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THERMOCHEMICAL DATA FOR CVD MODELING
FROM AB INITIO CALCULATIONS

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ABSTRACT

Ab initio electronic-structure calculations are combined with empirical bond-additivity corrections to yield thermochemical properties of gas-phase molecules. A self-consistent set of heats of formation for molecules in the Si-H, Si-H-Cl, Si-H-F, Si-N-H and Si-N-H-F systems is presented, along with preliminary values for some Si-O-C-H species.

INTRODUCTION

Developing a good model for a CVD process generally requires some description of the chemistry occurring in the process, either from an equilibrium or chemical kinetics point of view. Unfortunately, thermochemical data for many CVD systems of interest are often incomplete or inconsistent.

However, quantum chemistry has now reached the point where *ab initio* electronic-structure calculations yield usable thermochemical information for certain classes of compounds. For a number of years, we have been using the BAC-MP4 method, which combines calculations done at the MP4 level of theory (see next section) with empirical bond-additivity corrections (BACs), to obtain an extensive, self-consistent set of thermochemical data.

This method has been applied to over 2800 species, primarily molecules made up of first-row elements that are relevant to combustion,¹ but including a number of molecules relevant to the CVD of silicon-containing compounds. In this paper, we first review some of these earlier results before presenting some recent work on Si-O-C-H compounds. Detailed discussions of the Si-H, Si-H-Cl, Si-H-F, Si-N-H and Si-N-H-F systems are available elsewhere,²⁻⁵ as well as similar work on Si-C-H and Si-C-Cl-H that is not included in this paper.^{6,7}

THEORETICAL METHODS

The methods used in this work have been described in the literature,^{1,4,5} so only a short description is included here.

Electronic structure calculations were done using the Gaussian codes.⁸ Equilibrium geometries and harmonic vibrational frequencies were obtained at the HF/6-31G* level of theory (restricted Hartree-Fock theory,⁹ RHF, for closed shell molecules, and unrestricted Hartree-Fock theory,¹⁰ UHF, for open shell molecules, using the 6-31G* basis set^{11,12}). This level of theory provides sufficiently accurate equilibrium geometries, but does not provide total energies suitable for determining reaction energies involving the breaking of covalent bonds. Vibrational frequencies calculated at this level of theory are known¹³ to be systematically larger than experimental values, so each calculated frequency has been scaled by dividing it by 1.12 (determined by averaging the ratio of calculated to experimental vibrational frequencies over many known

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species). To determine atomization enthalpies, the effects of electron correlation were included in the calculation by performing single-point calculations at the HF/6-31G* geometries using Møller-Plesset (MP) perturbation theory¹⁴⁻¹⁶ with single, double, triple and quadruple substitutions and the 6-31G** basis set.^{11,12} This level of theory is generally a good compromise between the need for chemical accuracy in the calculated energies and limits on molecular size imposed by computational limitations. For most molecules, fourth-order perturbation calculations were done, but this was not possible for larger molecules like TEOS (tetraethoxysilane). In these cases, second-order perturbation calculations were done, which yields usable atomization enthalpies but with greater uncertainties than the MP4 calculations.

Empirical BACs are used to account for systematic errors in the *ab initio* calculations which result primarily from basis-set truncation. BACs are determined for each level of perturbation theory and depend mainly on the bond type and bond length, but there are small additional corrections for neighboring atoms. The BACs are obtained from reference compounds which have well-established experimental heats of formation or from analogous correction parameters for related classes of compounds. For Si-H, Si-Cl, Si-F and Si-C bonds, SiH₄, SiCl₄, SiF₄ and Si(CH₃)₃ were used as reference compounds, while Si₂H₆ was the reference compound for Si-Si bonds. For Si-N bonds, however, no good reference species was available, so we used parameters similar to those for Si-C bonds. For Si-O bonds, the BACs were based on a theoretical value obtained for H₃SiOH at a higher level of theory¹⁷ (vide infra). There are additional BAC terms for spin, both for open-shell molecules and for closed-shell molecules which are UHF unstable. These terms are discussed in detail elsewhere.^{1,4,5} The sum of the BAC terms are combined with the electronic energy from the perturbation theory calculation and the zero-point energy to obtain the heat of formation at 0K. Statistical-mechanics equations involving the calculated geometries and scaled frequencies are then used to determine entropies, heat capacities, enthalpies, and free energies at other temperatures.¹

The error estimates given in the tables are determined via a systematic, but ad hoc, procedure using the results from electronic structure calculations at lower levels of theory.^{1,4} These uncertainties only reflect the applicability of the calculational methods to the various species. As discussed in more detail elsewhere,^{3,4} the actual uncertainties may be somewhat larger for species for which we do not have good reference species, for example molecules with Si-N or Si-O bonds or with short Si-Si (multiple) bonds. In the case of the larger molecules that were only studied at the MP2 level of theory, we have not developed a method for systematically estimating errors, but consider the uncertainties in the heats of formation to be in the range of 5-7 kcal/mole.

