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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JUNE 2002

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BAC-MP4 Predictions of Thermochemistry for Gas-Phase Compounds in the Si–H–O–Cl System

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Received: January 23, 2002; In Final Form: April 8, 2002

A self-consistent set of thermochemical parameters for 39 molecules in the Si–H–O–Cl system have been calculated using the BAC-MP4 method. The BAC-MP4 method combines ab initio electronic structure calculations with empirical corrections to obtain accurate heats of formation. Both stable and radical species are included in the study, as well as several complexes formed by reaction with gas-phase water. Although there are almost no experimental data available for comparison, trends within homologous series and calculated bond dissociation energies are consistent with previous BAC-MP4 predictions for silicon compounds. Polynomial fits of the predicted thermodynamic data over the 300–3000 K temperature range are included in the Supporting Information. The thermodynamic data are used to evaluate the energetics of reactions that may be involved in the oxidation and hydrolysis of silicon tetrachloride, in particular the reactions of SiCl_3 and SiCl_2 with O_2 and H_2O .

I. Introduction

The oxidation of chlorinated silicon compounds, in particular silicon tetrachloride (SiCl_4), is of considerable industrial importance. Applications include the manufacture of silicon dioxide aerosols for a wide range of applications and the production of high-purity silica for telecommunications-grade optical fiber. Gas-phase chemical reactions are a key feature of silica manufacturing processes, which typically involve either flow reactors operating at high temperatures or methane/oxygen flames. Consequently, efforts to develop models capable of predicting silica formation rates must include chemical reactions at an elementary level. The high temperatures used indicate that a large number of silicon-containing species may be involved,¹ including silicon oxyhalides and compounds containing multiple silicon atoms.^{1–3} In contrast with silane oxidation/combustion, which has been extensively studied, very little is known about the thermochemistry and kinetics of species involved in SiCl_4 oxidation. Thermodynamic data (heats of formation, entropies, and heat capacities) for silicon oxyhalides are almost totally unavailable; in the Si–O–Cl system of monomeric silicon compounds, only two oxychloride species have been characterized: $\text{ClSiO}^{4,5}$ and $\text{Cl}_2\text{Si=O}$.^{4–6} Reaction rates relevant to SiCl_4 oxidation in the literature largely concern either qualitative observations or global reaction rates.^{3,7–10} Several investigations of the pyrolysis of chlorinated silanes have recently appeared,^{11–15} however, and reaction rates of SiCl_2 ¹⁶ and SiCl_3 ¹⁷ with molecular oxygen have been reported. The overall lack of information represents a major barrier to the construction of mechanisms composed of elementary chemical reactions.

Theoretical methods are now fully capable of providing molecular thermochemistry with sufficient accuracy for model-

ing purposes (± 2 kcal mol^{−1}). The literature contains several reports describing ab initio quantum-chemistry predictions of chlorinated silane thermochemistry;^{18–23} only a few applications to silicon oxychlorides are reported, however.^{4,5,24} In this paper we present the results of applying the bond additivity correction method at the level of fourth-order Møller–Plesset perturbation theory (BAC-MP4) to the prediction of thermochemical data for Si–H–O–Cl compounds. Prior to this investigation, we employed this method to predict thermochemistry for compounds in the related Si–H–Cl,^{18,19} Si–O–H,²⁵ and Si–C–O–H²⁶ systems. This earlier work established the bond additivity corrections needed to eliminate systematic errors in MP4 electronic energies caused by the use of finite basis sets and limited electron correlation. The current investigation focuses on the thermochemistry of monomeric silicon compounds containing bonds to H, O, and Cl. In addition to reporting the heats of formation for 39 molecules, we discuss bond energies for many of the compounds examined and trends exhibited by the various homologous series within the set. Comparisons with the predictions of the G2 method are also made for some selected cases; we find that G2 yields inconsistent results and cannot be considered reliable for compounds in this system. Finally, we use the thermochemistry obtained here to gain insight into some of the reactions involved in the oxidation of SiCl_4 in flames.

II. Theoretical Methods

The theoretical methods used here are described in detail in earlier works,^{19,27} so we present only a short description here. Electronic structure calculations were performed using Gaussian 94²⁸ and Gaussian 98.²⁹ Equilibrium geometries and harmonic vibrational frequencies were obtained at the HF/6-31G(d) level of theory. Restricted Hartree–Fock (RHF) theory was applied for the closed-shell molecules, and unrestricted Hartree–Fock

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TABLE 1: BAC Parameters for the BAC-MP4 (SDTQ) Level of Theory

bond	$A_{ij}(\text{MP4})^a$	$\alpha_{ij}(\text{MP4})^b$	bond	$A_{ij}(\text{MP4})^a$	$\alpha_{ij}(\text{MP4})^b$
Si–H	92.79	2.0	O–H	72.45	2.0
Si–O	7038.5	3.978	O–O	169.78	2.0
Si–Cl	721.930	2.0	Cl–O	355.14	2.0
atom	$B_k(\text{MP4})$		atom	$B_k(\text{MP4})$	
Si	0.2		O	0.225	
H	0.0		Cl	0.42	

^a In kcal mol^{−1}. ^b In Å^{−1}.

(UHF) theory was applied for the open-shell molecules, using the 6-31G(d) basis set. Vibrational frequencies calculated at this level of theory are known to be systematically larger than experimental values; thus, each calculated frequency was scaled by dividing it by 1.12.³⁰

To determine atomization enthalpies and thus heats of formation, the effects of electron correlation are included by performing single-point calculations, using Moller–Plesset perturbation theory and the HF/6-31G(d) geometries. MP4(SDTQ)/6-31G(d,p) calculations (fourth-order perturbation theory using the 6-31G(d,p) 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 our previous work, and we find that the errors remaining in the total energies are sufficiently systematic that empirical bond additivity corrections can provide enthalpies accurate to a few kilocalories per mole. The form of the BAC parameters α_{ij} , A_{ij} , and B_k used to calculate the corrections for individual molecules is given in eqs 1–4,

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

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

$$g_{kij} = (1 - h_{ik}h_{ji}) \quad (3)$$

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

using the example of a bond between atoms X_i and X_j in a molecule of the form $X_k-X_i-X_j$. 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 (Å). The factor B_k in eq 4 is used to derive a correction for the effects of neighboring atoms on the X_i-X_j bond (eq 3) and depends on the identity of atom k . Corrections for UHF instability and nonzero spin contamination are also applied; the form of these is also described elsewhere.¹⁹

Table 1 lists the parameters A_{ij} , α_{ij} , and B_k used in this work for each bond type, all of which were determined previously. Since there are no heats of formation for Si–O compounds that are sufficiently well established to determine the BAC for Si–O bonds, values of the Si–O BAC parameters²⁵ are based on heats of formation predicted by G2 calculations³¹ for two compounds, $\text{H}_2\text{Si}(\text{OH})_2$ and $\text{H}_2\text{Si}=\text{O}$. These species were chosen because their bonding is expected to be more representative of single and multiple bonds to oxygen in Si–O compounds than SiO and SiO₂, for which experimental heats of formation exist. BAC parameters for Si–Cl,¹⁸ Si–H,¹⁸ O–H,²⁷ and O–O²⁷ bonds are based on well-established heats of formation obtained from critical evaluations in the literature.

