Heats of Formation of SiH$_n$O and SiH$_n$O$_2$ Calculated by ab Initio Molecular Orbital Methods at the G-2 Level of Theory

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To help facilitate the study of the energetics and the mechanism of silane combustion and the oxidation of related silicon species, H$_m$Si–OH$_n$, H$_m$O–SiH$_n$–OH$_p$, and H$_m$Si–O–OH$_n$ have been examined by ab initio molecular orbital methods. Geometries have been optimized at the MP2/6-31G(d) level of theory, and vibrational frequencies have been computed at HF/6-31G(d). Heats of formation have been calculated at the G-2 level of theory (estimated mean absolute error of ±2 kcal/mol or less). The following theoretical heats of formation (at 298 K) have been obtained: SiO, –22.6; HSiO, 8.5; SiOH, 0.1; H$_2$SiO, –23.5; HSiOH, –23.7; H$_3$SiO, 1.0; H$_2$SiOH, –25.6; H$_3$SiOH, –67.5; OSiO, –66.2; OSiHO, –37.7; OSiOH, –72.9; OSiH$_2$O, –28.1; OSiHOH, –110.6; HOSiOH, –117.5; OSiH$_2$OH, –79.8; HOSiHOH, –104.2; HOSiH$_2$OH, –149.0; HSiOO, 47.7; SiOOH, 23.7; H$_2$SiOO, 35.5; HSiOOH, 0.2; H$_3$SiOO, –2.7; H$_2$SiOOH, 1.1; H$_3$SiOOH, –41.4 kcal/mol.

Introduction

Silane and oxygen form a highly explosive mixture, yet relatively little is known about the mechanism of combuation of silane.[1] Oxidation of silicon-containing species is also important in chemical vapor deposition processes used in the microelectronics industry[2] and the synthesis of ceramic powders.[3] Some rate constants have been measured[4–7] and some kinetic modeling has been carried out,[1,8,9] but good thermochemical and kinetic data for silicon–oxygen compounds is sparse. The energetics of the possible reactive intermediates in silane combustion can be expected to differ from those found in hydrocarbon combustion. For example, the lowest energy channel for dissociation of silane is to silylene and hydrogen molecule, whereas methane dissociates to methyl radical and hydrogen atom. Reliable experimental values for the thermochemistry of small, reactive silicon-containing molecules can be difficult to obtain,[10] and much of the thermochemistry for the proposed reactive silicon–oxygen intermediates has been estimated empirically rather than measured.[1a] Ab initio molecular orbital theory can be a valuable aid in developing a consistent set of thermochemical values for a variety of small molecules.[11] Heats of formation for small molecules can now be computed to an accuracy of ±3 kcal/mol or better[11] through the use of isodesmic reactions, bond additivity corrections,[12] and the G-1 and G-2 methods.[13,14]

In the present paper we have used the G-1 and G-2 methods to determine the energetics of neutral H$_m$Si–OH$_n$, H$_m$O–SiH$_n$–OH$_p$, and H$_m$Si–O–OH$_n$. A number of these species have been calculated previously[11–28] at levels of theory ranging from HF/3-21G to MP4/6-311G(d,p) and higher. However, it is not possible to piece together the data from these diverse studies to obtain a uniform estimate of the energetics of SiH$_m$O$_n$. The aim of the present work is to provide a consistent and reliable set of heats of formation for these simple silicon–oxygen compounds. These values also form the basis of a study of some of the elementary steps in silane combustion.[28]

Method

Molecular orbital calculations were carried out using the GAUSSIAN 92[29] series of programs using a variety of basis sets of split valence quality or better with multiple polarization and diffuse functions.[30] Equilibrium geometries were optimized by Hartree–Fock and second-order Møller–Plesset perturbation theory (HF/6-31G(d) and MP2(full)/6-31G(d), respectively) using a quasi-Newton optimization method.[31] Vibrational fre-

quencies and zero point energies were calculated at the HF/6-31G(d) level using the HF optimized geometries and analytical second derviatives.[32] Correlated energies were calculated by fourth-order Møller–Plesset perturbation theory[33] (MP4SDTQ, frozen core) and by quadratic configuration interaction with perturbative correction for triple excitations[34] (QCISD(T), frozen core) with the MP2(full)/6-31G(d) optimized geometries. In the G-1 method,[13] the energy computed at MP4/6-311G(d,p) is correct for the effect of diffuse functions obtained at MP4/6-311+G(d,p) for the effect of higher polarization functions obtained at MP4/6-311G(2df,p), and for the effect of electron correlated beyond fourth order obtained at QCISD(T)/6-311G(d,p). Higher level corrections for deficiencies in the wave function are estimated empirically[13] by comparing the calculated bond dissociation energy for H$_2$ with the exact value.

