−0.4	
$Si(OH)_3O$	−247.1 ± 3.3			
$HSi(OH)_2O$	−161.4 ± 1.3			
$H_2Si(OH)O$	−77.9 ± 1.1	−79.8		
H_3SiO	4.8 ± 1.2	1.0	4.0	−22.4[c]
$(HO)_2Si{=}O$	−192.3 ± 6.2			−213 ± 4[h]
$H(HO)Si{=}O$	−111.7 ± 3.4	−110.6	−112.6	−124.7[c]
$H_2Si{=}O$[m]	−23.5 ± 1.0	−23.5	−23.5	−27.5[c]
$HOSiO_2$	−117.1 ± 5.0			
$HOSi{=}O$ (cis)	−74.7 ± 1.5	−72.9	−74.9	−86.8[c]; −118 ± 4[h]
$HSi{=}O$	7.1 ± 3.6	8.5	6.9	
SiO	−26.7 ± 3.8	−22.6	−24.4	−24.0 ± 2.0[b]; −22.6[e]; −24.8 ± 1.6[g]; −18.3 ± 3[j]
$HSi({=}O)O$	−36.1 ± 2.3	−37.7	−37.3	−68.8[c]
SiO_2	−67.4 ± 2.1	−66.2	−68.8	−73.0 ± 8.0[b];−67.5[f]; −74.4 ± 10.0[g]; −66.9 ± 4[h]; −77.0 ± 2.5[i]
$H_3SiOSiH_3$	−79.3 ± 2.0			
H_3SiOOH	−38.5 ± 2.6	−41.1		−62.1[c]
H_3SiOO	2.0 ± 4.7	−2.7		−26.4[c]
H_2SiOOH	3.6 ± 3.0	1.1		−24.4[c]
HSiOOH	4.5 ± 4.6	0.2		
HSiOO	54.2 ± 5.2	47.7		
SiOOH	25.6 ± 4.9	23.7		
−O(SiH)O− (cyclic)	17.0 ± 8.4			
$-O(SiH_2)O(SiH_2)-$ (cyclic)	−155.6 ± 3.7		−157.3	
−O(SiH)O− (cyclic)	−24.5 ± 6.8	−28.1		−50.7[c]
−SiOSiO− (cyclic)	−92.2 ± 10.8		−99.0	
−(SiH2)OSiO− (cyclic)	−126.5 ± 7.5		−128.7	
OH	9.5 ± 1[k]			
O	59.4[k]			
H	52.1[k]			
SiH_4	8.2 ± 1[l]			
SiH_3	47.4 ± 1[l]			
SiH_2	64.8 ± 2[l]			
SiH	91.0 ± 1[l]			
Si	107.4[l]			
CH_3	34.9 ± 1[k]			
CH_3OH	−49.0 ± 1[k]			

[a] Reference 10. [b] Reference 6. [c] Reference 3. [d] Reference 11. [e] Dewar, M. J. S.; Friedheim, J.; Grady, G.; Healy, E. F.; Stewart, J. J. P. *Organometallics* **1986**, *5*, 375. [f] Dewar, M. J. S.; Jie, C. *Organometallics* **1987**, *6*, 1486. [g] Reference 37. [h] Reference 8. [i] Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1989; Vol. 2. [j] Reference 7. [k] Reference 13. [l] Reference 16. [m] Reference compound for this study.

Since the singlet−triplet splitting can be correlated with silylene (SiXY) reactivity, this energy difference was calculated for $Si(OH)_2$. Larger splittings are associated with smaller rates of insertion.[28] As in the case of all previous SiXY species examined, the singlet is found to be the ground state, with the triplet state lying 67.6 kcal mol^{-1} higher in energy. The trend in these splittings correlates well with the Allred−Rochow electronegativity,[29] although the relationship is not linear (Figure 3). The order of splittings for SiR_2, from largest to smallest, is R = F > OH > Cl > CH_3 > H > SiH_3 (75.7, 67.6, 50.4, 27.1, 19.8, and 7.8 kcal mol^{-1}). This is consistent with our earlier observations[18] and with similar trends observed in chlorine- and fluorine-substituted silylenes.[30]