Table 2 lists calculated bond lengths for each species as well as the MP4(SDTQ) BACs corresponding to each bond in the molecule and any spin or UHF-instability corrections. The sum of the BACs is combined with the MP4(SDTQ) electronic energy and the unscaled zero-point energy to obtain the heats

of atomization and formation at 0 K ($\sum D_0(0 \text{ K})$ and $\Delta H_f^\circ(0 \text{ K})$, respectively). Values of the atomic heats of formation at 0 K used in this calculation are given in Table 3 and were obtained from the *JANAF Thermochemical Tables*.³² 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, calculated geometries, and scaled frequencies. For consistency with earlier papers in this series,^{18,19,25–27,33–39} the unscaled frequencies are used for determining $\Delta H_f^\circ(0 \text{ K})$, while the scaled frequencies are used to calculate thermochemistry at higher temperatures. Minor differences that would result from using the scaled frequencies to calculate $\Delta H_f^\circ(0 \text{ K})$ are incorporated into the BACs. Contributions to the heat capacity and entropy from rotating groups are accounted for by substituting a hindered rotor for the corresponding vibrational frequency determined by the HF calculation.²⁷

There are two major sources of uncertainty in the calculated heats of formation: (1) uncertainties resulting from the applicability of the theoretical methods to a given molecule and (2) 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 calculations¹⁹ and is reported in Table 3:

$$\text{error}(\text{BAC-MP4}) = \{1.0 \text{ kcal mol}^{-1} + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP3}})^2 + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP4SDQ}})^2 + 0.25(E_{\text{BAC}}(\text{spin}_s^2) \text{ or } E_{\text{BAC}}(\text{spin}_{\text{UHF-I}}))^2\}^{1/2} \quad (5)$$

The second source of uncertainty can add a few kilocalories per mole to the uncertainty estimates 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 ± 2 – 7 kcal mol^{-1} range, as seen in Table 3.

Bond energies at 298 K for most compounds were calculated using the BAC-MP4 results. Where polyatomic ligands are involved that are not part of this study, BAC-MP4 heats of formation were taken from previous publications.^{19,25,27} In the case of atoms, the experimental atomic heats of formation (Table 3) were used.³²

III. Results and Discussion

A. Heats of Formation and Bond Energies. The results of applying the BAC-MP4 method to species in the Si–H–O–Cl system are given in Tables 2–5. The focus of this work, as in previous papers in this series, is on thermochemical parameters, rather than on the details of the ab initio calculations themselves. Thus, detailed information obtained from the calculations, including Hartree–Fock geometries (Table S7), total electronic energies at various levels of theory (Table S8), vibrational frequencies (Table S9), moments of inertia (Table S10), and polynomial fits in the Chemkin format⁴⁰ (Table S11), is reserved for the Supporting Information.

Heats of formation at 0 K ($\Delta H_f^\circ(0 \text{ K})$) at various levels of theory for the compounds included in this study are shown in Table 3 and are given to provide a measure of the accuracy of the calculations. For many species, the heats of formation predicted at the lower levels of theory are nearly the same as at

TABLE 2: Bond Additivity Corrections for the MP4(SDTQ) Level of Theory (kcal mol⁻¹)

species	spin or UHF- unstable correction ^a	Si-H bond length ^b (no.) ^c	BAC	Si-O bond length (no.)	BAC	Si-Cl bond length (no.)	BAC	O-H bond length (no.)	BAC	O-O bond length (no.)	BAC	Cl-O bond length (no.)	BAC
Cl ₃ SiOH				1.613	11.12	2.023	12.13	0.949	10.87				
						2.038 (2)	11.79						
Cl ₂ Si(OH) ₂				1.619 (2)	10.89	2.036 (2)	11.87	0.948 (2)	10.87				
SiCl(OH) ₃				1.619	10.93	2.050	11.58	0.948	10.88				
				1.620	10.89			0.947	10.89				
				1.625	10.66			0.947	10.90				
HSiCl ₂ (OH)		1.451	5.09	1.618	11.03	2.050 (2)	11.69	0.948	10.88				
H ₂ SiCl(OH)		1.460	5.01	1.631	10.62								
		1.466	4.94			2.067	11.44	0.947	10.90				
H ₂ SiCl(O)	0.62 (s)	1.462	4.99	1.669	9.12	2.053	11.79						
		1.462	4.99										
SiCl ₃ O	0.59 (s)			1.661	9.23	2.026	12.08						
						2.022 (2)	12.16						
SiCl(OH) ₂	0.18 (s)			1.625	10.75	2.080	11.05	0.950	10.84				
				1.635	10.34			0.947	10.89				
Cl(OH)Si=O (OSiOH cis)				1.490	18.11	2.006	12.64	0.951	10.82				
				1.604	11.61								
Cl(OH)Si=O (OSiOH trans)				1.487	18.35	2.024	12.21	0.948	10.88				
				1.600	11.79								
SiCl(O)(OH) ₂				1.610	11.29	2.041	11.81						
				1.619	10.93			0.948	10.88				
				1.662	9.24			0.947	10.89				
SiCl ₂ (OH)O	0.58 (s)			1.611	11.23	2.021	12.22	0.949	10.86				
				1.664	9.13	2.032	11.97						
SiCl ₂ OH (C _s)	0.17 (s)			1.622	10.85	2.061 (2)	11.44	0.950	10.85				
SiCl(O) ₂ (C _{2v})	0.69 (s)			1.486	18.45	2.001	12.78						
				1.641	10.04								
SiHCl(OH)	0.18 (s)	1.468	4.92	1.636	10.40	2.076	11.24	0.947	10.89				
Cl ₂ Si=O				1.487	18.21	2.008 (2)	12.56						
HClSi=O		1.457	5.03	1.491	18.37	2.021	12.44						
SiClOH (trans ¹ A')				1.637	10.36	2.090	10.94	0.949	10.85				
SiClOH (trans triplet)	0.20 (s)			1.645	10.04	2.069	11.40	0.948	10.87				
SiClOH (cis ¹ A')				1.629	10.69	2.124	10.23	0.950	10.84				
ClSiO	0.73 (s)			1.497	17.94	2.049	11.79						
Cl ₃ SiO ₂ H				1.647	9.60	2.024	12.12	0.951	10.81	1.407	10.02		
						2.031	11.94						
						2.024	12.12						
Cl ₂ HSiO ₂ H		1.452	5.09	1.656	9.37	2.034	12.07	0.951	10.81	1.409	9.97		
						2.043	11.85						
ClH ₂ SiO ₂ H		1.463	4.98	1.670	8.96	2.051	11.85	0.950	10.83	1.413	9.92		
		1.460	5.00										
Cl ₃ SiOO	0.83 (s)			1.673	8.67	2.018	12.27			1.331	11.64		
						2.022 (2)	12.18						
Cl ₂ SiOOCl	0.21 (s)			1.680	8.53	2.039	11.96			1.395	9.71	1.669	11.90
						2.044	11.84						
Cl ₂ SiO ₂ (triplet)	0.83 (s)			1.682	8.44	2.041	11.92			1.334	11.58		
						2.041	11.92						
ClSiOOCl				1.692	8.23	2.078	11.22			1.395	9.71	1.669	11.92
HClSiO ₂ H (ClSiOO trans)	0.19 (s)	1.471	4.90	1.675	8.77	2.058	11.68	0.950	10.84	1.411	9.96		
HClSiO ₂ H (ClSiOO cis)	0.17 (s)	1.469	4.91	1.666	9.08	2.060	11.61	0.950	10.84	1.406	10.04		
HClSiO ₂ (triplet)	0.82 (s)	1.467	4.94	1.692	8.21	2.052	11.82			1.333	11.62		
Cl ₂ SiO ₂ H	0.21 (s)			1.662	9.15	2.046	11.79	0.950	10.83	1.409	9.99		
						2.048	11.74						
ClSiO ₂ H (ClSiOO trans, SiOOH trans)				1.670	8.94	2.090	10.94	0.950	10.84	1.407	10.02		
ClSiO ₂ (² A')	0.85 (s)			1.667	9.05	2.089	10.99			1.338	11.48		
-OSi(Cl)O- (cyclic)	0.33 (s)			1.627 (2)	10.51	2.032	12.13			1.527	7.78		
-O(SiCl ₂)O- (cyclic)	1.03 (u)			1.613	10.96	2.002	12.65			1.541	7.56		
				1.613	10.95	2.002	12.65						
Cl ₃ Si-OH ₂ (weak complex)	0.2 (s)					2.046	11.74	0.947 (2)	10.89				
						2.048 (2)	11.69						
Cl ₃ Si-OH ₂	0.2 (s)					2.062	0.975	0.949 (2)	10.87				
						2.058 (2)	0.975						
Cl ₂ Si-OH ₂				2.174	1.23	2.139 (2)	9.91	0.954 (2)	10.75				

^a u, UHF-unstable correction; s, spin-contamination correction. ^b In angstroms. ^c Number of bonds.

