

Ab Initio Study of the Initial Reactions in Silane Combustion: $\text{SiH}_3 + \text{O}_2 \rightarrow \text{Products}$

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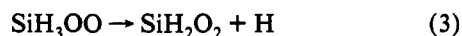
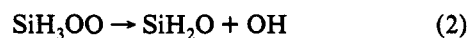
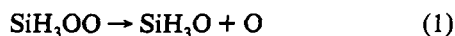
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To help understand the mechanism and kinetics of silane combustion, the initial steps of silane oxidation have been studied by ab initio molecular orbital theory. Geometries have been optimized at the MP2/6-31G(d) level of theory and vibrational frequencies have been computed at HF/6-31G(d); relative energies and barrier heights have been calculated at the G-2 level of theory. Silyl radical and O_2 react to form H_3SiOO , which undergoes a 1,3-hydrogen shift to form H_2SiOOH , via a transition state that is 17.5 kcal/mol below that of the reactants. A low barrier of ca. 4 kcal/mol separates H_2SiOOH from H_2SiO and OH. Hydroxyl radical can abstract a hydrogen from H_2SiO to form $\text{HSiO} + \text{H}_2\text{O}$ or it can add to H_2SiO to form $\text{H}_2\text{Si}(\text{O})\text{OH}$ —both processes appear to be barrierless. The latter intermediate can lose hydrogen to form $\text{HSi}(\text{O})\text{OH}$ or rearrange to form $\text{HSi}(\text{OH})_2$.

Introduction

The mechanism and kinetics of gas phase silane oxidation are relevant to silane combustion and explosions,^{1,2} chemical vapor deposition of silicon dioxide films,³ and the formation of silicon dioxide nanoparticles.⁴ Analogous to hydrocarbon oxidation, it is generally agreed that the first steps in silane combustion are the generation of SiH_3 radical followed by the reaction of SiH_3 with O_2 . Reaction rates for $\text{SiH}_3 + \text{O}_2$ have been measured by several groups^{5–8} and there is good agreement between the various methods that the rate is ca. $1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The first intermediate, SiH_3OO , has not been observed directly. It is formed with considerable excess energy (more than 50 kcal/mol) and three decay channels have been postulated:¹



The branching ratios for these pathways (ca. 0.1, 0.3, 0.6) have been deduced from monitoring the products SiH_3O (by mass spectroscopy),⁸ H, and OH (by LIF).⁹ A number of studies have modeled the kinetics of silane combustion and explosion.^{1,2,10–12} Even though these studies are largely based on approximate rate constants and estimated thermochemistry, they have been able to reproduce some of the unusual behavior of silane combustion.

Although no theoretical studies have considered the entire mechanism for silane combustion, a number of relevant reactions have been examined at various levels of ab initio molecular orbital theory. Barriers for silanone rearrangement and decomposition, $\text{H}_2 + \text{SiO} \rightleftharpoons \text{SiH}_2\text{O} \rightleftharpoons \text{HSiOH} \rightleftharpoons \text{Si} + \text{H}_2\text{O}$, have been calculated by a number of groups.^{13–17} Likewise, several studies are available for $\text{HSiO} \rightleftharpoons \text{SiOH}$ ^{18–20} and $\text{SiH}_2 + \text{H}_2\text{O} \rightarrow \text{SiH}_3\text{OH}$.^{17,21–23} Theoretical investigations of $\text{SiH}_2\text{O} + \text{H}_2\text{O}$,¹⁴ $\text{SiO} + \text{H}_2\text{O}$,²³ and $\text{SiH}_2 + \text{O}_2$ ^{23–25} have also been reported. Several of these species have been shown experimentally to be stable, observable intermediates.^{26–28} There are also a number of theoretical studies on dimer formation^{23,29–31} that go beyond the scope of this study.