RESULTS AND DISCUSSION

Tables I and II list our calculated heats of formation and entropies at 298K for molecules in the Si-H, Si-H-Cl, Si-H-F, Si-N-H and Si-N-H-F systems. Detailed information on energies, vibrational frequencies and geometries from the *ab initio* calculations, can be found in the full papers.²⁻⁵

There are some general trends observable in the heats of formation. For example, the heats of formation of the SiH_nCl_(4-n), SiH_nF_(4-n), and SiH_n(NH₂)_(4-n) (0 ≤ n ≤ 4) species show nearly linear dependences on n, indicating that the successive replacement of Si-H bonds with Si-Cl, Si-F or Si-NH₂ bonds is accompanied by monotonic changes in stabilization. This is also true for the replacement of Si-F bonds by Si-NH₂ bonds in the SiF_n(NH₂)_(4-n) species. In contrast, the heats of

formation for the SiH_n , SiCl_n , SiF_n , SiH_nNH_2 and SiF_nNH_2 compounds do not vary smoothly with n . In addition, the first and third successive Si-X ($X = \text{H}, \text{Cl}, \text{F}$) bond dissociation energies (BDEs) are significantly higher than the second and fourth successive BDEs. These observations are manifestations of the change in hybridization of the silicon from sp^3 to s^2p^2 at SiX_2 .

Our calculated heats of formation compare favorably with the literature, especially for the saturated species. For example, for the $\text{SiH}_n\text{Cl}_{(4-n)}$ and $\text{SiH}_n\text{F}_{(4-n)}$ species, our values agree quite well with those given in the JANAF tables¹⁸ and by Walsh.¹⁹ Our values for Si_3H_8 and Si_2F_6 also agree well with those given in the CATCH tables.²⁰ For the molecules with Si-N bonds, however, virtually no data are available in the literature for comparison with our heats of formation. For H_3SiNH_2 , Jolly and Bakke²¹ have estimated a heat of formation of $-12 \text{ kcal mol}^{-1}$, which agrees well with our calculated value of $-11.45 \text{ kcal mol}^{-1}$. The literature data for radical species are much sparser. The heat of formation of SiH_2 has been the subject of much recent study,²² and our current calculated value of $64.8 \text{ kcal mol}^{-1}$ is in good agreement with the value of 65.2 now recommended by Walsh.²³ For two isomers of Si_2H_4 , our calculated values for H_3SiSiH and $\text{H}_2\text{Si}=\text{SiH}_2$ are $74.9 \text{ kcal mol}^{-1}$ and $62.9 \text{ kcal mol}^{-1}$, respectively, which agree well with the experimental values of 74.6 ± 2.0 and $\leq 62.3 \text{ kcal mol}^{-1}$ obtained by Walsh.²³

In some cases, substantial differences exist in the literature and our results support one value over another. For example, our values of -76.0 and $-237.4 \text{ kcal mol}^{-1}$ for SiCl_3 and SiF_3 , respectively, support the values in the literature of -80 and $-239 \text{ kcal mol}^{-1}$ derived from bond dissociation energy measurements,¹⁹ rather than the values of -93.3 and $-259.4 \text{ kcal mol}^{-1}$ derived from effusion/mass-spectrometric studies.¹⁸ There are, of course, other cases in which disagreement between our values and literature values cannot be explained simply, some cases where disagreements may not be significant because the literature values are very uncertain, and many cases where no literature value exists.

We have also applied our calculational methods to a number of transition states that give insight into decomposition mechanisms. For example, several transition states relevant to disilane decomposition are included in Table I. Although disilane decomposes primarily to SiH_2 and SiH_4 , it can also form $\text{Si}_2\text{H}_4 + \text{H}_2$. Our results indicate that, although $\text{H}_2\text{Si}=\text{SiH}_2$ has a lower heat of formation than H_3SiSiH , disilane decomposition will initially produce H_3SiSiH because of the high transition state energy for the $\text{Si}_2\text{H}_6 \rightarrow \text{H}_2\text{Si}=\text{SiH}_2 + \text{H}_2$ reaction. H_3SiSiH then has a low barrier for isomerization to $\text{H}_2\text{Si}=\text{SiH}_2$. Transition states for the decomposition of silylamine are also included in Table II. In contrast with disilane decomposition, the silylamine decomposition pathway for H_2 elimination is significantly lower in energy than the pathway for silylene elimination.