Selected bond dissociation enthalpies (BDEs) are listed in Table 6, from which several general observations can be made. First, the Si−OH bond is quite strong; at 122.8 kcal mol^{-1} in H_3SiOH, it is nearly 30 kcal mol^{-1} stronger than the H_3C−OH bond in methanol (93.4 kcal mol^{-1}). Second, the strength of the Si−OH bond increases with increasing substitution of OH for H, a trend that parallels those seen in other silicon compounds.[15−18] In the case of OH for H substitution, the amount of stabilization per OH substitution is not constant. Addition of the second OH increases the Si−OH BDE by 7.5

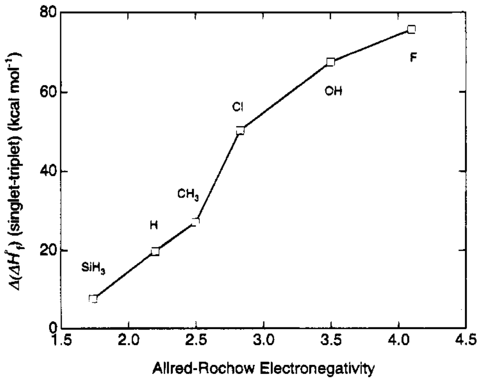

Figure 3. Singlet−triplet splittings for SiR_2 species as a function of the Allred−Rochow electronegativity. The identity of R is shown on the figure.

TABLE 5: Thermochemical Parameters at Various Temperatures (K)

species	ΔH°_f[a] 298	S°[b] 298	ΔG°_f[a] 300	600	1000	1500	2000	2500
$Si(OH)_4$	−320.8	81.9	−296.0	−271.0	−238.1	−198.7	−158.2	−117.1
$HSi(OH)_3$	−234.6	76.4	−215.5	−196.1	−170.6	−139.7	−107.4	−74.3
$H_2Si(OH)_2$	−149.0	68.7	−135.0	−120.2	−100.2	−76.2	−50.4	−23.9
H_3SiOH	−65.8	61.8	−57.0	−47.8	−34.7	−18.6	−0.6	18.4
$Si(OH)_3$	−185.8	77.6	−171.8	−157.5	−139.2	−117.0	−93.0	−68.2
$HSi(OH)_2$	−103.4	70.5	−94.6	−85.5	−73.5	−58.8	−42.2	−24.5
H_2SiOH	−24.2	62.3	−20.2	−15.7	−9.3	−1.4	8.5	19.7
$Si(OH)_2$	−115.4	64.7	−109.5	−103.3	−94.9	−84.3	−71.6	−57.5
HSiOH(trans)	−20.5	57.8	−19.8	−18.8	−16.8	−14.2	−9.3	−2.9
SiOH	1.4	57.0	−2.4	−5.9	−10.0	−14.8	−16.9	−17.5
$Si(OH)_3O$	−247.1	82.0	−227.0	−207.0	−180.9	−149.6	−116.8	−83.3
$HSi(OH)_2O$	−161.4	75.7	−146.8	−132.1	−112.6	−89.0	−63.9	−37.8
$H_2Si(OH)O$	−77.9	68.3	−68.4	−58.4	−44.9	−28.5	−10.3	9.0
H_3SiO	4.8	61.3	9.1	13.9	20.9	29.6	40.2	52.1
$(HO)_2Si{=}O$	−192.3	70.0	−180.6	−168.8	−152.9	−133.3	−111.6	−88.9
$H(HO)Si{=}O$	−111.7	63.8	−105.5	−99.0	−89.8	−78.4	−64.9	−50.1
$H_2Si{=}O$	−23.5	56.0	−22.3	−20.6	−17.7	−13.9	−7.9	−0.4
$HOSiO_2$	−117.1	71.1	−110.5	−103.7	−94.5	−83.5	−70.6	−56.4
$HOSi{=}O$(cis)	−74.7	64.8	−73.5	−72.1	−69.9	−66.9	−61.6	−55.2
$HSi{=}O$	7.1	57.5	3.2	−0.4	−4.8	−9.9	−12.5	−13.6
$HSi{-}O$	30.7	58.4	26.6	22.6	17.8	11.9	8.6	6.7
SiO	−26.7	50.5	−33.2	−39.5	−47.5	−57.1	−64.2	−69.6
$HSi({=}O)O$	−36.1	64.2	−34.7	−33.0	−30.5	−27.2	−21.8	−15.0
SiO_2	−67.4	55.3	−68.0	−68.5	−69.0	−69.5	−67.8	−64.6
$H_3SiOSiH_3$	−79.3	83.7	−66.5	−53.1	−34.2	−11.2	15.5	44.1
H_3SiOOH	−38.5	69.3	−24.7	−10.1	9.7	33.9	59.4	85.7
H_3SiOO	2.0	68.6	11.4	21.4	35.0	51.4	69.5	88.5
H_2SiOOH	3.6	70.1	12.5	21.9	34.6	50.1	67.5	85.7
HSiOOH	4.5	69.5	9.0	13.5	19.9	27.7	37.5	48.5
HSiOO	54.2	65.3	55.3	56.6	58.4	60.6	64.9	70.6
SiOOH	25.6	67.3	26.1	26.8	28.1	29.6	33.5	33.8
−O(SiH)O−(cyclic)	17.0	63.2	18.7	20.7	23.6	27.2	33.0	40.1
$-O(SiH_2)O(SiH_2)-$(cyclic)	−155.6	67.3	−139.8	−123.1	−100.0	−71.7	−39.4	−5.0
−O(SiH)O−(cyclic)	−24.5	61.2	−17.6	−10.2	0.2	12.9	27.6	43.4
−SiOSiO−(cyclic)	−92.2	64.6	−94.2	−96.0	−98.0	−100.2	−97.6	−92.1
$-(SiH_2)OSiO-$(cyclic)	−126.5	67.2	−120.0	−112.9	−102.8	−90.4	−73.5	−54.1