the highest level, BAC-MP4(SDTQ), resulting in ad hoc uncertainties for ΔH_f° (298 K) that are ± 2 kcal mol⁻¹ or less (evaluated using eq 5). Larger uncertainties, up to ± 5.6 kcal

mol⁻¹, are associated with sub-tetravalent species (radicals) containing O-O bonds (which is also true of similar compounds in the Si-O-H system²⁵). Heats of formation for cyclic

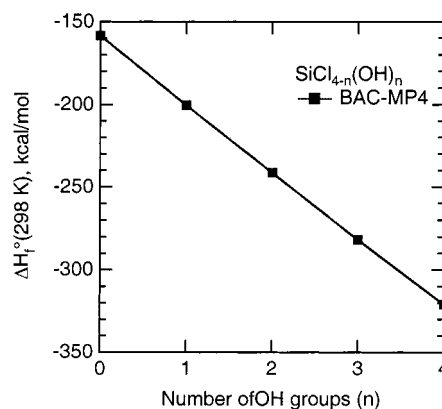
TABLE 3: Calculated Heats of Formation for Si–H–O–Cl Compounds at Various Levels of Theory (0 K) and at 298 K (with Estimated Error), kcal mol^{−1}

species	0 K				BAC-MP4	
	MP4	BAC-MP2	BAC-MP3	BACSDQ	SDTQ (0 K)	SDTQ (298 K)
SiCl ₃ OH	−141.3	−198.8	−200.0	−199.5	−199.0	−200.3 ± 1.5
SiCl ₂ (OH) ₂	−171.8	−238.9	−240.8	−240.0	−239.1	−241.2 ± 2.2
SiCl(OH) ₃	−202.0	−278.5	−281.4	−280.1	−278.8	−281.7 ± 3.1
HSiCl ₂ (OH)	−105.7	−156.2	−156.5	−156.1	−156.0	−158.0 ± 1.1
H ₂ SiCl(OH)	−66.9	−110.3	−109.8	−109.7	−109.8	−112.3 ± 1.0
H ₂ SiCl(O)	−6.8	−37.5	−37.8	−37.9	−38.3	−40.1 ± 1.2
SiCl ₃ O	−78.0	−122.7	−124.4	−124.3	−124.2	−125.2 ± 1.0
SiCl(OH) ₂	−94.7	−150.1	−148.8	−148.6	−148.7	−150.5 ± 1.0
Cl(OH)Si=O (OSiOH cis)	−98.6	−150.8	−155.3	−153.5	−151.8	−153.2 ± 4.1
Cl(OH)Si=O (OSiOH trans)	−96.3	−148.3	−153.2	−151.3	−149.5	−150.8 ± 4.3
SiCl(O)(OH) ₂	−139.8	−203.8	−207.7	−206.6	−205.4	−207.6 ± 2.7
SiCl ₂ (OH)O	−109.3	−163.7	−166.6	−166.0	−165.3	−166.7 ± 1.7
SiCl ₂ OH (C _s)	−67.5	−113.2	−112.0	−111.8	−112.2	−113.2 ± 1.1
SiCl(O) ₂ (C _{2v})	−35.9	−75.1	−80.1	−78.9	−77.9	−78.4 ± 2.6
SiHCl(OH)	−30.9	−69.7	−67.9	−68.0	−68.5	−70.1 ± 1.3
Cl ₂ Si=O	−67.4	−109.6	−112.3	−111.5	−110.8	−111.2 ± 1.9
HClSi=O	−33.3	−68.5	−69.8	−69.3	−69.1	−70.1 ± 1.2
SiClOH (trans ¹ A')	−42.7	−73.3	−72.2	−73.2	−74.8	−75.7 ± 3.2
SiClOH (trans triplet)	−15.5	−19.1	−16.1	−16.3	−17.0	−17.8 ± 1.6
SiClOH (cis ¹ A')	−44.8	−75.1	−74.0	−74.8	−76.5	−77.4 ± 3.2
ClSiO	−8.0	−37.8	−35.9	−37.0	−38.5	−38.5 ± 3.1
Cl ₃ SiO ₂ H	−101.8	−168.9	−167.4	−167.6	−168.4	−169.9 ± 1.6
Cl ₂ HSiO ₂ H	−66.5	−126.5	−124.1	−124.4	−125.6	−127.8 ± 2.2
ClH ₂ SiO ₂ H	−28.3	−81.2	−78.0	−78.5	−79.8	−82.6 ± 2.5
Cl ₃ SiOO	−67.2	−124.7	−122.5	−124.1	−125.0	−125.7 ± 2.9
Cl ₂ SiOOCl	6.3	−49.5	−44.3	−45.7	−47.9	−48.6 ± 4.3
Cl ₂ SiO ₂ (triplet)	4.8	−40.4	−36.2	−38.1	−39.9	−40.4 ± 4.2
ClSiOOCl	28.4	−12.0	−6.9	−9.3	−12.7	−13.2 ± 6.8
HClSiO ₂ H (ClSiOO trans)	8.3	−40.1	−35.7	−36.4	−38.1	−39.9 ± 3.1
HClSiO ₂ H (ClSiOO cis)	7.8	−40.6	−36.6	−37.2	−38.8	−40.6 ± 2.9
HClSiO ₂ (triplet)	40.2	1.8	6.5	4.5	2.8	1.7 ± 4.2
Cl ₂ SiO ₂ H	−28.9	−84.1	−80.1	−80.8	−82.6	−83.7 ± 3.2
ClSiO ₂ H (ClSiOO trans, SiOOH trans)	−6.4	−46.3	−42.5	−44.2	−47.2	−48.1 ± 5.6
ClSiO ₂ (² A')	34.1	3.9	6.9	4.4	1.7	1.4 ± 5.9
−OSi(Cl)O− (cyclic)	13.3	−28.2	−22.3	−24.9	−28.0	−28.6 ± 6.5
−O(SiCl ₂)O− (cyclic)	−57.4	−111.7	−110.1	−111.6	−113.2	−114.1 ± 3.7
Cl ₂ SiCl−OH ₂ (weak complex)	−76.5	−134.1	−132.6	−132.7	−133.6	−134.0 ± 1.7
Cl ₃ Si−OH ₂	−80.5	−137.7	−135.3	−135.5	−136.8	−137.6 ± 2.3
Cl ₂ Si−OH ₂	−60.6	−102.3	−98.5	−99.7	−103.1	−104.5 ± 5.8
H ^a					51.6	52.1 ± 1.0
O (³ P) ^a					59.0	59.4 ± 1.0
Si (³ P) ^a					106.7	107.4 ± 1.0
Cl ^a					28.6	29.0 ± 1.0

^a Reference 32.

compounds also have high degrees of uncertainty, as do compounds with a high degree of unsaturation, such as ClSiO. In both cases, the greater uncertainty arises from oscillation in the electronic energy predicted at different levels of theory, rather than corrections associated with either spin contamination or UHF instability (eq 5). The importance of the BAC corrections to the prediction of accurate heats of formation should also be noted; uncorrected heats of formation at the MP4 level are considerably more positive than those obtained after the corrections are applied.

Heats of formation for several homologous series are contained in Table 3 and are plotted in Figures 1–3. Linear variations in the heat of formation are observed for all three series. For SiCl_{4−n}(OH)_n (Figure 1), the heats of formation obtained from a linear least-squares fit deviate from the BAC-MP4 values by less 1.0 kcal mol^{−1} for each compound. The slope is −40.6 kcal mol^{−1}, indicating that compounds are stabilized by the substitution of OH for Cl. Similar linear behavior is observed for Cl_nH_{n−3}SiOOH (Figure 2), in which chlorine substitution for hydrogen decreases $\Delta H_f^\circ(298\text{ K})$ by 43.9 kcal mol^{−1} per substitution. Such trends are not limited to tetravalent species, but can also be observed for trivalent radicals

**Figure 1.** Heat of formation (298 K) for compounds in the series SiCl_{4−n}(OH)_n, n = 0–4.

in the series SiCl_{3−n}(OH)_n (Figure 3). Here, the $\Delta H_f^\circ(298\text{ K})$ decreases by 36.7 kcal mol^{−1} per Cl substitution. These trends are consistent with ones observed for compounds of silicon with other ligands, which show that increasing ligand electronegativity imparts greater molecular stability.