$$E(\text{G-1}) = E(\text{MP4/6-311G(d,p)}) + \Delta E(+) + \Delta E(2\text{df}) + \Delta E(\text{QCI}) + \Delta E(\text{HLC}) + \text{ZPE(HF/6-31G(d))} \quad (1)$$

with

$$\Delta E(+) = E(\text{MP4/6-311+G(d,p)}) - E(\text{MP4/6-311G(d,p)}) \quad (2)$$

$$\Delta E(2\text{df}) = E(\text{MP4/6-311G(2df,p)}) - E(\text{MP4/6-311G(d,p)}) \quad (3)$$

$$\Delta E(\text{QCI}) = E(\text{QCISD(T)/6-311G(d,p)}) = E(\text{MP4/6-311G(d,p)}) \quad (4)$$

$$\Delta E(\text{HLC}) = -0.00614 n_{\text{paired}} - 0.00019 n_{\text{unpaired}} \text{ au} \quad (5)$$

where n_{paired} and n_{unpaired} are the number of electron pairs and the number of unpaired electrons, respectively. The G-2 method[14a] overcomes some limitations caused by additivity assumptions in the G-1 method by using an extra calculation at the MP2/6-311G(3df,2p) level:

$$E(\text{G-2}) = E(\text{G-1}) + E(\text{MP2/6-311G(3df,2p)}) - E(\text{MP2/6-311G(2df,p)}) - E(\text{MP2/6-311+G(d,p)}) + E(\text{MP2/6-311G(d,p)}) + 0.00114 n_{\text{paired}} \quad (6)$$

The average absolute error of the remainng additivity assumptions in the G-2 level of theory is only 0.30 kcal/mol.[14b] At the G-2 level of theory, the mean absolute error for 125 well-characterized