In our earlier paper,³² we used the G-1 and G-2 methods^{33,34} to obtain a consistent and reliable set of theoretical heats of formation for SiH_nO and SiH_nO_2 . Lucas, Curtiss, and Pople³⁵ have also published a study at the G-2 level of theory in which

they compute the heats of formation, ionization energies, and proton affinities of SiH_nO . Previous studies³⁴ have demonstrated that energy differences computed by the G-2 method have a mean absolute error of less than 2 kcal/mol when compared to reliable experimental data. Calculations show that the previous estimates of the heats of formation of some silicon–oxygen compounds¹ are in error by as much as 20 kcal/mol. Such errors in the thermochemistry can have a profound effect on our understanding of the mechanism and kinetics of silane combustion. In the present paper, we use the G-2 level of theory to compute transition structures, relative energies, and barrier heights for the initial reactions in silane combustion.

Method

Molecular orbital calculations were carried out by using the GAUSSIAN 92 series of programs,³⁶ using a variety of basis sets of split valence quality or better with multiple polarization and diffuse functions.³⁷ 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) by using a quasi-newton optimization method.³⁸ Vibrational frequencies and zero-point energies were calculated at the HF/6-31G(d) level by using the HF optimized geometries and analytical second derivatives.³⁹ Correlated energies were calculated by fourth order Møller–Plesset perturbation theory⁴⁰ (MP4SDTQ, frozen core) and by quadratic configuration interaction with perturbative correction for triple excitations⁴¹ (QCISD(T), frozen core) with the MP2(full)/6-31G(d) optimized geometries. In the G-1 method,³³ the energy computed at MP4/6-311G(d,p) is corrected 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 correlation beyond fourth order obtained at QCISD(T)/6-311G(d,p). Higher level corrections for deficiencies in the wave function are estimated empirically³³ by comparing the calculated bond dissociation energy for H_2 with the exact value. The G-2 method^{34a} overcomes some limitations caused by additivity assumptions in the G-1 method by using an extra calculation at the MP2/6-311+G(3d,2p) level. The average absolute error of the remaining additivity assumptions in the G-2 level of theory is only 0.30 kcal/mol.^{34b} At the G-2 level of theory, the mean absolute error for 125 well-characterized atomization energies, ionization energies, electron affinities, and proton affinities is 1.3 kcal/mol.^{34a}

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TABLE 1: Total Energies, Zero-Point Energies, and Thermal Corrections for Transition Structures^a

	MP2/6-31G(d)	MP4/6-311G(2df,p)	QCISD(T)/6-311G(d,p)	G-1	G-2	ZPE ^c	thermal
TS-1 H ₃ SiOO → H ₂ SiOOH	-440.63152	-440.90334	-440.79269	-440.94840	-440.94738	16.03	2.53
TS-2 H ₂ SiOOH → SiH ₂ O + OH	-440.65654	-440.92732	-440.84176	-440.98738	-440.98799	18.33	2.92
TS-3 SiH ₂ O + OH → HSiO + H ₂ O	-440.71128	-440.97827	-440.87317	-441.02389	-441.02585	15.87	3.29
TS-4 HSiO + H ₂ O → SiOH + H ₂ O	-440.71409	-440.98429	-440.88152	-441.03822	-441.04017	16.56	3.58
TS-5 HSi(O)OH + H → H ₂ SiO(OH)	-440.78845	-441.05712	-440.94028	-441.10196	-441.10369	16.45	2.87
TS-6 H ₂ SiO(OH) → HOSiOH	-440.78837	-441.06077	-440.94347	-441.10323	-441.10389	18.30	2.53

^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; see Figure 1, 2, and 3 for geometries. ^c Zero-point energies computed at the HF/6-31G(d) level and scaled by 0.8929.