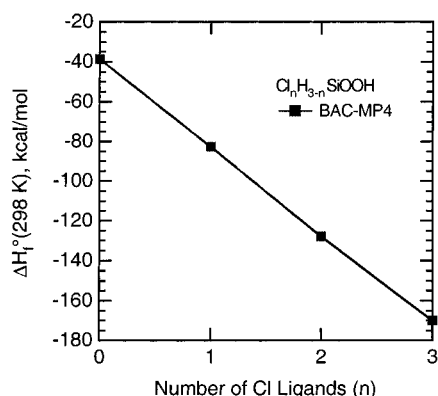


Figure 2. Heat of formation (298 K) for compounds in the series $\text{Cl}_n\text{H}_{3-n}\text{SiOOH}$, $n = 0-3$.

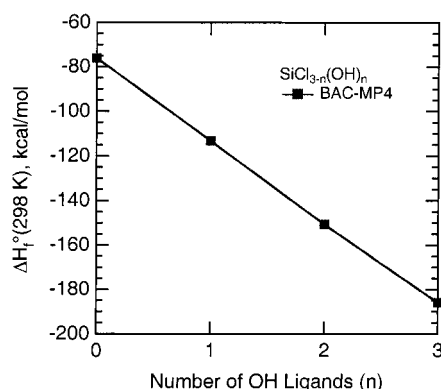


Figure 3. Heat of formation (298 K) for compounds in the series $\text{SiCl}_{3-n}(\text{OH})_n$, $n = 0-3$.

The near-perfect linearity of the $\text{SiCl}_{4-n}(\text{OH})_n$ series suggests that the bonding in these compounds is essentially local (i.e., the strength of a given bond is not affected by the identity of neighboring ligands), behavior that is observed for a number of other ligand combinations in silicon compounds, such as H and Cl, H and F, and H and CH_3 . However, comparison with the analogous $\text{Si}(\text{OH})_n\text{H}_{4-n}$ series,²⁵ for which the heats of formation do not change linearly with n , suggests that, at least for compounds with OH ligands, trends in heats of formation reflect a balance of interacting forces among the ligands. For example, the $\Delta H_f^\circ(298 \text{ K})$ values predicted by BAC-MP4 for SiH_4 and H_3SiOH differ by 74 kcal mol⁻¹, while those for $\text{HSi}(\text{OH})_3$ and $\text{Si}(\text{OH})_4$ differ by 86 kcal mol⁻¹.²⁵ Changes in Si–OH bond lengths in the $\text{Si}(\text{OH})_n\text{H}_{4-n}$ compounds also provide evidence of nonlocal bonding. The Si–OH bond length decreases from 1.647 Å in H_3SiOH to 1.629 Å in $\text{Si}(\text{OH})_4$, while in the $\text{SiCl}_{4-n}(\text{OH})_n$ series it actually increases with increasing n (to 1.613 Å in Cl_3SiOH , Table 2), even though the heat of formation decreases with n . Thus, the bonding picture in these molecules is not as simple as one might initially conclude and likely results from a combination of factors, including ligand electronegativity, ability to form π back-bonds, and possibly ligand size.

Bond dissociation energies (BDEs) in these molecules (Table 5) do not vary significantly from values in other silicon compounds containing H, Cl, and OH ligands. In tetravalent compounds, the Si–OH bonds range from 133.8 kcal mol⁻¹ in Cl_3SiOH to 144.5 kcal mol⁻¹ in $\text{Si}(\text{OH})_4$. The effect of substituting chlorine for hydrogen is to increase the Si–OH bond energy; for example, the Si–OH bond is worth only 122.8 kcal mol⁻¹ in H_3SiOH .²⁵ In contrast, Si–OH bond energies decrease

in trivalent compounds $\text{SiCl}_{3-n}(\text{OH})_n$ as n increases, dropping from 86.5 kcal mol⁻¹ in SiCl_2OH to 80.0 kcal mol⁻¹ in $\text{Si}(\text{OH})_3$. The divalent molecule SiClOH again has a strong (124.7 kcal mol⁻¹) Si–OH bond. The “high–low–high” alternation of the Si–OH BDE displayed in the tetravalent–trivalent–divalent series is seen in all silicon compounds examined to date, regardless of the ligands involved, and is due to the stabilization of the divalent state relative to the trivalent one. The effect is even more pronounced in $\text{SiH}_{3-n}(\text{OH})_n$ compounds.²⁵

Bonds to oxygen atoms (as opposed to OH groups) in the ketone analogues (i.e., $\text{XYSi}=\text{O}$ compounds, where X, Y = Cl or OH) are also quite strong, but they are not significantly stronger than the Si–OH bonds in tetravalent species, even though they contain significant multiple-bond character. This is exhibited by the fact that the Si–O bonds are considerably shorter than the single bonds to OH in tetravalent hydroxides. For example, the Si–OH bond distance in Cl_3SiOH is 1.613 Å, while the Si–O bond distance in $\text{Cl}_2\text{Si}=\text{O}$ is 1.488 Å. The Si–O bond energy in these compounds ranges from 133.4 kcal mol⁻¹ in $\text{Cl}_2\text{Si}=\text{O}$ to 145.5 kcal mol⁻¹ in $\text{Cl}(\text{OH})\text{Si}=\text{O}$, values that are comparable to or somewhat higher than those of the Si–OH bonds (see Table 5). These values can be compared with the analogous BDEs in $\text{H}_2\text{Si}=\text{O}$ (147.7 kcal mol⁻¹) and $\text{H}(\text{OH})\text{Si}=\text{O}$ (150.7 kcal mol⁻¹), indicating that Cl ligands reduce the strength of the adjacent Si–O bond.

The remaining bond types in Si–H–O–Cl compounds are very similar in strength to those in analogous compounds examined previously and display the same trends.^{18,25} Silicon–chlorine bond strengths in the tetravalent compounds follow the same trend as Si–OH bonds; namely, they increase in strength as the number of OH groups increases. In SiCl_4 , the Si–Cl BDE is 111.4 kcal mol⁻¹, while in $\text{SiCl}(\text{OH})_3$ it is nearly 125 kcal mol⁻¹. In trivalent compounds, the Si–Cl BDEs are considerably smaller than in tetravalent compounds, ranging from 68.8 kcal mol⁻¹ in SiCl_3 to 64.1 kcal mol⁻¹ in $\text{SiCl}(\text{OH})_2$, again illustrating the stabilization of divalent bonding relative to trivalent bonding. Qualitatively similar behavior is exhibited by Cl_3SiO and $\text{Cl}_2\text{Si}=\text{O}$. In the former molecule, the Si–Cl bond is very weak (43 kcal mol⁻¹), due to the great stability of the latter compound, which is created when one Cl atom is removed. In contrast, the Si–Cl bonds in $\text{Cl}_2\text{Si}=\text{O}$ are much stronger (101.7 kcal mol⁻¹). In the only silylene examined in this study, ClSiOH , the Si–Cl bond is again very strong (124.7 kcal mol⁻¹). Si–H bonds, though substantially weaker than Si–Cl bonds, exhibit much the same behavior. These bonds are also strengthened by the presence of the more electronegative ligands OH and Cl in the molecule. Finally, O–H bonds are very strong in the tetravalent hydroxides, with BDEs around 126 kcal mol⁻¹. In contrast, these bonds are much weaker in the trivalent hydroxides, because loss of the hydrogen atom creates a formaldehyde analogue. BDEs in the range 49–54 kcal mol⁻¹ are thus observed.