TABLE I: MP2/6-31G(d) Optimized Geometries

molecule[a]	symmetry	parameters[b]
1 SiO	$C_{\infty v}$	$R(SiO) = 1.5423$
2 HSiO	C_s	$R(SiO) = 1.5468$, $R(SiH) = 1.5245$, $\angle HSiO = 122.7$
3 SiOH	C_s	$R(SiO) = 1.6739$, $R(OH) = 0.9736$, $\angle SiOH = 115.9$
4 H$_2$SiO	C_{2v}	$R(SiO)$ 1.5451, $R(SiH) = 1.4830$, $\angle HSiO = 124.2$
5 HSiOH *cis*	C_s	$R(SiO) = 1.6734$, $R(SiH)$ 1.5387, $R(OH) = 0.9719$, $\angle HSiO = 97.9$, $\angle SiOH = 117.0$
6 HSiOH *trans*	C_s	$R(SiO) = 1.6775$, $R(SiH) = 1.5194$, $R(OH) = 0.9725$, $\angle HSiO = 94.9$, $\angle SiOH = 112.1$
7 H$_3$SiO (^{2}A′)	C_s	$R(SiO) = 1.6970$, $R(SiH_1) = 1.4823$, $R(SiH_2) = 1.4812$, $\angle H_1SiO = 102.5$, $\angle H_2SiO = 111.5$, $\angle H_2SiOH_1 = 118.6$
8 H$_2$SiOH	C_1	$R(SiO) = 1.6750$, $R(SiH_1) = 1.4821$, $R(SiH_2) = 1.4893$, $R(OH) = 0.9695$, $\angle H_1SiO = 105.8$, $\angle H_2SiO = 112.8$, $\angle SiOH = 115.5$, $\angle H_1SiOH = 176.6$, $\angle H_2SiOH = -63.1$
9 H$_3$SiOH	C_s	$R(SiO) = 1.6705$, $R(SiH_1) = 1.4775$, $R(SiH_2) = 1.4874$, $R(OH) = 0.9688$, $\angle H_1SiO = 105.8$, $\angle H_2SiO = 112.1$, $\angle SiOH = 116.4$, $\angle H_1SiOH = 180$, $\angle H_2SiOH_1 = 119.5$
10 OSiO	$D_{\infty h}$	$R(SiO) = 1.5313$
11 OSiHO	C_s	$R(SiO_1) = 1.5330$, $R(SiO_2) = 1.6707$, $R(SiH) = 1.4749$, $\angle OSiO = 127.1$, $\angle HSiO_2 = 102.8$
12 OSiOH *cis*	C_s	$R(SiO_1) = 1.5420$, $R(SiO_2) = 1.6523$, $R(OH) = 0.9759$, $\angle OSiO = 129.4$, $\angle SiOH = 115.4$, $\angle OSiOH = 0$
13 OSiOH *anti*	C_s	$R(SiO_1) = 1.5374$, $R(SiO_2) = 1.6541$, $R(O_2H) = 0.9729$, $\angle OSiO = 127.7$, $\angle SiOH = 115.9$, $\angle OSiOH = 180$
14 OSiH$_2$O	C_{2v}	$R(SiO) = 1.6719$, $R(OO) = 1.6280$, $R(SiH) = 1.4738$, $\angle HSiO = 118.9$
15 OSiHOH	C_s	$R(SiO_1) = 1.5355$, $R(SiO_2) = 1.6401$, $R(SiH)$ 1.4700, $R(OH) = 0.9733$, $\angle OSiO = 128.1$, $\angle HSiO_1 = 127.3$, $\angle SiOH = 115.6$, $\angle OSiOH = 0$
16 HOSiOH *trans, trans*	C_{2v}	$R(SiO) = 1.6667$, $R(OH) = 0.9716$, $\angle OSiO = 97.4$, $\angle SiOH = 113.2$, $\angle OSiOH = 180$
17 HOSiOH *cis, trans*	C_s	$R(SiO_1) = 1.6623$, $R(SiO_2) = 1.6810$, $R(O_1H) = 0.9760$, $R(O_2H) = 0.9716$, $\angle OSiO = 98.6$, $\angle SiO_1H = 114.6$, $\angle SiO_2H = 114.5$, $\angle O_2SiO_1H = 0$, $\angle O_1SiO_2H = 180$
18 OSiH$_2$OH	C_1	$R(SiO_1) = 1.6459$, $R(SiO_2) = 1.6895$, $R(SiH_1) = 1.4722$, $R(SiH_2) = 1.4832$, $R(O_1H) = 0.9698$, $\angle OSiO = 115.3$, $\angle H_1SiO_1 = 104.9$, $\angle H_2SiO_1 = 112.9$, $\angle SiO_1H = 117.4$, $\angle H_1SiO_1O_2 = 120.1$, $\angle H_2SiO_1O_2 = -114.5$, $\angle O_2SiO_1H = 61.5$
19 HOSiHOH *gauche, gauche*	C_s	$R(SiO) = 1.6701$, $R(SiH) = 1.4786$, $R(OH) = 0.9693$, $\angle HSiO = 104.9$, $\angle SiOH = 116.3$, $\angle OSiHO = 122.8$, $\angle HSiOH = 195.3$
20 HOSiHOH *gauche, gauche′*	C_1	$R(SiO_1) = 1.6703$, $R(SiO_2) = 1.6697$, $R(SiH) = 1.4877$, $R(OH_1) = 0.9708$, $R(OH_2) = 0.9722$, $\angle HSiO_1 = 103.3$, $\angle HSiO_2 = 111.4$, $\angle SiOH_1 = 115.4$, $\angle SiOH_2 = 116.2$, $\angle OSiHO = 122.9$, $\angle HSiOH_1 = 186.7$, $\angle HSiOH_2 = -50.2$
21 HOSiH$_2$OH	C_2	$R(SiO) = 1.6642$, $R(SiH) = 1.4784$, $R(OH) = 0.9699$, $\angle OSiO = 113.9$, $\angle HSiO = 103.5$, $\angle SiOH = 116.0$, $\angle HSiOO = 121.5$, $\angle OSiOH = 65.6$
22 HSiOO *cis*	C_s	$R(SiO) = 1.7076$, $R(OO) = 1.3656$, $R(SiH) = 1.5213$, $\angle SiOO = 118.8$, $\angle HSiO = 96.3$, $\angle HSiOO = 0$
23 HSiOO *trans*	C_s	$R(SiO) = 1.7141$, $R(OO) = 1.3598$, $R(SiH) = 1.5137$, $\angle SiOO = 118.1$, $\angle HSiO = 88.6$, $\angle HSiOO = 180$
24 SiOOH	C_s	$R(SiO) = 1.6855$, $R(OO) = 1.4481$, $R(OH) = 0.9771$, $\angle SiOO = 113.1$, $\angle OOH = 98.6$, $\angle SiOOh = 180$
25 H$_2$SiOO	C_1	$R(SiO) = 1.7482$, $R(OO) = 1.3057$, $R(SiH_1) = 1.4839$, $R(SiH_2) = 1.4878$, $\angle SiOO = 122.5$, $\angle H_1SiO = 98.0$, $\angle H_2SiO_1 = 106.1$, $\angle H_1SiO_1O_2 = -145.8$, $\angle H_2SiO_1O_2 = -27.2$
26 HSiOOH	C_1	$R(SiO) = 1.6932$, $R(OO) = 1.4864$, $R(SiH) = 1.5215$, $R(OH) = 0.9775$, $\angle SiOO = 107.8$, $\angle HSiO = 88.1$, $\angle OOH = 97.4$, $\angle HSiOO = 179.0$, $\angle SiOOH = 161.9$
27 H$_3$SiOO (^{2}A″)	C_s	$R(SiO) = 1.7420$, $R(OO) = 1.3426$, $R(SiH_1) = 1.4783$, $R(SiH_2) = 1.4752$, $\angle SiOO = 104.7$, $\angle H_1SiO = 103.4$, $\angle H_2SiO = 109.1$, $\angle H_1SiOO = 180$, $\angle H_2SiOH_1 = 118.8$
28 H$_2$SiOOH	C_1	$R(SiO) = 1.6814$, $R(OO) = 1.4868$, $R(SiH_1) = 1.4861$, $R(SiH_2) = 1.4884$, $R(OH) = 0.9778$, $\angle SiOO = 101.9$, $\angle H_1SiO = 102.2$, $\angle H_2SiO = 111.0$, $\angle OOH = 98.2$, $\angle H_1SiOO = 178.0$, $\angle H_2SiOO = -63.0$, $\angle SiOOH = 121.8$
29 H$_3$SiOOH	C_1	$R(SiO) = 1.7033$, $R(OO) = 1.4890$, $R(SiH_1) = 1.4818$, $R(SiH_2) = 1.4818$, $R(SiH_3) = 1.4786$, $R(OH) = 0.9779$, $\angle SiOO = 99.8$, $\angle H_1SiO = 102.9$, $\angle H_2SiO = 110.9$, $\angle H_3SiO = 111.5$, $\angle OOH = 98.3$, $\angle H_1SiOO = 177.4$, $\angle H_2SiOH_1 = 118.1$, $\angle H_3SiOH_1 = -118.8$, $\angle SiOOH = 119.5$