[a] In kcal mol^{-1}. [b] In cal mol^{-1} K^{-1}.

kcal mol^{-1}, while addition of the fourth OH increases the BDE by only 3.8 kcal mol^{-1}. This is evidently not caused by steric hindrance, since there is more than enough room on the silicon atom to accommodate four OH groups, but may be the result of hyperconjugation,[10,27] electrostatic repulsion between the OH groups, or increasing electron density at silicon. The Si−H BDE also increases with increasing OH substitution. Finally, sequential removal of OH groups from $Si(OH)_4$ produces a high−low−high pattern of Si−OH BDEs, which is determined by the stability of SiX_4 relative to SiX_3 and of SiX_2 relative to SiX. This trend is also consistent with all previously examined silicon compounds.

As noted previously,[20] Si−OH bonds are 10−12 kcal mol^{-1} stronger than $Si{-}OCH_3$ bonds, presumably due to the somewhat higher electronegativity of carbon relative to hydrogen. In contrast, substitution of OCH_3 for OH has only a slight effect on the BDEs of other Si−OH or $Si{-}OCH_3$ bonds in a molecule. Similarly, O−H BDEs are essentially unaffected by replacement of OH groups with OCH_3 groups (and vice versa). These observations are consistent with localized bonding in these compounds, in which substitutions at more distant H atoms have a much smaller effect on adjacent bonds to Si than does substitution at Si itself.

BDEs for Si−OH and Si−H bonds in the $SiH_{3-n}(OH)_n$ (n = 0−3) series are much weaker than those in the saturated ($SiH_{4-n}(OH)_n$, n = 0−4) series. For example, the Si−OH BDE in $Si(OH)_3$ is 80 kcal mol^{-1}, while the same bond in $Si(OH)_4$ is 144.5 kcal mol^{-1}. This dramatic weakening is due to the enhanced stability of the divalent silylene (SiXY) molecules relative to the trivalent silyl radicals and has been observed in all other silicon systems examined. However, this so-called divalent-state stabilization energy (DSSE), defined by Walsh as DSSE = $BDE(R_3Si{-}R) - BDE(R_2Si{-}R)$,[31] at 64 kcal mol^{-1} is the largest predicted so far. For comparison, the DSSEs predicted by BAC-MP4 for R = H, CH_3, Cl, and F are 21.8, 29.9, 42.6, and 61.0 kcal mol^{-1}, respectively.