Table III lists calculated thermochemical parameters for species in the Si-O-C-H system. For the smaller species, calculated heats of formation are given for both the BAC-MP4 and BAC-MP2 levels of theory. For the larger molecules, only results from BAC-MP2 calculations are listed. In general, the BAC-MP2 numbers appear to be within a few kcal/mole of the BAC-MP4 numbers, with no systematic variations. In several cases, Table III lists heats of formation that were estimated using bond additivity methods because the MP2 calculations have not finished yet. We expect that these estimated values will be within 2–3 kcal/mole of the BAC-MP2 values.

The heats of formation listed in this table are somewhat preliminary; the BAC for Si-O bonds may need refinement. The present correction for Si-O bonds was developed

during work on Si-O-H compounds and is based on a higher level (G2) calculation for H_3SiOH .¹⁷ There is, however, some literature data for Si-O-C-H species that may support the use of a different reference compound for the correction. Walsh²³ lists heats of formation of -119.5, -281.8 and -314.3 kcal/mole for $(\text{CH}_3)_3\text{SiOH}$, $\text{Si}(\text{OCH}_3)_4$, and $\text{Si}(\text{OC}_2\text{H}_5)_4$, respectively. These values are somewhat less negative than our values, and may warrant an adjustment after calculations are done for species such as TEOS and $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$.

The ΔH_f° s in Table III were used to analyze possible TEOS decomposition reactions, shown in Table IV. The first two reactions, involving simple breaking of Si-O and O-C bonds, are very endothermic (≥ 100 kcal/mole), and will not be significant under the conditions used for TEOS CVD. The next two reactions, involving the formation of $\text{O}=\text{Si}(\text{OC}_2\text{H}_5)_2$, are also quite endothermic (≥ 70 kcal/mole). These reactions are multicenter reactions, and are expected to have substantial kinetic barriers in addition to the endothermicities. These reactions will probably also not be significant under TEOS CVD conditions. The last two reactions, involving the formation of the $\text{HSi}(\text{OC}_2\text{H}_5)_3$ and $\text{HOSi}(\text{OC}_2\text{H}_5)_3$ species, have lower endothermicities of 46 and 11 kcal/mole, respectively. These are both 4-center reactions and are expected to have additional kinetic barriers, but the endothermicities indicate that the last reaction is the most reasonable pathway for TEOS decomposition. To investigate this further, transition states for the elimination of ethylene from $\text{CH}_3\text{CH}_2\text{OSi}(\text{OH})_3$ and $\text{CH}_3\text{CH}_2\text{OSiH}_3$ were studied and the results included in Table III. These calculations confirmed the presence of substantial kinetic barriers. For the $\text{CH}_3\text{CH}_2\text{OSi}(\text{OH})_3 \rightarrow \text{C}_2\text{H}_4 + \text{Si}(\text{OH})_4$ and $\text{CH}_3\text{CH}_2\text{OSiH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{SiH}_4$ reactions, the activation energies are 70 and 68 kcal/mole, respectively, while the endothermicities are 12 kcal/mole. These results are consistent with recent experiments by Lin and coworkers,²⁴ who report that $k = 5 \times 10^{13} \exp(-61500/\text{RT})$ for the gas phase decomposition of TEOS.

CONCLUSION

The combination of high level *ab initio* electronic-structure calculations and empirical bond-additivity corrections has proven useful in obtaining thermochemical properties of gas-phase molecules for modeling CVD processes. In some cases, the calculated values help choose between conflicting measurements in the literature; in other cases, the calculated values are the only ones available. In addition to providing information on reaction endo/exothermicities, these calculational methods can also provide energetic and geometric information on transition states. Thus, likely reaction pathways can be identified and evaluated.

The calculational methods described in this paper can generally be applied to compounds comprised of elements in the first three rows of the periodic table and are limited to molecules with a relatively small number of heavy atoms. This is primarily caused by computational requirements that scale with higher powers of the number of atoms. The results for the smaller molecules, can, however, be used to develop bond-additivity methods for reliably estimating the thermochemistry of larger gas-phase species and possibly surface species. These types of calculations are also limited by the need for a reference species for each bond type. For many CVD systems, particularly MOCVD systems, good experimental data are sparse enough that we have to resort to estimates based on analogous species, leading to larger uncertainties in the calculated values.