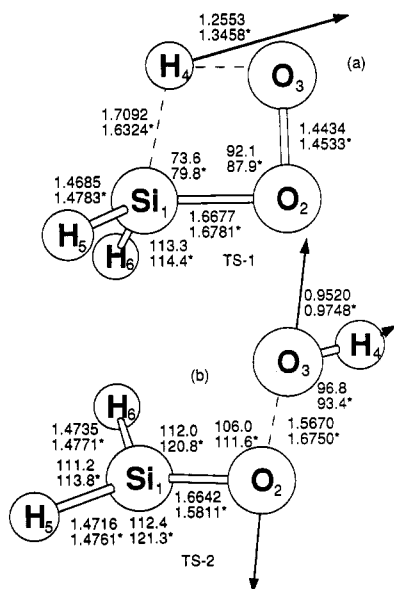


Figure 1. Transition states for (a) H₃SiOO → H₂SiOOH and (b) H₂SiOOH → H₂SiO + OH, optimized at HF/6-31G(d) (no superscript) and MP2(full)/6-31G(d) (asterisk) for (a) ∠O₂SiO₃H₄ = -6.1, -5.3*, ∠H₅Si₁O₂O₃ = 170.1, 171.8*, and ∠H₆Si₁O₂O₃ = -100.3, -100.8* and for (b) ∠Si₁O₂O₃H₄ = 133.2, 128.2*, ∠H₅Si₁O₂O₃ = 63.1, 81.5*, and ∠H₆Si₁O₂O₃ = -63.1, -74.7*.

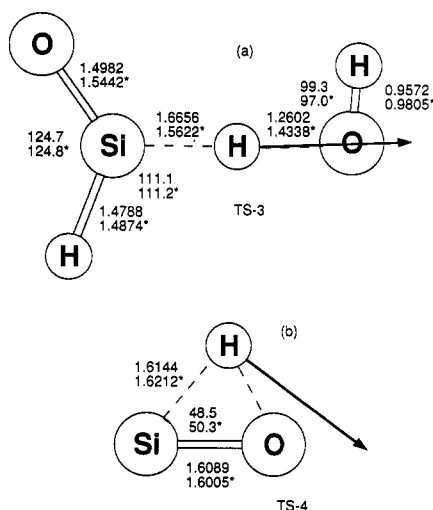


Figure 2. Transition states for (a) H₂SiO + OH → HSiO + H₂O and (b) HSiO ⇌ SiOH, optimized at HF/6-31G(d) (no superscript) and MP2(full)/6-31G(d) (asterisk).

Results and Discussion

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 I along with zero-point energies and thermal corrections. Optimized geometries for the transition states are collected in Figures 1–3; vibrational frequencies for the transition states are summarized in Table II. Total energies, geometries, and vibrational and vibrational frequencies for the reactants, inter-

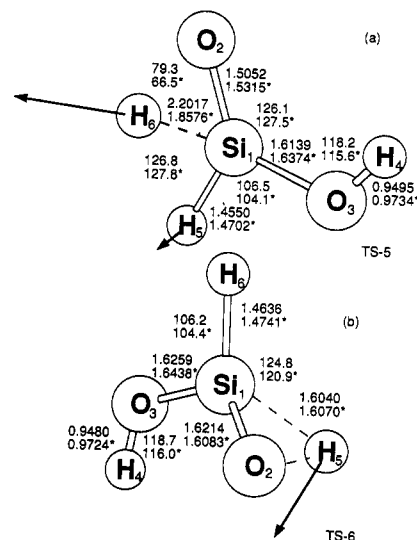


Figure 3. Transition states for (a) H₂Si(O)OH → HSi(O)OH + H and (b) H₂Si(O)OH → HSi(OH)₂, optimized at HF/6-31G(d) (no superscript) and MP2(full)/6-31G(d) (asterisk) for (a) ∠O₂SiO₃H₄ = -6.1, -5.3*, ∠H₅Si₁O₂O₃ = 170.1, 171.8*, and ∠H₆Si₁O₂O₃ = -100.3, -100.8* and for (b) ∠H₆Si₁O₃H₄ = 175.1, 176.1*, ∠H₆Si₁O₃O₂ = 138.4, 149.7*, and ∠H₆Si₁O₂H₅ = 112.1, 104.7*.

mediates, and products were reported previously.³² The G-1 and G-2 energies are used to compute the relative enthalpies listed in Table III; Figure 4 summarizes the mechanism and energetics for some of the initial reactions in silane combustion.