[a] See Figure 1 for structure numbers, conformations, and numbering of atoms. [b] Bond lengths in Å, angles in deg.

atomization energies, ionization energies, electron affinities, and proton affinities is 1.3 kcal/mol.[14a] A similar level of accuracy can be expected in the present study.

Results and Discussion

Geometries optimized at the MP2/6-31G(d) level are collected in Table I, and the conformations are shown in Figure 1. Total energies at the MP2/6-31G(d), MP4/6-311G(2df,p), QCISD-(T)/6-311G(d,p), G-1, and G-2 levels are listed in Table II, and

vibrational frequencies are summarized in Table III. The structures and relative energies are discussed very briefly below. The G-1 and G-2 energies are then used to compute the heats of formation listed in Table IV. Bond dissociation enthalpies calculated from the heats of formation calculated at the G-2 level are given in Table V.

H$_m$SiOH$_n$. Silicon monoxide has been calculated previously at the G-2 level, and the heat of formation is within 1.7 kcal/mol of the experimental value.[14,35] Both HSiO and SiOH are bent
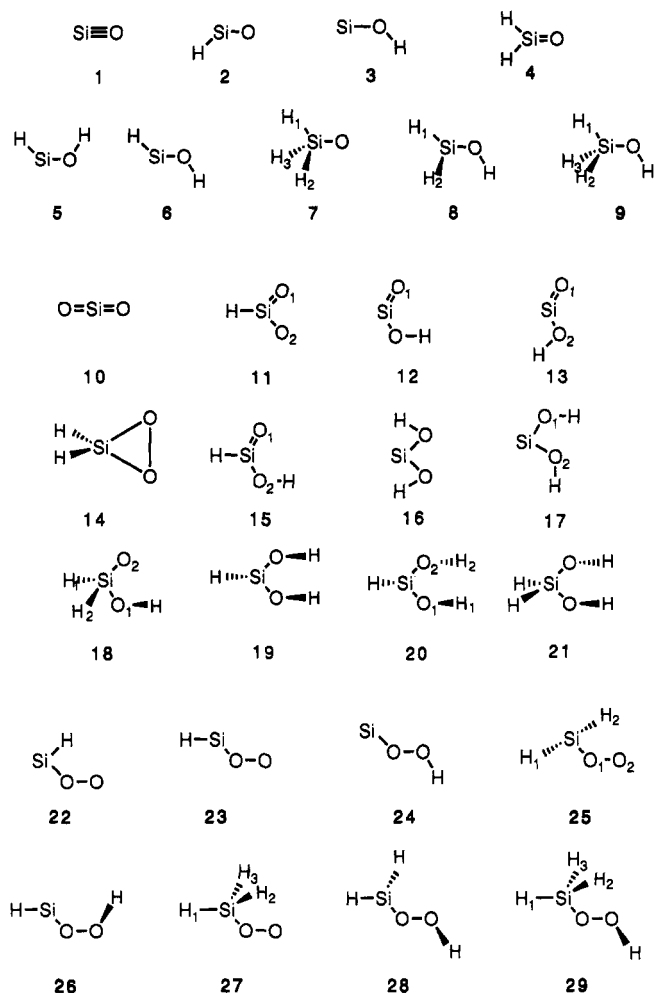
Figure 1. Structure numbers, conformations, and atom numbering for the molecules used in the present study.