Combining the Si−OH BDE in H_3SiOH with those of analogous $H_3Si{-}X$ species from our previous BAC-MP4 studies allows trends across the periodic table to be examined. Figure 4 shows the H_3Si-X BDE plotted versus the Allred−Rochow electronegativity[29] for first- and second-row R groups. The figure shows that a strong, linear correlation exists between electronegativity and the BDE, although the slopes differ for first- and second-row substitutents. This result is consistent with earlier theoretical work that identified the σ-bonding interaction as the dominant feature of Si−X bonds, with π-bonding playing a secondary role.[32] Such correlations have been used successfully by Luo and Bensen to develop group additivity schemes for silicon compounds.[33−35] Note that hydrogen, which is capable of forming only σ bonds, appears to behave more like the second-row substituents than the first-row ones, falling on the line between SiH_3 and Cl.

Table 6 also shows that Si−O double bonds are very strong, with BDEs as high as 151 kcal mol^{-1} in $H(OH)Si{=}O$. These are the strongest of the Si=X double bonds. By comparison, the double bonds in $H_2Si{=}CH_2$[18] and $H_2Si{=}NH$[17] are 116.9 and 110.8 kcal mol^{-1}, respectively. The stability of compounds with Si=O bonds is also revealed by the weakness of the O−H

TABLE 6: Calculated Bond Dissociation Enthalpies (BDE) at 298 K for Selected Compounds in the Si−O−H System (kcal mol^{-1})

Si−O bonds	BDE	Si−H bonds	BDE	O−H bonds	BDE
$(OH)_3Si-OH$	144.5			$(OH)_3SiO-H$	125.8
$(OH)_2HSi-OH$	140.7	$(OH)_3Si-H$	100.8	$(OH)_2HSiO-H$	125.3
$(OH)H_2Si-OH$	134.3	$(OH)_2HSi-H$	97.6	$(OH)H_2SiO-H$	123.2
H_3Si-OH	122.8	$(OH)H_2Si-H$	93.7	H_3SiO-H	122.7
		H_3Si-H	91.3		
$(OH)_2Si-OH$	80.0			$(OH)_2SiO-H$	45.6
$(OH)HSi-OH$	92.5	$(OH)_2Si-H$	40.1	$(OH)HSiO-H$	43.8
H_2Si-OH	98.5	$(OH)HSi-H$	55.8	H_2SiO-H	52.7
$(OH)Si-OH$	126.3	H_2Si-H	69.4		
$HSi-OH$	121.0			$(OH)SiO-H$	92.7
$Si-OH$	115.5	$(OH)Si-H$	73.9	$HSiO-H$	79.6
				$SiO-H$	24.0
$(OH)_2OSi-OH$	64.3				
$(OH)H(O)Si-OH$	59.2				
$H_2(O)Si-OH$	63.9				
$OH(O)Si-OH$	127.1				
$H(O)Si-OH$	128.3				
$OSi-OH$	57.5				
$O(O)Si-OH$	59.2				
$(OH)_3Si-O$	120.7				
$(OH)_2HSi-O$	117.4	$(OH)_2OSi-H$	21.2		
$(OH)H_2Si-O$	113.1	$(OH)H(O)Si-H$	18.2		
H_3Si-O	102.1	$H_2(O)Si-H$	23.8		
$(OH)_2Si{=}O$	136.3				
$H(OH)Si{=}O$	150.7	$OH(O)Si-H$	89.0		
$H_2Si{=}O$	147.7	$H(O)Si-H$	82.7		
$HOSi{=}O$	135.5	$OSi-H$	18.3		
$HSi-O$	143.3	$O(O)Si-H$	20.8		
$Si-O$	193.5				
$HO(O)Si-O$	101.8	$H_3SiOO-H$	92.6		
$H(O)Si-O$	102.6	$H_2(HOO)Si-H$	94.2		
$OSi-O$	100.1				
SiH_3O-SiH_3	131.6				