Several silicon peroxide species are also included in this study, since these may form in the initial stages of SiCl_4 oxidation (see discussion below, section D). The Si–H and Si–Cl BDEs are similar to those of other compounds discussed above. In the tetravalent compounds, the Si–OOH BDE ranges from ~95 to 98 kcal mol⁻¹, while the SiO–OH bond is relatively weak, with a BDE of 49–54 kcal mol⁻¹. Most interesting, however, are the bond strengths in the trivalent radicals Cl_2SiOOH and ClHSiOOH . In these species, the calculated SiO–OH BDE is actually negative (–20 and –18 kcal mol⁻¹, respectively); in H_2SiOOH (calculated previously²⁵),

TABLE 4: BAC-MP4 Thermochemical Parameters for Si–O–Cl–H Compounds at Various Temperatures

species	ΔH_f° ^a	S° ^b			ΔG_f° ^a			
	298 K	298 K	300 K	600 K	1000 K	1500 K	2000 K	2500 K
Cl ₃ SiOH	−200.3	84.61	−188.4	−176.9	−161.9	−143.6	−123.5	−102.4
Cl ₂ Si(OH) ₂	−241.2	84.02	−225.2	−209.5	−189.0	−164.2	−137.7	−110.3
SiCl(OH) ₃	−281.7	83.73	−261.5	−241.5	−215.6	−184.2	−151.2	−117.6
HSiCl ₂ (OH)	−158.0	77.20	−147.2	−136.4	−121.9	−104.3	−84.8	−64.3
H ₂ SiCl(OH)	−112.3	69.69	−102.6	−92.4	−78.6	−61.6	−42.8	−23.0
H ₂ SiCl(O)	−40.1	69.05	−34.8	−29.2	−21.4	−11.9	−0.4	12.3
SiCl ₃ O	−125.2	81.22	−116.9	−108.7	−97.5	−83.5	−67.2	−49.5
SiCl(OH) ₂	−150.5	78.02	−140.6	−130.7	−117.9	−102.4	−84.9	−66.4
SiCl(OH)O (OSiOH cis)	−153.2	71.69	−146.0	−138.8	−129.1	−117.1	−102.9	−87.5
SiCl(OH)O (OSiOH trans)	−150.8	72.08	−143.8	−136.7	−127.1	−115.3	−101.4	−86.5
SiCl(O)(OH) ₂	−207.6	83.30	−191.9	−176.2	−155.6	−131.1	−105.0	−78.1
SiCl ₂ (OH)O	−166.7	83.50	−155.1	−143.6	−128.7	−110.8	−91.1	−70.5
SiCl ₂ OH (C _s)	−113.2	79.75	−107.9	−102.8	−96.1	−87.9	−77.6	−66.1
SiCl(O) ₂ (C _{2v})	−78.4	72.18	−76.1	−73.8	−70.6	−66.7	−60.7	−53.2
SiHCl(OH)	−70.1	70.41	−65.3	−60.1	−53.1	−44.6	−34.0	−22.2
Cl ₂ Si=O	−111.2	72.19	−108.3	−105.3	−101.2	−96.2	−88.9	−80.3
HClSi=O	−70.1	65.74	−68.5	−66.7	−63.8	−60.2	−54.3	−47.0
SiClOH (trans ¹ A′)	−75.7	66.84	−74.5	−73.0	−70.8	−67.9	−62.7	−56.1
SiClOH (trans triplet)	−17.8	69.56	−17.4	−16.8	−15.6	−14.1	−10.3	−5.0
SiClOH (cis ¹ A′)	−77.4	66.92	−76.2	−74.7	−72.6	−69.7	−64.5	−57.9
ClSiO	−38.5	66.41	−41.8	−45.0	−48.9	−53.5	−55.6	−56.1
Cl ₃ SiOOH	−169.9	91.43	−152.7	−135.7	−113.4	−86.8	−58.8	−30.0
Cl ₂ HSiOOH	−127.8	84.08	−111.8	−95.5	−74.0	−48.0	−20.6	7.8
ClH ₂ SiOOH	−82.6	76.86	−67.7	−52.4	−31.8	−6.5	20.0	47.5
Cl ₃ SiOO	−125.7	90.82	−113.0	−100.6	−84.8	−66.0	−45.5	−24.0
Cl ₂ SiOOC	−48.6	93.78	−36.8	−25.3	−10.5	7.2	26.7	47.1
Cl ₂ SiOO (triplet)	−40.4	84.32	−33.7	−27.3	−19.0	−9.2	2.3	14.9
ClSiOOC	−13.2	83.01	−6.2	0.7	9.6	20.3	33.0	46.8
HClSiOOH (ClSiOO trans)	−39.9	78.31	−30.1	−20.0	−6.4	9.9	27.9	47.0
HClSiOOH (ClSiOO cis)	−40.6	78.72	−30.9	−21.2	−8.1	7.7	25.5	44.2
HClSiOO (triplet)	1.7	76.66	7.3	13.0	20.6	29.8	40.9	53.1
Cl ₂ SiOOH	−83.7	86.24	−73.0	−62.2	−48.2	−31.4	−12.7	6.9
ClSiOOH (ClSiOO trans, SiOOH trans)	−48.1	75.77	−42.2	−36.3	−28.5	−19.0	−7.4	5.4
ClSiO ₂ (² A′)	1.4	73.94	3.2	4.9	7.2	9.8	14.7	20.9
−OSi(Cl)O− (cyclic)	−28.6	71.64	−26.1	−23.6	−20.2	−16.1	−9.8	−2.2
−O(SiCl ₂)O− (cyclic)	−114.1	78.09	−105.6	−97.2	−86.2	−72.8	−57.5	−41.0
Cl ₂ SiCl−OH ₂ (weak complex)	−134.0	113.93	−126.3	−119.1	−109.9	−99.1	−86.6	−73.2
Cl ₃ Si−OH ₂	−137.6	99.73	−125.6	−114.1	−99.1	−81.1	−61.4	−40.8
Cl ₂ Si−OH ₂	−104.5	84.84	−96.0	−87.8	−76.8	−63.4	−48.0	−31.5

^a In kcal mol^{−1}. ^b In cal mol^{−1} K^{−1}.

the SiO–OH BDE is −17.6, continuing the trend toward more positive values as the non-oxygen ligands on silicon become less electronegative. Negative bond energies indicate that the fragments are more stable than the parent compound. The Si–H, Si–OOH, and Si–Cl BDEs in these molecules are comparable to those in similar trivalent compounds (Table 5), indicating that the negative BDEs are not the result of the MP4-(SDTQ) calculation erroneously locating an electronic excited state, rather than the ground state. If this had occurred, one would expect all BDEs to be abnormally low. This is not the case, however. For example, the Si–Cl BDE in Cl₂SiOOH is 64.6 kcal mol^{−1}, while in Cl₂SiOH it is 64.8 kcal mol^{−1}. In HClSiOOH the Si–H BDE is 44.6 kcal mol^{−1}; in HClSiOH, the Si–H BDE is 44.8 kcal mol^{−1}. The situation is similar for H₂SiOOH and H₂SiOH. We therefore conclude that these hydroperoxy radicals are very unstable and would likely have extremely short lifetimes, since there should be no significant kinetic barrier to SiO–OH bond fission. We note that our findings are consistent with bond energies derived from G2-level calculations for H₂SiOOH.³¹

B. G2 Results. Our initial intention in this investigation was to use the BAC-G2 method to determine heats of formation, which we found in an earlier study provides accurate heats of formation for group III compounds.^{38,39} The accuracy of the G2 method for small main-group compounds, including those of silicon,^{20,31} appears to be well established. However, we find

that the method behaves erratically when applied to compounds in the Si–H–O–Cl system, yielding highly inaccurate predictions for some species, while performing well for others. Some of the data resulting from these calculations are shown in Table 6.