Silyl radical reacts with oxygen to form a stable complex H₃SiOO of C_s symmetry, 52.2 kcal/mol below reactants. A stability analysis shows that the lowest electronic state for H₃SiOO is ²A'. From this intermediate, one could break an SiH bond to form H₂SiOO + H (38.1 kcal/mol relative to SiH₃ + O₂), break the O–O bond to form H₃SiO + ³O (11.0 kcal/mol relative to SiH₃ + O₂), or eliminate H₂ to form HSiOO + H₂ (-2.9 kcal/mol relative to SiH₃ + O₂), but the transition state for this reaction probably lies considerably higher). The lowest energy unimolecular process for H₃SiOO involves a 1,3-hydrogen shift from silicon to oxygen, forming H₂SiOOH. The transition state TS-1 has C_s symmetry with an ²A' electronic state and is 17.5 kcal/mol below SiH₃ + O₂. The transition state resembles the product more than the reactant with significant shortening of the Si–O bond (1.678 Å compared to 1.742 Å in the reactant and 1.681 Å in the product) and elongation of the O–O bond (1.453 Å compared to 1.343 Å in the reactant and 1.487 Å in the product). The product of the 1,3-shift, H₂SiOOH, lies 48.5 kcal/mol below SiH₃ + O₂.

From H₂SiOOH, breaking the Si–O bond leads to SiH₂ + OOH (16.1 kcal/mol relative to SiH₃ + O₂) and breaking the Si–H bond leads to HSiOOH + H (2.8 kcal/mol relative to SiH₃ + O₂). The lowest barrier for unimolecular reactions of H₂SiOOH involves the elimination of OH via the transition state TS-2, shown in Figure 1, to form H₂SiO + OH. The transition state TS-2 is relatively late, with the Si–O bond close to a double bond (1.581 Å compared to 1.681 Å in the reactant and 1.545

TABLE 2: Calculated Vibrational Frequencies for Transition Structures^a

	frequencies, cm ⁻¹
TS-1 H ₃ SiOO → H ₂ SiOOH	2573 i, 181, 519, 717, 796, 820, 878, 930, 1046, 1825, 2415, 2432
TS-2 H ₂ SiOOH → SiH ₂ O + OH	849 i, 182, 240, 268, 750, 810, 883, 1038, 1315, 2383, 2404, 4084
TS-3 SiH ₂ O + OH → HSiO + H ₂ O	2689 i, 111, 155, 239, 407, 707, 779, 907, 1346, 1424, 2348, 4011
TS-4 HSiO → SiOH	2423 i, 975, 1915
TS-5 HSi(O)OH + H → H ₂ Si(O)OH	795 i, 252, 298, 369, 497, 688, 886, 972, 997, 1316, 2507, 4107
TS-6 H ₂ Si(O)OH → HOSiHOH	2346 i, 288, 412, 575, 743, 856, 890, 974, 1041, 1984, 2445, 4125

^a Calculated at the HF/6-31G(d) level; calculated frequencies are unscaled.

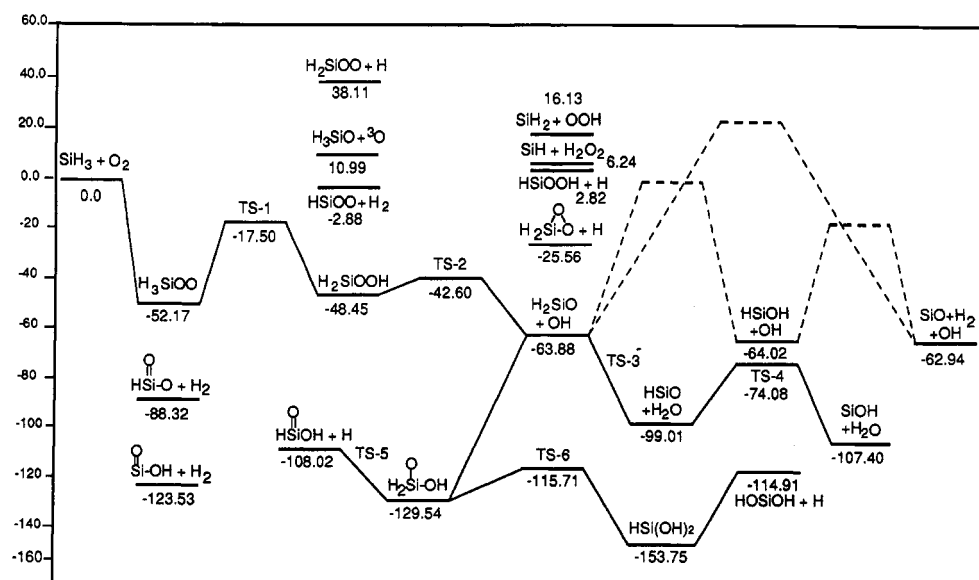
TABLE 3: Calculated Relative Enthalpies at 298 K (kcal/mol)