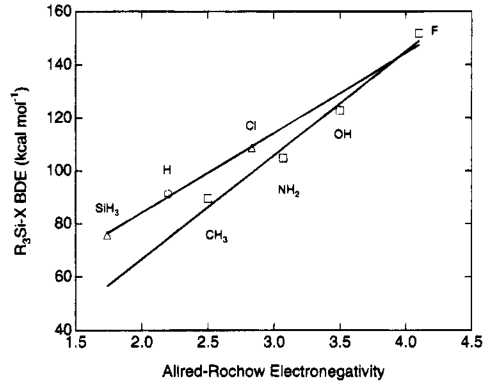

Figure 4. Si−X bond dissociation energies for R_3SiX compounds as a function of the Allred−Rochow electronegativity. Triangles indicate BDEs for second-row X groups, hydrogen is indicated by a circle, and squares indicate BDEs for first-row X groups. Lines shown are linear least-squares fits to each set.

bond in the corresponding hydroxysilyl molecule. For example, the O−H BDE in H_2SiOH is only 52.7 kcal mol^{-1}. The strength of the Si−O π bond in $H_2Si{=}O$ can be determined from the equation

$$D_\pi = \mathrm{BDE}_\sigma(\mathrm{Si{-}H}) + \mathrm{BDE}_\sigma(\mathrm{O{-}H}) - \mathrm{BDE}(\mathrm{H{-}H}) + \Delta H_{\mathrm{hyd}} \quad (5)$$

where ΔH_{hyd} is the hydrogenation energy of the Si=X bond. A value of 70.0 kcal mol^{-1} is found, which is stronger than the π bond in C_2H_4 (66.1 kcal mol^{-1}) and considerably stronger than the π bond in $H_2Si{=}CH_2$[18] (41.1 kcal mol^{-1}) or $H_2Si{=}SiH_2$[16] (28.7 kcal mol^{-1}). This estimate of D_π for $H_2Si{=}O$ is higher than an earlier one (55.8 kcal mol^{-1}) by Schleyer and Kost[36] based on isodesmic reactions and another by Schmidt et al.[37] (50 kcal mol^{-1}) using eq 5. The earlier studies assumed values of BDE_σ(SiO−H) considerably lower than the BDEs predicted by BAC-MP4, as a result of the erroneous assumption that this bond strength is similar to that in organic alcohols.

B. Comparisons with Literature Values. As discussed earlier, experimental measurements of thermochemistry are available for only two gas-phase compounds in the Si−O−H system: SiO and SiO_2. The JANAF[6] and CATCH[38] Tables, two large compilations of thermodynamic data, contain heats of formation for these species and the experimental sources are summarized in the JANAF Tables. The BAC-MP4 prediction (−26.7 ± 3.8 kcal mol^{-1}) for SiO falls within the range of experimental values discussed in the JANAF Tables (−23 to −28 kcal mol^{-1}) and the recommended values in both compilations are within the estimated uncertainty of the BAC-MP4 calculation (see Table 4). An additional experimental measurement reported by Hildenbrand and Murad just after the information on SiO in the JANAF Tables was compiled yielded a heat of formation of −18.3 ± 3 kcal mol^{-1},[7] which is slightly outside the uncertainty range of our calculation (these authors used the heat of formation for SiO found in the JANAF Tables in their most recent publication[8]).