Comparison of the heats of formation in Table 6, which do not include any BAC corrections, with those in Table 3 shows that values for all species in the series SiCl_n(OH)_{4−n} (*n* = 1–3) are in considerable disagreement with the BAC-MP4 results. The differences exceed 100 kcal mol^{−1} in some cases. In contrast, G2 predicts virtually the same heats of formation for H₂SiCl(OH) and HSiCl₂OH as BAC-MP4. The two methods are also in agreement for SiH_{4−n}Cl_n (*n* = 1–3) compounds,^{19,20} and the G2 prediction for SiCl₄ (−156.8 kcal mol^{−1}) agrees well with experiment.^{32,41} Predictions for silicon radicals are also erratic; for example, BAC-MP4 obtains −76.0 kcal mol^{−1} for SiCl₃, while G2 predicts −157.1 kcal mol^{−1} (interestingly, in a paper published by Su and Schlegel reporting heats of formation at the G2 level for SiH_mCl_n species,²⁰ the G2 electronic energy for SiCl₃ is not reported). Again, however, the G2 predictions are inconsistent for silicon radicals in general; G2 results in the series SiH_mCl_n²⁰ are in excellent agreement with the analogous BAC-MP4 predictions,^{18,19} as well as with the value for SiHCl(OH), while disagreeing markedly for SiCl₂–OH, SiCl(OH)₂, and SiCl₃O. While there are no data to confirm the accuracy of the BAC-MP4 heats of formation for most mixed

TABLE 5: Selected Bond Dissociation Energies (kcal mol⁻¹) for Si–H–O–Cl Compounds at 298 K

species	Si–H	Si–OH	Si–O	Si–Cl	O–O	O–H
SiCl ₃ OH		133.8		116.1		127.2
SiCl ₂ (OH) ₂		137.5		119.7		126.6
SiCl(OH) ₃		140.7		124.9		126.2
HSiCl ₂ (OH)	96.9	133.5		116.9		127.4
H ₂ SiCl(OH)	94.3	129.7		117.1		
H ₂ SiCl(O)	22.1		107.4	45.6		
SiCl ₃ O			108.6	43		
SiCl(OH) ₂		82.6		64.1		49.4
Cl(OH)Si=O		124.2	135.2	107.5		
(OSiOH cis)						
Cl(OH)Si=O		121.8	132.8	105.1		
(OSiOH trans)						
SiCl(O)(OH) ₂		63.9	116.5	44.3		
SiCl ₂ (OH)O		65	112.9	42.5		
SiCl ₂ OH (C _s)		86.5		64.8		54.1
SiCl(O) ₂ (C _{2v})			99.3	40		
HSiCl(OH)	44.8	95.5		78.6		52.1
Cl ₂ Si=O			134.4	101.7		
HClSi=O	83.7		145.4	106.2		
SiClOH (cis ¹ A')		124.7		107.8		91.0
ClSiO			135.7	40.8		
Cl ₃ SiO ₂ H			98.2	115.2	54.2	96.3
Cl ₂ HSiO ₂ H	96.2		98.1	116.2	54.6	
ClH ₂ SiO ₂ H	94.1		94.8	115.2		
Cl ₃ SiOO			49.7			
Cl ₂ SiOOCl				64.4	–33.4	
HClSiO ₂ H	44.6		60.8	74.1	–20	
(ClSiOO cis)						
Cl ₂ SiO ₂ H			51.8	64.6	–18	
ClSiO ₂ H			90.2	102.7	19.1	
(ClSiOO trans, SiOOH trans)						
ClSiO ₂ (² A')			36.4	–39.8		
–OSi(Cl)O– (cyclic)				–9.8		
–O(SiCl ₂)O– (cyclic)				114.5		

Si–H–O–Cl species, the heat of formation of SiCl₃ is not in doubt, indicating that a serious problem exists.

Table 6 also gives the heats of formation obtained at various intermediate levels of theory used by the G2 method. These results show that the problem evidently involves the calculations at the MP4 level of theory, since the G2MP2 heat of formation is in reasonable agreement with the BAC-MP4 results. Problems exist with both the G1 and G2 levels of theory, since the heats of formation based on both calculations are in sharp disagreement with the G2MP2 and BAC-MP4 results. In contrast, the heats of formation predicted by G1, G2MP2, and G2 are very similar in cases where the method appears to be working correctly, such as HSiCl₂(OH). Raw MP4 and MP2 electronic energies obtained from the three basis sets involved in the G2 calculation suggest (Table 6) that the problem lies with the MP4/6-311G(2df,p) calculation. In cases where inconsistent results are produced, the difference between the MP4/6-311G(2df,p) and MP4/6-311G(d,p) energies ($\Delta(2df)$ in the table) is anomalously large relative to $\Delta(2df)$ for species that do not display this problem, as well as to $\Delta(2df)$ at the MP2 level for species with the problem. For example, the MP4 $\Delta(2df)$ for SiCl₃OH is –0.484 hartree (over 300 kcal mol⁻¹), while the same quantity for HSiCl₂(OH) is only 0.204 hartree (128 kcal mol⁻¹). A similar discrepancy exists when $\Delta(2df)$ values at the MP4 and MP2 levels for SiCl₃OH are compared, whereas these values are similar for HSiCl₂(OH).

To conclude, the problem apparently lies with the MP4/6-311G(2df,p) calculation, although we did not investigate the problem further to determine its precise cause. However, the problem only occurs in tetravalent and trivalent species and only those that do not contain at least one Si–H bond. The presence

of oxygen in the molecule is not a requirement, since, as already observed, the prediction for SiCl₃ is in error. Divalent species and species containing Si=O bonds are apparently not affected by this problem. Fortunately, the erroneous results yielded by G2 are readily identifiable if one compares the predictions obtained at the G2MP2, G1, and G2 levels of theory. (The problem is also readily apparent when our ad hoc error estimate, eq 5, is determined.) However, when such errors occur, they make it impossible to use the G2 method to treat a large number of species within a class, such as with the present study.

C. Comparison with the Literature. There are very few reported heats of formation for silicon oxychlorides. Among the monosilicon species examined here, the only experimentally measured values we are aware of are those of Dittmer and Nieman,⁴² who obtained –167.8 kcal mol⁻¹ for Cl₂Si=O and –86.8 kcal mol⁻¹ for ClSiO. Both values are considerably more negative than the BAC-MP4 prediction, as well as calculated values reported by others. Heats of formation for these molecules were calculated by Junker and Schnöckel using density functional theory (DFT; B3LYP/TZVPP), yielding values (298 K) of –105.2 kcal mol⁻¹ and –39.96 kcal mol⁻¹,^{5,6} respectively. Their value for Cl₂Si=O is about 6 kcal mol⁻¹ more positive than that of the BAC-MP4 model, while DFT prediction for ClSiO is in good agreement with it. Stewart and Gordon also calculated the heat of formation for Cl₂Si=O, obtaining –121.2 kcal mol⁻¹ from the semiempirical MNDO-PM3 method and –110.1 kcal mol⁻¹ from a calculation at the MP2/6-31G(d) level; the latter value is in very good agreement with the BAC-MP4 prediction. Bond lengths and angles predicted by DFT methods are in good agreement with the HF/6-31G(d) geometry reported here; both indicate a bent structure for ClSiO and a short Si–O bond in Cl₂Si=O consistent with double-bond character.^{4–6}

The only other report addressing silicon oxyhalide thermochemistry concerns Si–Cl bond dissociation energies for SiCl_n(OH)_{4–n} ($n = 1–4$) species. Wichmann and Jug calculated these at both the HF and MP2 levels, obtaining values that are in all cases lower than the BAC-MP4 values (Table 5).⁵¹ At their highest level of theory (MP2/6-311+G(2d) + zero-point energy), they underpredict the Si–Cl BDE by 7–9 kcal mol⁻¹. This result is not surprising, since it is well-known that bond energies obtained at such low levels of theory are rather inaccurate unless empirical corrections are applied (as is the case in the various BAC methods) or isodesmic or isogyric reactions are employed to remove systematic errors resulting from the use of finite basis sets.