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Table I: Calculated Enthalpies (kcal mol⁻¹) and Entropies (cal mol⁻¹ K⁻¹) for Si-H, Si-H-Cl and Si-H-F Compounds

Species	ΔH_f° (298) ^a	S° (298)
SiH ₄ ^b	8.19±1.00	48.9
SiH ₃	47.43±1.01	51.8
SiH ₂	64.80±2.20	49.5
SiH	91.01±1.14	46.0
SiCl ₄ ^b	-158.39±1.00	79.7
SiCl ₃	-76.00±1.58	75.6
SiCl ₂	-36.15±3.73	67.5
SiCl ² Π	37.76±2.34	55.8
SiH ₃ Cl	-32.03±1.06	60.0
SiH ₂ Cl ₂	-74.42±1.09	68.8
SiHCl ₃	-117.14±1.05	75.4
SiH ₂ Cl	7.91±1.13	62.7
SiHCl ₂	-33.98±1.38	71.1
SiHCl	15.85±2.5	60.1
Si ₂ H ₆ ^b	19.11±1.00	65.9
Si ₂ H ₅	55.39±1.02	70.0
H ₃ SiSiH	74.91±2.73	68.0
H ₂ Si=SiH ₂ (¹ A _g)	62.90±2.30	65.6
HSiSiH ₂	102.05±2.48	66.3
Si(H ₂)Si	95.62±1.70	58.8
Si(H)Si	118.82±2.86	59.1
Si ₂ (³ Σ _g ⁻)	145.79±1.31	54.8
Si ₃ H ₈	28.36±1.03	83.9
TS1 ^c	87.94±2.25	64.6
TS2 ^c	104.77±2.71	69.0
TS3 ^c	70.91±2.19	69.1
TS4 ^c	66.48±1.58	68.3
SiF ₄ ^b	-385.99±1.00	68.2
SiF ₃	-237.42±1.87	67.8
SiF ₂	-149.86±4.00	61.4
SiF	-12.42±2.89	52.7
SiHF ₃	-288.63±1.34	66.6
SiH ₂ F ₂	-186.38±1.47	62.8
SiH ₃ F	-85.50±1.21	57.0
SiHF ₂	-139.57±1.89	65.1
SiH ₂ F	-42.16±1.37	59.7
SiHF	-35.70±2.85	57.1
Si ₂ F ₆	-569.62±3.47	97.2

^a See text for discussion of error estimates.

^b Reference compound

^c Transition states for the 1) H₃SiSiH → H₂Si=SiH₂ isomerization, 2) Si₂H₆ → H₂Si=SiH₂ + H₂ reaction, 3) Si₂H₆ → H₃Si=SiH + H₂ reaction, and 4) Si₂H₆ → SiH₂ + SiH₄ reaction.

Table II. Calculated Enthalpies (kcal mol⁻¹) and Entropies (cal mol⁻¹ K⁻¹) for Si-N-H and Si-N-H-F Compounds

Species	ΔH_f° (298) ^a	S° (298)
H ₃ SiNH ₂	-11.45±1.47	65.7
H ₃ SiNH	51.32±1.38	65.5
H ₂ SiNH ₂	28.03±1.26	65.8
H ₃ SiN	96.56±1.31	59.5
H ₂ SiNH	40.99±3.26	59.9
HSiNH ₂	26.33±1.62	59.8
H ₂ SiN ² A ₁	141.40±4.40	57.2
HSiNH	84.80±4.96	60.6
SiNH ₂	48.67±1.55	58.6
HSiN	92.98±24.3	54.8
SiNH	38.39±5.41	51.7
SiN ² Π	130.72±5.67	52.3
SiN ² Σ ⁺	115.55±8.85	52.0
H ₃ SiNHSiH ₃	-14.32±2.03	83.5
H ₃ SiNSiH ₃	48.90±2.49	83.7
H ₂ Si(NH ₂) ₂	-37.30±2.65	74.4
HSi(NH ₂) ₃	-64.86±3.80	82.8
HSi(NH ₂) ₂	5.62±2.23	75.3
Si(NH ₂) ₄	-92.88±5.15	90.0
Si(NH ₂) ₃	-18.77±3.21	84.3
TS5 ^b	62.67±3.45	62.8
TS6 ^b	51.72±1.18	64.3
F ₃ SiNH ₂	-317.89±2.93	80.0
F ₃ SiNH	-249.65±2.21	82.2
F ₂ SiNH ₂	-167.24±1.48	77.2
F ₃ SiN	-200.02±1.59	73.9
F ₂ SiNH	-146.94±1.38	70.9
FSiNH ₂	-80.01±1.92	65.8
F ₂ SiN	-63.11±3.47	70.5
FSiNH	-13.57±2.63	68.9
FSiN	54.37±8.57	63.7
F ₃ SiNHSiH ₃	-320.19±3.16	96.0
F ₃ SiNSiH ₃	-252.84±3.80	97.6
F ₂ Si(NH ₂) ₂	-247.30±4.52	82.8
FSi(NH ₂) ₃	-170.70±5.19	88.0
FSi(NH ₂) ₂	-95.47±2.54	79.7

^a See text for discussion of error estimates.