structures. Peyerimhoff,[15] Schaefer,[16] and Grein[17] have studied the HSiO ⇌ SiOH isomerization and find SiOH 10–20 kcal/mol lower. At the G-2 level SiOH is more stable by 8.4 kcal/mol. The structures of H$_2$SiO an HSiOH are analogous to formaldehyde and hydroxycarbene, respectively. The isomerization and decomposition of H$_2$SiO and HSiOH have been examined by Nagase,[18] Yamabe,[19] Jordan,[20] and Gordon;[21] they find that HSiOH is 2–5 kcal/mol more stable than H$_2$SiO (by contrast, hydroxycarbene is ca. 50 kcal/mol higher than formaldehyde) and that both structures have high barriers (50–90 kcal/mol) to isomerization and decomposition. At the G-2 level cis-HSiOH, trans-HSiOH, and H$_2$SiO are equal in energy within ±0.2 kcal/mol.

Gordon et al.[21] have calculated H$_3$SiO, H$_2$SiOH, and H$_3$SiOH in a study of the thermal decomposition of silanol. The formation of H$_3$SiOH from SiH$_2$ and H$_2$O has also been calculated by Raghavachari[22] and Zachariah.[23] The proton affinity and gas-phase acidity of silanol have been calculated at the G-1 level.[24] The G-2 level of theory indicates that H$_2$SiOH is 24.6 kcal/mol more stable than H$_3$SiO, reflecting the difference in the Si–H and O–H bond strengths. The heats of reaction for silanol dissociation calculated by Gordon[21] are within 2–10 kcal/mol of the more accurate G-2 values.

H$_m$O–SiH$_n$–OH$_p$. The heat of formation of SiO$_2$ has been calculated previously at the G-2 level.[14] The 8 kcal/mol difference between the calculated and experimental heats of formation is much larger than for CO$_2$ (2.7 kcal/mol) and may signal a problem with the experimental value. Like HCO$_2$,[36] HSiO$_2$ suffers from a symmetry-breaking instability when calculated by single reference methods. The energy of the C_{2v} form may be a few kcal/mol lower. The O=Si–OH isomer **12** is 35 kcal/mol more

stable than HSiO$_2$ and ca. 100 kcal/mol more stable than HSiOO and SiOOH (**23** and **24**, see below). Of the SiH$_2$O$_2$ isomers, dihydroxysilylene is the most stable and prefers the cis, trans geometry, **17**. Silanoic acid, **15**, is the next most stable isomer (7 kcal/mol higher than Si(OH)$_2$) and adopts a O–Si–O–H cis conformation.[25] The most stable SiH$_2$O$_2$ isomer with 2 SiH bonds is the 3-membered ring **14**, siladioxirane,[26] and lies ca. 90 kcal/mol above dihydroxysilylene.

Dihydroxysilyl radical, SiH(OH)$_2$, adopts a *gauche, gauche* conformation, **19**; however, the *gauche, gauche'* conformation, **20**, is only 0.4 kcal/mol higher. The O–SiH$_2$–OH radical, **18**, is 25 kcal/mol less stable, reflecting the difference in the Si–H and O–H bond strengths. The lowest energy conformer of O–SiH$_2$–OH has a *gauche* orientation for the O–Si–O–H dihedral angle (*syn* and *anti* are both transition states for OH rotation). Like its carbon analogue, silanediol (**21**) is a *gauche, gauche'* structure with C_2 symmetry[27] as a result of the anomeric effect.[37]