	G-1	G-2
Reactants, Intermediates, and Products		
SiH ₃ + O ₂	0.00	0.00
H ₃ SiOO	-52.94	-52.17
H ₂ SiOO + H	36.68	38.11
H ₃ SiO + ³ O	10.47	10.99
HSiOO + H ₂	-3.79	-2.88
H ₂ SiOOH	-49.11	-48.45
SiH ₂ + OOH	17.29	16.13
HSiOOH + H	1.51	2.82
H ₂ SiOO + H	-26.83	-25.56
H ₂ SiO + OH	-63.18	-63.88
HSiOH + OH	-63.65	-64.02
SiO + H ₂ + OH	-63.94	-62.94
HOSiHOH	-153.60	-153.75
H ₂ Si(O)O	-129.82	-129.54
SiOH + H ₂ O	-106.09	-107.40
HSiO(OH) + H	-108.46	-108.02
SiH + H ₂ O ₂	7.47	6.24
HSiO + H ₂ O	-97.80	-99.01
HSi(O)O + H ₂	-88.63	-88.32
O=SiOH + H ₂	-124.13	-123.53
HSiOH + OH	-63.65	-64.02
HOSiOH + H	-115.65	-114.91
Transition Structures		
TS-1 H ₃ SiOO → H ₂ SiOOH	-18.53	-17.50
TS-2 H ₂ SiOOH → H ₂ SiO + OH	-42.61	-42.60
TS-3 H ₂ SiO + OH → HSiO + H ₂ O	-65.14	-65.97
TS-4 HSiO + H ₂ O → SiOH + H ₂ O	-73.25	-74.08
TS-5 HSi(O)OH + H → H ₂ Si(O)OH	-114.56	-115.25
TS-6 H ₂ Si(O)OH → HOSiHOH	-115.69	-115.71

Å in the product) and the H₂Si group more than halfway to planarity ($\angle\text{H}_6\text{Si}_1\text{O}_2\text{H}_5 = 157.7^\circ$). The transition state is 42.6 kcal/mol below SiH₃ + O₂ and only 5.9 kcal/mol above H₂-SiOOH. This is probably the mechanism for the formation of OH measured by the experiments of Koshi.⁹

The unimolecular reactions of H₂SiO have relatively high barriers:¹³⁻¹⁷ ca. 60 kcal/mol for isomerization to HSiOH, ca. 90 kcal/mol for H₂SiO → H₂ + SiO, ca. 50 kcal/mol for HSiOH → H₂ + SiO, and ca. 100 kcal/mol for H₂SiO → H₂O + ¹Si. Because these processes are unlikely to contribute to silane combustion, the transition states have not been recalculated at the G-2 level. However, there are a number of bimolecular reactions of H₂SiO that are of interest. Hydrogen can be abstracted from H₂SiO by OH via the transition state TS-3, shown in Figure 2, to form the products HSiO + H₂O. The transition state is planar, has C_s symmetry with a ²A' electronic state, and has a Si-H bond that is only 5% elongated compared to H₂SiO. A barrier of 5.4 kcal/mol was calculated at MP2/6-31G(d), but when larger basis sets and higher levels of theory were used with the MP2/6-31G(d) geometry, the energy of the transition state was lower than that of the reactants. The calculated G-2 energy for TS-3 is 2.1 kcal/mol below that of the reactants, primarily because of contributions from the QCISD(T)/6-311G(d,p) level. Thus, there is little or no barrier for hydrogen abstraction from H₂SiO by OH. The products, HSiO + H₂O, are 99.0 kcal/mol below SiH₃ + O₂. The transition state for HSiO ⇒ SiOH isomerization, TS-4, is shown in Figure 2. This reaction has been studied previously by a number of groups;¹⁸⁻²⁰ the present calculations give a barrier of 24.9 kcal/mol at the G-2 level.