D. Silicon Tetrachloride Oxidation. The thermodynamic data obtained from the BAC-MP4 calculations can be used to evaluate the energetics of potential reaction pathways for the oxidation of silicon tetrachloride, which is an important industrial process, as discussed earlier. Reaction enthalpies can be a useful qualitative indicator of the speed of reactions. In particular, the relative rates of simple bond-breaking reactions can be estimated, since these proceed without an activation barrier and often have comparable Arrhenius preexponential factors. In more complex reactions, such as multichannel processes involving the formation of a hot intermediate complex (“chemically activated” reactions), reaction enthalpies can be combined with chemical intuition concerning the nature of the transition states that may be involved to predict the most favorable channel. Clearly, transition-state calculations or direct measurements are required to obtain quantitative information concerning rate constants. Since both of these can be complex and difficult to perform, analyses of the type described here can allow one to narrow the scope of an investigation to the

TABLE 6: Electronic Energies (hartrees) at the MP2 and MP4 Levels Obtained from G2 Calculations and Heats of Formation at 0 K (kcal mol⁻¹) for Selected Si–H–O–Cl Compounds at Various Levels of Theory Employed by the G2 Method

species		6-311G(d,p)	6-311+G(d,p)	$\Delta(+)^a$	6-311G(2df,p)	$\Delta(2df)^b$	G1 ^c	G2MP2 ^c	G2 ^c
SiCl ₃ OH (cis)	MP4	-1743.880247	-1743.896907	-0.016660	-1744.364364	-0.484117	-333.7	-199.9	-328.7
	MP2	-1743.821947	-1743.837708	-0.015761	-1744.065500	-0.243553			
SiCl ₂ (OH) ₂	MP4	-1359.908099	-1359.926774	-0.018675	-1360.370308	-0.462209	-370.6	-238.6	-367.6
	MP2	-1359.854663	-1359.872063	-0.017400	-1360.082787	-0.228124			
SiCl(OH) ₃	MP4	-975.934449	-975.955738	-0.021289	-976.374754	-0.440305	-407.1	-277.7	-406.6
	MP2	-975.886709	-975.906600	-0.019891	-976.099876	-0.213167			
H ₂ SiCl(OH)	MP4	-825.650679	-825.659256	-0.008577	-825.785907	-0.135228	-110.3	-111.6	-109.7
	MP2	-825.609335	-825.617289	-0.007953	-825.731676	-0.122341			
HSiCl ₂ (OH)	MP4	-1284.768709	-1284.780936	-0.012226	-1284.972377	-0.203667	-157.0	-157.2	-154.2
	MP2	-1284.718479	-1284.729863	-0.011384	-1284.901382	-0.182904			
SiCl ₃	MP4	-1668.091555	-1668.101561	-0.010006	-1668.447632	-0.356077	-161.9	-78.3	-157.1
	MP2	-1668.039443	-1668.048717	-0.009274	-1668.237847	-0.198404			
SiCl ₂ OH	MP4	-1284.112520	-1284.125888	-0.013368	-1284.447640	-0.335120	-196.2	-113.7	-193.0
	MP2	-1284.066696	-1284.079190	-0.012494	-1284.270240	-0.203543			
SiCl(OH) ₂	MP4	-900.133632	-900.262927	-0.129295	-900.448178	-0.314546	-301.4	-150.3	-300.2
	MP2	-900.093567	-900.110364	-0.016797	-900.261935	-0.168368			
SiHCl(OH)	MP4	-824.997527	-825.008155	-0.010628	-825.132705	-0.135179	-69.3	-70.4	-68.3
	MP2	-824.960425	-824.970431	-0.010005	-825.101003	-0.140577			
SiCl ₂ (¹ A ₁)	MP4	-1208.398415	-1208.405001	-0.006586	-1208.555414	-0.156999	-42.9	-42.6	-39.4
	MP2	-1208.354662	-1208.360692	-0.006030	-1208.494224	-0.139562			
SiClOH (trans singlet)	MP4	-824.422924	-824.434547	-0.011622	-824.558093	-0.135169	-79.2	-79.8	-77.4
	MP2	-824.385170	-824.396109	-0.010939	-824.508433	-0.123263			
SiClOH (trans triplet)	MP4	-824.330062	-824.341257	-0.011195	-824.463537	-0.133476	-16.6	-17.7	-15.5
	MP2	-824.297646	-824.308217	-0.010571	-824.418651	-0.121005			
SiCl ₃ O	MP4	-1743.181166	-1743.321882	-0.140716	-1743.637281	-0.456115	-325.2	-127.6	-319.2
	MP2	-1743.117261	-1743.131623	-0.014362	-1743.358033	-0.240772			
Cl ₂ Si=O	MP4	-1283.520751	-1283.533224	-0.012474	-1283.727282	-0.206531	-110.9	-111.7	-108.0
	MP2	-1283.474649	-1283.486616	-0.011967	-1283.661270	-0.186620			
Cl(OH)Si=O	MP4	-899.548687	-899.565077	-0.016390	-899.735210	-0.186523	-150.7	-152.6	-149.4
	MP2	-899.509575	-899.525343	-0.015768	-899.682002	-0.172427			
ClSiO	MP4	-823.774604	-823.785189	-0.010585	-823.910276	-0.135672	-37.2	-38.4	-35.3
	MP2	-823.739588	-823.749947	-0.010359	-823.864037	-0.124449			

^a Energy difference (hartrees) between the MP4/6-311+G(d,p) and MP4/6-311(d,p) calculations. ^b Energy difference (hartrees) between the MP4/6-311G(2df,p) and MP4/6-311(d,p) calculations. ^c Heat of formation at 0 K, kcal mol⁻¹.

most likely pathways. In the case of silicon tetrachloride oxidation, the number of possible reactions is very large. Thus, we address only a limited set of reactions that could ultimately lead to SiO formation, which is thought to be the immediate precursor to oxygenated silicon clusters.⁴³ Note that all heats of reaction (ΔH_r°) shown are for 298 K.

We begin with the supposition that SiCl₄ oxidation is initiated by the pyrolysis reactions,



the rates of which were measured in shock-tube experiments by Kunz and Roth.^{14,15} These processes may be accelerated through chain reactions involving radicals such as H atoms:



There is no evidence we are aware of suggesting that gas-phase SiCl₄ can react directly with either O₂ or H₂O at temperatures below those required for reaction R1 to proceed, although the formation of Cl₃SiOH and HCl by reaction of SiCl₄ with H₂O is slightly exothermic (-6.2 kcal mol⁻¹). In a recent investigation using density functional theory, Ignatyev and Schaefer were unable to locate any stable complexes of SiCl₄ with H₂O whose energies lie below those of the reactants.⁴⁴ Thus, the silicon-containing species most likely to react with combustion gases

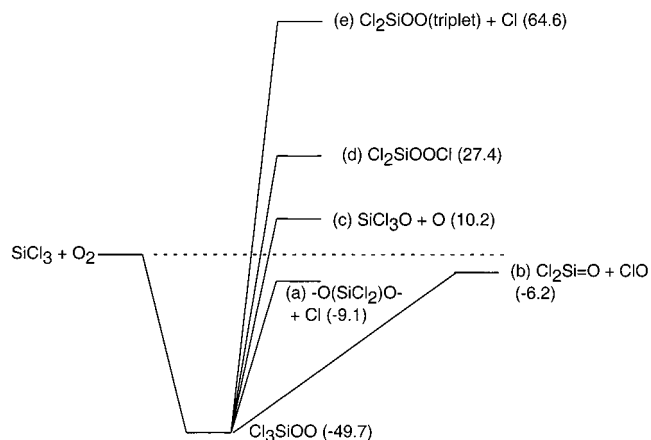


Figure 4. Energy diagram for SiCl₃ + O₂. Energies (kcal mol⁻¹) are relative to those of the reactants.

are SiCl₃ and SiCl₂. Although the high temperatures produced by the flames used to oxidize SiCl₄ (up to 3000 K⁴⁵) will produce a large number of other species as well, some of which may play an important role, oxygen and H₂O are the oxygen-containing species that will be present in greatest concentration. Consequently, we will now focus on the pathways by which SiCl₃ and SiCl₂ can react with these gases.