H$_m$Si–O–OH$_n$. The SiH$_m$O$_2$ structures with one Si–O bond and one O–O bond can formally arise from the reaction of SiH$_m$ with O$_2$ (perhaps followed by rearrangement). These species are 70–100 kcal/mol less stable than their counterparts with two Si–O bonds, largely because of the strength of the Si–O bond and the weakness of the O–O bond. The SiOOH isomer is *trans* whereas HSiOO is *cis*; the former is 24 kcal/mol more stable because of the difference in the SiH and OH bond energies. Nagase[26] has found that the structure of H$_2$SiOO, **25**, is more like a complex between SiH$_2$ and O$_2$ rather than the silicon analogue of carbonyl oxide (**25** could not be found at the Hartree–Fock level). The HSiOOH isomer, **26**, is more stable than **25**, but both are over 100 kcal/mol higher in energy than dihydroxysilylene, **16**. The reaction between SiH$_3$ and O$_2$ forms H$_3$SiOO without a barrier;[28] H$_3$SiOO and its 1,3 hydrogen shift isomer, H$_2$SiOOH, are nearly equal in energy but are 80–105 kcal/mol less stable than OSiH$_2$OH and SiH(OH)$_2$. Like methyl peroxide, silyl peroxide has a gauche conformation, with the cis and trans geometries representing transition states for rotation about the O–O bond.

Heats of Formation. The calculated heats of formation are collected in Table IV. These are obtained by computing the enthalpies of atomization at 298 K using the G-1 and G-2 energies in Table II with the appropriate thermal corrections. The computed atomization enthalpies are combined with the experimental $\Delta H_f°$ for the atoms to give the heats of formation in Table IV. The mean absolute errors in the $\Delta H_f°$ values calculated at the G-2 level are expected to be 1.3 kcal/mol.[14] The relative energies of various isomers have been considered above; bond energies derived from the calculated heats of formation are discussed below. Also listed in Table IV are some empirical estimates of heats of formation based on bond energy assumptions.[1a] Many of the differences can be traced to a poor estimate for the heat of formation of SiH$_3$O. The G-2 calculations provide, for the first time, a reliable and consistent set of heat of formation of these silicon–oxygen species.

Bond Energies. The heats of formation in Table IV can be combined to yield bond energies for the various species in this study. Table V lists Si–H, Si–O, O–H, and O–O bond energies for selected molecules. The Si–H bond energy is 92–97 kcal/mol for saturated sp^3 silicon and 84–90 for sp^2 silicon. The large variation in the Si–H bond strengths for the silyl radicals reflects the increasing stability of the product silylenes with increasing electronegative substitution. This also highlights the danger of using simple bond energies to estimate the heats of formation of reactive intermediates. The Si–H bond energies for the substituted silylenes are better behaved.

The Si–O bond energies in SiH$_3$OH and SiH$_2$(OH)$_2$ differ by 8 kcal/mol. The same magnitude effect is found for the Si–F bonds in SiH$_{4-n}$F$_n$[38] and reflects the stabilizing electrostatic and hyperconjugative interactions between multiple electronegative

TABLE II: Total Energies, Zero Point Energies, and Thermal Corrections[a]