^b Transition states for the 5) H₃SiNH₂ → SiH₂+NH₃, and 6) H₃SiNH₂ → HSiNH₂+H₂ reactions.

Table III. Preliminary Values for ΔH_f° (298) at Two Levels of Theory (kcal mol⁻¹) and Entropies (cal mol⁻¹ K⁻¹) for Some Si-O-C-H Compounds

Species	ΔH_f° (298) ^a		S° (298)
	BAC-MP4	BAC-MP2	
Si(OCH ₃) ₄		-285.5	123.2
Si(OH)(OCH ₃) ₃		-294.8	113.2
Si(OCH ₃) ₂ (OH) ₂	-304.8±6.5	-302.5	103.9
SiOH(OCH ₃) ₂	-172.3±2.2	-172.7	98.3
O=Si(OCH ₃) ₂	-174.9±8.4	-174.0	92.3
CH ₃ OSi(OH) ₃	-316.0±6.0	-314.2	91.9
Si(OH) ₂ OCH ₃	-180.9±1.8	-181.9	88.2
O=SiOHOCH ₃	-184.1±8.0	-183.6	81.3
CH ₃ OSi(OH) ₂ O	-242.3±5.9	-239.1	92.8
CH ₂ OSi(OH) ₃	-270.1±6.7	-268.5	92.1
Si(OC ₂ H ₅) ₄		-320.0 ^c	
Si(OH)(OC ₂ H ₅) ₃		-321.0	137.1
Si(OH) ₂ (OC ₂ H ₅) ₂		-321.9	117.5
CH ₃ CH ₂ OSi(OH) ₃	-324.6±5.7	-322.8	99.0
CH ₃ CH ₂ OSiH ₃	-67.5±1.1	-67.8	79.9
HSi(OC ₂ H ₅) ₃		-235.0	132.4
(CH ₃) ₃ SiOH	-121.1±1.1	-121.2	90.9
TS7 ^b	-254.2±3.1	-252.8	101.5
TS8 ^b	1.0±7.1	1.4	84.5
Si(OC ₂ H ₅) ₃		-187.0 ^c	
OSi(OC ₂ H ₅) ₃		-248.8 ^c	
O=Si(OC ₂ H ₅) ₂		-189.1 ^c	
Si(OH) ₄	-325.2±5.6	-323.9	81.9
SiH(OH) ₃	-238.4±2.8	-238.7	76.4
SiH ₂ (OH) ₂	-152.0±1.2	-153.0	68.7
H ₃ SiOH	-67.5±1.0	-68.4	61.8
Si(OH) ₃	-189.9±1.6	-191.4	77.6
OSi(OH) ₃	-251.6±5.4	-248.9	82.0
O=Si(OH) ₂	-192.1±7.4	-192.0	70.0
SiO	-25.0±4.0	-23.3	50.5

^a See text for discussion of error estimates.

^b Transition states for the 7) CH₃CH₂OSi(OH)₃ → C₂H₄ + Si(OH)₄ and 8) CH₃CH₂OSiH₃ → C₂H₄ + SiH₄ reactions.

^c Estimated using bond additivity

Table IV. Thermochemistry for various TEOS decomposition pathways

Reaction		$\Delta H_{rxn}(298)$
$\text{Si}(\text{OC}_2\text{H}_5)_4$	$\longrightarrow \text{Si}(\text{OC}_2\text{H}_5)_3 + \text{OC}_2\text{H}_5$	132
	$\longrightarrow \text{OSi}(\text{OC}_2\text{H}_5)_3 + \text{C}_2\text{H}_5$	100
	$\longrightarrow \text{O}=\text{Si}(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{OH}$	86
	$\longrightarrow \text{O}=\text{Si}(\text{OC}_2\text{H}_5)_2 + \text{O}(\text{C}_2\text{H}_5)_2$	71
	$\longrightarrow \text{HSi}(\text{OC}_2\text{H}_5)_3 + \text{O}=\text{C}(\text{CH}_3)\text{H}$	46
	$\longrightarrow \text{HOSi}(\text{OC}_2\text{H}_5)_3 + \text{C}_2\text{H}_4$	11

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