The BAC-MP4 prediction for the heat of formation of SiO_2 (−67.4 ± 2.1 kcal mol^{-1}), however, is significantly more positive than either the value recommended in the JANAF Tables (−73.0 ± 8.0 kcal mol^{-1}) or the value listed in the CATCH Tables (−74.4 ± 10.0 kcal mol^{-1}). G-2 calculations by Darling and Schlegel have also suggested that there may be a problem with the experimental heat of formation for this molecule.[10] The amount of experimental data available for SiO_2 at the time the JANAF and CATCH compilations were published was considerably smaller than that available for SiO, resulting in correspondingly higher uncertainties (±2 kcal mol^{-1}

for SiO reported in the JANAF Tables, for example) for the recommended value. However, the BAC-MP4 prediction is in excellent agreement with the experimental value recently reported by Hildenbrand and Lau[8] (-66.9 ± 4 kcal mol^{-1}). Values for the SiO_2 heat of formation predicted by the other high-level calculations listed in Table 4 are similar to the value reported here. Thus, these results suggest that the correct heat of formation for SiO_2 is 4−7 kcal mol^{-1} more positive than the values in the JANAF and CATCH Tables.

Hildenbrand and Lau also report heats of formation for $HOSi{=}O$ and $(HO)_2Si{=}O$.[8] Using an effusion-cell source coupled to a mass spectrometer, they measured the equilibrium constant for the reactions $SiO + OH \leftrightarrow HOSi{=}O$ and $SiO + 2OH \leftrightarrow (HO)_2Si{=}O$. Heats of formation were determined by a third-law calculation, which yielded -118 ± 4 kcal mol^{-1} for $(HO)Si{=}O$ and -213 ± 4 kcal mol^{-1} for $(HO)_2Si{=}O$. By comparison, we predict -74.7 ± 1.5 kcal mol^{-1} for $HOSi{=}O$ and -192.3 ± 6.2 kcal mol^{-1} for $(HO)_2Si{=}O$. One possible source of the disagreement between our predicted values and those measured experimentally are the frequencies used by Hildenbrand and Lau to calculate $S°_{298}$ for the third-law calculation. A comparison of the corrected HF/6-31G* frequencies reported here with those used by Hildenbrand and Lau shows that there are significant differences. However, a recalculation of the third-law-derived heats of formation using the corrected frequencies obtained from our Hartree−Fock calculation results in a change of only 1.1−1.5 kcal mol^{-1}.[39] In the case of $HOSi{=}O$, a second possible explanation is that the application of a very large correction for fragmentation by Hildenbrand and Lau to obtain the $HOSi{=}O$ concentration is incorrect. Recalculation of the equilibrium constant, using only the $HOSi{=}O$ parent ion signal, results in a heat of formation that is 33 kcal mol^{-1} more positive (i.e., −85 kcal mol^{-1} rather than −118 kcal mol^{-1}),[39] which is in considerably better agreement with the BAC-MP4 prediction.

The heats of formation obtained in this study provide an opportunity to compare calculations at different levels of theory and using three different basis sets. Table 4 lists, in addition to the results of this study using the 6-31G** basis set, Darling and Schlegel's G-2 calculations using basis sets up to 6-311G-(3df,2p),[10] and the BAC-MP4 results of Zachariah and Tsang,[11] which were carried out using the extended basis sets 6-311G-(2df,p) and 6-31G(d,p) (cyclic species only). Comparison of our BAC-MP4 calculations with those of Zachariah and Tsang shows that they generally differ by less than 2.0 kcal mol^{-1}, which is within the combined uncertainty for the two calculations. The BAC-MP4 results of this study and the G-2 calculations are also in good agreement (less than 2.0 kcal mol^{-1} difference), with a few exceptions. Disparities between the two sets of predictions for the peroxy species are the greatest and are likely caused by the assumption in the BAC-MP4 calculations that O−O bonds in these compounds are similar to the O−O bonds in H_2O_2 and O_2. The generally small differences between BAC-MP4 and G-2 and between the BAC-MP4 calculations using different basis sets suggest that BAC-MP4 can provide results comparable to G-2. Note, however, that BAC-MP4 requires a reference bond energy obtained from either reliable experimental data, G-2, or some higher-level calculation to achieve this level of agreement. Improved theoretical accuracy will likely occur only after reliable heats of formation for more compounds in the Si−O−H system are established. Presently, it is not clear that the potentially higher accuracy provided by the use of larger basis sets or higher levels of theory adequately compensates for the higher computational costs and consequent limitation on the number of heavy atoms that can be treated.