molecule[b]	theory					ZPE[c]	thermal
	MP2/6-31G(d)	MP4/6-311G(2df,p)	QCISD(T)/6-311G(d,p)	G-1	G-2		
Si	−288.882 07	−288.925 45	−288.909 32	−288.933 78	−288.933 24	0	0.89
O	−74.882 00	−74.964 78	−74.934 02	−74.982 05	−74.982 03	0	0.89
H	−0.498 23	−0.499 81	−0.499 81	−0.500 00	−0.500 00	0	0.89
1 SiO	−364.059 41	−364.191 10	−364.119 13	−364.218 92	−364.216 18	1.80	1.49
2 HSiO	−364.575 86	−364.722 57	−364.651 60	−364.749 07	−364.747 90	5.37	1.84
3 SiOH	−364.585 60	−364.733 14	−364.667 82	−364.762 28	−364.761 28	7.53	1.85
4 H₂SiO	−365.196 65	−365.358 87	−365.286 53	−365.379 71	−365.379 68	11.41	1.90
5 HSiOH cis	−365.187 95	−365.353 64	−365.287 67	−365.380 30	−365.379 89	12.39	1.95
6 HSiOH trans	−365.189 18	−365.353 81	−365.287 76	−365.380 52	−365.379 97	12.60	1.94
7 H₃SiO	−365.723 49	−365.901 73	−365.839 59	−365.921 85	−365.921 66	15.80	2.12
8 H₂SiOH	−365.768 09	−365.944 56	−365.877 98	−365.963 71	−365.964 15	17.36	2.27
9 H₃SiOH	−366.403 78	−366.596 97	−366.529 67	−366.610 74	−366.611 71	23.15	2.35
10 OSiO	−439.095 01	−439.318 18	−439.188 28	−439.364 05	−439.361 00	4.31	1.98
11 OSiHO	−439.616 39	−439.852 52	−439.735 33	−439.897 75	−439.896 54	8.66	2.13
12 OSiOH cis	−439.676 66	−439.909 94	−439.789 34	−439.954 55	−439.952 86	10.16	2.26
14 OSiH₂O	−440.173 40	−440.423 43	−440.299 67	−440.463 33	−440.461 92	14.05	2.12
15 OSiHOH	−440.305 86	−440.555 23	−440.432 72	−440.593 69	−440.593 60	15.89	2.29
17 HOSiOH cis, trans	−440.311 36	−440.561 23	−440.446 86	−440.605 30	−440.604 76	16.96	2.39
18 OSiH₂OH	−440.823 22	−441.088 64	−440.977 39	−441.125 61	−441.125 77	19.97	2.70
19 HOSiHOH gauche, gauche	−440.864 13	−441.127 07	−441.011 65	−441.164 37	−441.165 24	21.38	2.99
21 HOSiH₂OH	−441.505 57	−441.785 61	−441.669 61	−441.815 84	−441.817 04	27.40	2.83
22 HSiOO cis	−439.471 60	−439.710 72	−439.608 62	−439.762 88	−439.760 71	7.43	2.33
24 SiOOH	−439.520 43	−439.752 50	−439.648 21	−439.800 98	−439.799 27	10.08	2.54
25 H₂SiOO	−440.071 76	−440.323 79	−440.208 11	−440.362 71	−440.361 06	13.86	2.49
26 HSiOOH	−440.125 55	−440.374 37	−440.267 26	−440.419 29	−440.417 83	14.82	2.83
27 H₃SiOO	−440.699 81	−440.964 87	−440.860 60	−441.003 43	−441.002 84	18.50	2.66
28 H₂SiOOH	−440.701 86	−440.961 78	−440.853 37	−440.997 72	−440.997 28	20.08	2.89
29 H₃SiOOH	−441.338 84	−441.615 14	−441.505 34	−441.645 58	−441.645 69	25.96	2.93

[a] Total energies in au (1 au = 627.51 kcal/mol), zero point and thermal energies in kcal/mol, MP2 energies are full, MP4 and QCI energies are frozen core, G-1 and G-2 energies include zero point energy. [b] See Figure 1 for structure numbers and conformations. [c] Zero point energies computed at the HF/6-31G(d) level and scaled by 0.8929.

TABLE III: Calculated Vibrational Frequencies[a]

molecule	
1 SiO	1407
2 HSiO	761, 1324, 2121
3 SiOH	884, 919, 4100
4 H₂SiO	785, 809, 1124, 1355, 2432
5 HSiOH cis	662, 827, 922, 1069, 2104, 4126
6 HSiOH trans	698, 874, 932, 1050, 2202, 4122
7 H₃SiO	422, 698, 873, 1013, 1047, 1091, 2409, 2411, 2417
8 H₂SiOH	247, 738, 860, 923, 955, 1020, 2328, 2388, 4143
9 H₃SiOH	205, 736, 793, 913, 958, 1041, 1068, 1107, 2365, 2381, 2425, 4146
10 OSiO	329, 329, 1111, 1604
11 OSiHO	402, 634, 901, 960, 1393, 2497
12 OSiOH cis	329, 446, 863, 945, 1308, 4071
13 OSiOH anti	349, 355, 853, 917, 1327, 4123
14 OSiH₂O	539, 772, 774, 831, 880, 1080, 1161, 2482, 2489
15 OSiHOH	371, 521, 674, 891, 982, 1007, 1393, 2509, 4103
16 HOSiOH trans, trans	364, 460, 511, 854, 881, 951, 980, 4132, 4134
17 HOSiOH cis, trans	350, 499, 558, 869, 882, 934, 986, 4079, 4129
18 OSiH₂OH	178, 358, 547, 731, 843, 921, 966, 1021, 1055, 2437, 2444, 4142
19 HOSiHOH gauche, gauche	80, 282, 359, 734, 831, 940, 972, 977, 2407, 4147, 4150
20 HOSiHOH gauche, gauche'	188, 263, 399, 728, 843, 936, 966, 987, 2355, 4100, 4135
21 HOSiH₂OH	252, 277, 412, 672, 821, 886, 949, 953, 989, 1058, 1069, 2424, 2432, 4135, 4137
22 HSiOO cis	316, 383, 774, 915, 1199, 2238
23 HSiOO anti	307, 470, 774, 945, 1196, 2248
24 SiOOH	114, 320, 802, 1011, 1556, 4095
25 H₂SiOO	286, 374, 670, 731, 758, 926, 1862, 2271, 2325
26 HSiOOH	30, 333, 447, 802, 949, 1160, 1575, 2211, 4105
27 H₃SiOO	170, 286, 743, 762, 844, 1036, 1048, 1065, 1224, 2435, 2437, 2443
28 H₂SiOOH	212, 225, 292, 742, 826, 893, 1001, 1153, 1551, 2354, 2388, 4098
29 H₃SiOOH	213, 231, 291, 751, 772, 862, 1039, 1054, 1077, 1151, 1547, 2407, 2421, 2425, 4097