A second bimolecular reaction between H₂SiO and OH is addition of OH to the silicon end of the double bond. This proceeds without a barrier and yields H₂Si(O)OH, which is 129.5 kcal/mol below SiH₃ + O₂. In principle, H₂Si(O)OH can also be reached by a 1,2-hydroxyl shift in H₂SiOOH, but extensive searching at the HF/6-31G(d) and MP2/6-31G(d) levels did not reveal any unimolecular pathway from H₂SiOOH to H₂Si(O)OH. The transition state TS-5, shown in Figure 3, describes the elimination of H from H₂Si(O)OH to form HSi(O)OH + H. This reaction is endothermic by 21.5 kcal/mol. The transition

**Figure 4.** Theoretical estimates of the relative energies at the G-2 level for the SiH₃ + O₂ system.

state is relatively late with the Si₁-H₆ rather extended and the Si₁-O₂ bond displaying essentially double bond character (1.532 Å versus 1.536 Å in the product). The barrier for the reverse reaction, HSi(O)OH + H → H₂Si(O)OH, is 9.8 kcal/mol at the MP2/6-31G(d) level but disappears at the G-2 level of calculation.

Bimolecular reactions of H₂SiO with other species, such as O₂, H₂O, H, etc., are potentially important contributors to the overall mechanism of silane combustion. In particular, Kudo and Nagase¹⁴ have shown there is no barrier for the addition of H₂O to H₂SiO to form H₂Si(OH)₂. This probably accounts for the absence of H₂O as a product in combustion processes rich in silane.¹ However, these subsequent bimolecular reactions are outside the scope of the present study.

The addition of OH to H₂SiO to form H₂Si(O)OH followed by H elimination to give HSi(O)OH + H is probably the source of H atoms measured by Koshi in his study of branching ratios.⁹ This suggestion is supported by experimental work by Niki et al.,⁴² who found that the reaction of SiH₃ + O₂ yielded an aerosol product with IR bands that could be interpreted as [-HSi(OH)O-]_n, i.e., a polymeric form of HSi(O)OH. The only other thermodynamically feasible candidate for the source of H atoms is cyclic H₂SiO₂ + H (25.56 kcal/mol below SiH₃ + O₂). However, no transition structures could be found for the formation of cyclic H₂SiO₂ + H directly from H₃SiOO or H₂SiOOH.

A second, lower energy unimolecular path for H₂Si(O)OH involves a 1,2-hydrogen shift from silicon to oxygen. The transition state TS-6 has the Si₁-H₅ partially broken (1.607 Å versus 1.472 Å in the reactant) and the O₂-H₅ bond partially formed (1.391 Å versus 0.969 Å in the product). The barrier is 13.8 kcal/mol and the product HSi(OH)₂ is the lowest energy structure in this reaction scheme (153.8 kcal/mol below SiH₃ + O₂).

Summary

The calculated energetics for some of the initial reactions in silane combustion are summarized in Figure 4. The reaction of SiH₃ and O₂ produces H₃SiOO, which rearranges via a 1,3-hydrogen shift, whose transition state lies 17.5 kcal/mol below that of the reactants. The product of this rearrangement, H₂SiOOH, has a low barrier for a subsequent reaction to form H₂SiO and OH. At this point, a bimolecular reaction between H₂SiO and OH can proceed in either of two directions: abstraction of H to form HSiO + H₂O or addition to silicon to form H₂Si(O)OH. Further unimolecular rearrangements of these products is also possible. Subsequent bimolecular reactions between these intermediates and oxygen-containing species are needed to yield the final products of silane combustion, SiO₂ and H₂O.

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