In addition to the calculated results discussed above, Hartmann et al. estimated heats of formation using bond additivity methods for a number of Si−O−H species relevant to silane combustion.[3] These results are also shown in Table 4. Differences between these estimates and our BAC-MP4 predictions are large, as much as 27 kcal mol^{-1} for H_3SiO. This is in part due to the assumption by Hartmann et al. that the O−C bond in H_3SiOCH_3 is the same as that in H_3COCH_3 (82.0 kcal mol^{-1}) and that the O−H bond strength in silanols is the same as in organic alcohols (104 kcal mol^{-1}), contrary to the results presented here and elsewhere.[10,11] In a previous paper,[18] we reported thermochemistry for several methoxy silanes. Although that work did not include H_3SiOCH_3, $SiO{-}CH_3$ bonds in several related compounds such as $H_3C{-}OSi(OH)_3$ suggest that the strength of the $R{-}OCH_3$ bond in silicon-containing compounds is closer to 100 kcal mol^{-1}. The O−H bond in silanols is also predicted by BAC-MP4 to be considerably stronger than in the corresponding organic alcohols; Table 6 shows that these BDEs are predicted to be greater than 122 kcal mol^{-1}.

Finally, Lucas et al.[12] reported the results of G-2 calculations from which they obtained heats of formation at 0 K for species in the $SiOH_n$ ($n = 0{-}4$) series. Their results are compared to the prediction of this study in Table 3. Agreement between the two calculations is good, with most values at the G-2 level within 4 kcal mol^{-1} of the BAC-MP4 prediction. However, the G-2 predictions, with the exception of $HSi{=}O$, are systematically lower in energy than the BAC-MP4 predictions. Since energy differences are relatively unaffected by changing the temperature from 0 to 298 K, a direct comparison between BDEs predicted by the G-2 and BAC-MP4 calculations can be made. Again, satisfactory agreement between the G-2 and BAC-MP4 calculations is found. In H_3SiOH, for example, the G-2 predictions for the O−H, Si−H, and Si−OH BDEs are 119.3, 92.6, and 121.9 kcal mol^{-1}, respectively, while the BAC-MP4 predictions are 122.7, 93.7, and 122.8 kcal mol^{-1}, respectively.

IV. Summary and Conclusions

We have used *ab initio* calculations coupled with empirical bond additivity corrections to arrive at a set of thermodynamic data for species in the Si−O−H system. The lack of measured heats of formation for all but four of the molecules considered makes experimental validation of the calculations impossible at this time. However, agreement between these calculations and those of previous studies using different basis sets and at the G-2 level (a higher level of calculation) suggests that the predicted heats of formation for most of the molecules reported here should be accurate within the reported uncertainties. Additional confidence is gained from the accuracy of BAC-MP4 calculations observed for a wide range of previously examined silicon-containing species. The self-consistent thermochemistry provided by this work, coupled with the earlier analysis of silane oxidation,[11] should greatly improve our understanding of a variety of practical technologies involving silicon oxides.

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Appendix

Data contained in the supporting information are as follows: Table 7 presents **Z** matrices[40] for each of the molecular species obtained from the HF/6-31G* geometry optimization calculations. Molecular geometries can be obtained from these **Z** matrices. Table 8 gives moments of inertia in atomic units (amu Bohr^2), while Table 9 lists scaled vibrational frequencies obtained at the same level of theory. Table 10 presents electronic energies resulting from various perturbation-theory calculations using the 6-31G** basis set. The projected UHF (PUHF) and projected UMP2 (PUMP2) energies[41] are given for reference, although they are not used in the derivation of the BACs.

Table 11 gives polynomial coefficients for C_p, H, and S as a function of temperature for the species considered in this paper. These fits can be used with the CHEMKIN package of software[42] and are defined by

$$C_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

Supporting Information Available: Tables 7−11 as described in the Appendix (17 pages). Ordering information is given on any current masthead page.

References and Notes

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