[a] In cm⁻¹ calculated at the HF/6-31G* level, except for H₂SiOO which was calculated at the MP2/6-31G* level; calculated frequencies are unscaled.

substituents on the same center. The hydroxysilylenes show a similar progression. The trend in the hydroxysilyl radicals would appear to be the opposite, but this is misleading because the changes are due to the stabilization of the product silylenes (see the discussion of the Si–H bond energies in substituted silylenes, above). The Si–O double bond dissociation energies in H₂Si=O and O=SiHOH are 145–150 kcal/mol. However, this is only

20% higher than the single bond in SiH₃OH; the triple bond in SiO is only 50% higher. The problem with Si–O multiple bonds is not that they are weak but that the single bonds are very strong.

The O–H bond dissociation energies of H₂O, SiH₃OH, SiH₂(OH)₂, and O=SiHOH are nearly constant, as are those of HOO–H and H₃SiOO–H. For the other SiH_mO_n species, there are large variations, primarily because of special stabilizing effects

TABLE IV: Heats of Formation at 298 K (in kcal/mol)

molecule	G-1	G-2	experimental[a]	previous estimates[b]
1 SiO	−24.0	−22.6	−24.2	
2 HSiO	8.1	8.5		
3 SiOH	−0.2	0.1		
4 H$_2$SiO	−23.2	−23.5		−27.5
6 HSiOH	−23.7	−23.7		
7 H$_3$SiO	1.2	1.0		−22.4
8 H$_2$SiOH	−24.9	−25.6		
9 H$_3$SiOH	−66.5	−67.5		
10 OSiO	−67.7	−66.2	−74.3	
11 OSiHO	−38.1	−37.7		−68.8
12 OSiOH	−73.6	−72.9		−86.8
14 OSiH$_2$O	−28.7	−28.1		−50.7
15 OSiHOH	−110.3	−110.6		−124.7
17 HOSiOH	−117.5	−117.5		
18 OSiH$_2$OH	−79.3	−79.8		
19 HOSiHOH	−103.3	−104.2		
21 HOSiH$_2$OH	−147.9	−149.0		
22 HSiOO	46.7	47.7		
24 SiOOH	23.0	23.7		
25 H$_2$SiOO	34.9	35.5		−16.5
26 HSiOOH	−0.3	0.2		
27 H$_3$SiOO	−2.7	−2.7		−26.4
28 H$_2$SiOOH	1.2	1.1		−24.4
29 H$_3$SiOOH	−41.0	−41.1		−62.1

[a] From the JANAF tables, ref 35. [b] Bond energy based estimates, ref 1a.

TABLE V: Bond Dissociation Enthalpies (in kcal/mol)

Si−H

H−SiH$_3$	91.8	H−SiHOH	54.0
H−SiH$_2$OH	94.0	H−SiHOOH	51.2
H−SiH$_2$OOH	94.6	H−Si(OH)$_2$	38.8
H−SiH(OH)$_2$	96.9	H−SiH	76.2
H−SiHO	84.1	H−SiOH	75.9
H−Si(O)OH	89.8	H−SiOOH	75.6
H−SiH$_2$	69.7		

O−H

H−OH	119.3	H−OSiHO	125.0
H−OSiH$_3$	120.6	H−OOH	99.2
H−OSiH$_2$OH	121.3	H−OOSiH$_3$	90.8

Si−O

SiH$_3$−OH	124.8	OHSi−OH	127.0
HOSiH$_2$−OH	132.8	SiH$_2$=O	148.6
SiH$_2$−OH	100.5	HOSiH=O	146.5
HOSiH−OH	89.9	Si=O	189.7
HSi−OH	122.7		

O−O

HO−OH	51.4	HO−O	65.5
SiH$_3$O−OH	41.4	SiH$_3$O−O	63.3

[a] Calculated from the G-2 values for the heats of formation in Table IV and ref 14.

in the products of O–H dissociation. Silyl substituents appear to have a destabilizing effect relative to hydrogen on the O–O bond in peroxide but not in peroxyl radical.

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