Reactions of SiCl₃ + O₂. An energy diagram for potential reactions of SiCl₃ with O₂ is given in Figure 4. The immediate product of this reaction is the complex Cl₃SiOO, formation of which is exothermic by 50 kcal mol⁻¹. This hot product must therefore be stabilized by collisions with the bath gas; whether significant quantities of ground-state Cl₃SiOO form depends on the pressure and the rates of energy transfer. The excess energy

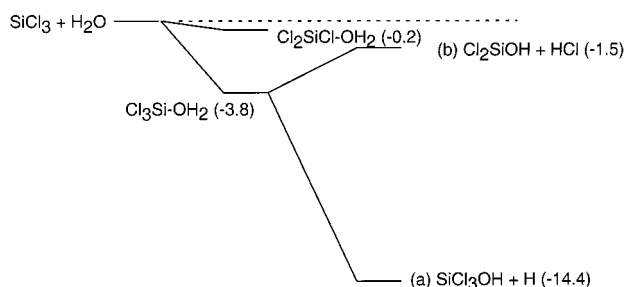


Figure 5. Energy diagram for $\text{SiCl}_3 + \text{H}_2\text{O}$. Energies (kcal mol^{-1}) are relative to those of the reactants.

present in the molecule can cause other reaction channels to open; this is a so-called “chemically activated” reaction.⁴⁶ Two exothermic pathways exist (paths a and b in Figure 4); however, tight transition states are expected for these reactions, yielding nonzero activation energies and relatively low preexponential (*A*) factors. In contrast, path c in the figure is only endothermic by 10 kcal mol^{-1} and can proceed via a unimolecular bond-cleavage reaction coordinate. This route will thus have no activation barrier and a significantly larger *A* factor than either path a or b. The product of path c, Cl_3SiO , can decompose further through a second bond-cleavage reaction to yield $\text{Cl}_2\text{-Si=O}$, an analogue of formaldehyde that we expect to have relatively high thermal stability.

Other pathways are much more endothermic: (path d) a 1,2-Cl shift, which should have a large activation energy, and (path e) Si–Cl bond cleavage to form triplet Cl_2SiOO . We were unable to obtain a converged structure for the singlet state of Cl_2SiOO (see the discussion below for $\text{SiCl}_2 + \text{O}_2$). Although the heat of reaction for its formation may be lower than that for path e, it seems likely that this compound will rearrange to form cyclic $-\text{O}(\text{SiCl}_2)\text{O}-$, the exothermic product of path a, as predicted by Nagase et al. for the analogous Si–H–O system.⁴⁷

We note that Darling and Schlegel published an extensive study of the reaction of $\text{SiH}_3 + \text{O}_2$ at the G2 level of theory.⁴⁸ There are two important factors that contribute to the substantial differences between this reaction and that of $\text{SiCl}_3 + \text{O}_2$. First, the Si–Cl bond is much stronger than the Si–H bond, leading to stabilization of intermediates or products with these bonds. Second, the formation of O–H bonds is far more favorable thermodynamically than the formation of O–Cl bonds, so that formation of H_2SiOOH via a 1,2-hydrogen shift is exothermic in the case of $\text{SiH}_3 + \text{O}_2$, whereas formation of Cl_2SiOOCl by rearrangement of Cl_3SiOOCl is endothermic (path d).

Reactions of $\text{SiCl}_3 + \text{H}_2\text{O}$. Two complexes between water and SiCl_3 were located (Figure 5). The first is a weakly bound one in which oxygen interacts at long distance (3.50 \AA) with a chlorine atom. The second, more stable complex involves bonding between silicon and the water oxygen, with a Si–O distance of 2.95 \AA . Loss of a H atom by the latter molecule via a unimolecular bond-cleavage reaction is exothermic relative to $\text{SiCl}_3 + \text{H}_2\text{O}$ by $14.4 \text{ kcal mol}^{-1}$ (path a). A 1,2-elimination reaction could also occur (path b), but is somewhat less favorable, being exothermic by only $1.5 \text{ kcal mol}^{-1}$. Path b is expected to have a high activation barrier. If SiCl_3OH forms, however, its thermal decomposition is relatively difficult; the Si–Cl bond ($116 \text{ kcal mol}^{-1}$) is even stronger than in SiCl_4 , but is actually the weakest bond in the molecule. Formation of HCl and $\text{Cl}_2\text{Si=O}$ via a 1,2-elimination reaction is endothermic by 8 kcal mol^{-1} and would also have an activation barrier. Thus, the efficient pathways to decomposition of this product may well be through abstraction reactions involving flame radicals

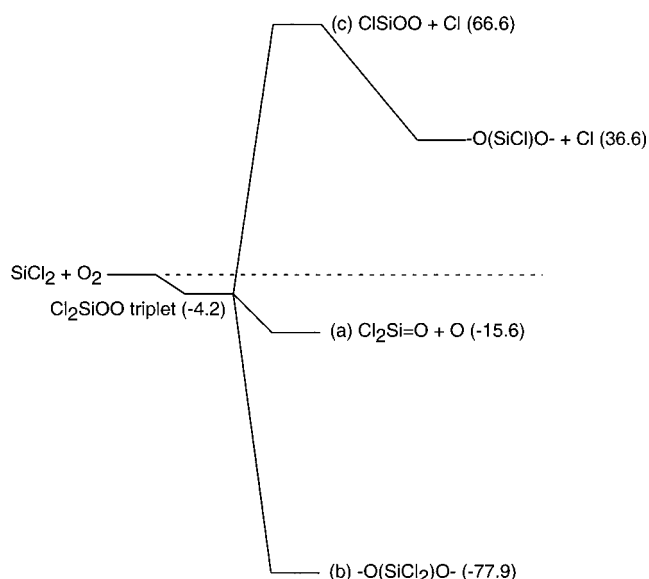


Figure 6. Energy diagram for $\text{SiCl}_2 + \text{O}_2$. Energies (kcal mol^{-1}) are relative to those of the reactants.

such as H (as in reaction R3 above), rather than via unimolecular processes.

Reactions of $\text{SiCl}_2 + \text{O}_2$. The energetics of possible reactions between dichlorosilylene and O_2 are shown in Figure 6. Formation of Cl_2SiOO is exothermic by about 4 kcal mol^{-1} . The ground electronic state of this molecule is predicted to be a triplet, which is consistent with earlier experimental and theoretical work by Akasaka et al. showing that the adduct between R_2Si and O_2 has the R_2SiOO structure and a triplet ground state.⁴⁹ Once formed, Cl_2SiOO can lose an oxygen atom to form $\text{Cl}_2\text{Si=O}$ through a reaction that is exothermic by an additional 12 kcal mol^{-1} (path a), a reaction that we expect will proceed with a negligible barrier. It is thus likely that $\text{Cl}_2\text{-SiOO}$ will form only as an intermediate transition-state complex and rapidly decompose to $\text{Cl}_2\text{Si=O}$. A second possibility, however, is that Cl_2SiOO rearranges to form the cyclic compound $-\text{O}(\text{SiCl}_2)\text{O}-$ (path b), a reaction that is far more exothermic than path a. This reaction, however, requires a curve crossing of different spin states and will have an activation barrier, which presumably includes the energy to first pair the electrons to form the singlet state. A theoretical investigation by Nagase et al. of the singlet H_2SiOO molecule indicates that this molecule rapidly rearranges to form cyclic siladioxirane ($-\text{O}(\text{SiH}_2)\text{O}-$), the barrier being only $2\text{--}6 \text{ kcal mol}^{-1}$, suggesting that this may also be the case with Cl_2SiOO . Unfortunately, we were unable to determine the energy of singlet Cl_2SiOO (all input geometries used converged to $-\text{O}(\text{SiCl}_2)\text{O}-$), possibly because the HF/6-31G(d) calculation employed by the BAC-MP4 method to predict molecular geometries does not accurately model singlet states with significant biradical character.⁴⁷ The only remaining pathway, unimolecular loss of Cl (path c), is energetically quite unfavorable relative to the other two pathways and for that reason probably does not play an important role.

Reactions of $\text{SiCl}_2 + \text{H}_2\text{O}$. We expect dichlorosilylene (SiCl_2) to react with water vapor in combustion atmospheres (Figure 7). Complex formation can occur exothermically ($-10.5 \text{ kcal mol}^{-1}$), followed by a highly exothermic rearrangement to yield HCl_2SiOH ($-64.0 \text{ kcal mol}^{-1}$). This reaction will likely have an activation barrier; calculations of the transition-state energy for the analogous reaction of SiH_2 indicate a barrier of $2.5\text{--}9 \text{ kcal mol}^{-1}$.^{43,50} Theoretical studies and experimental

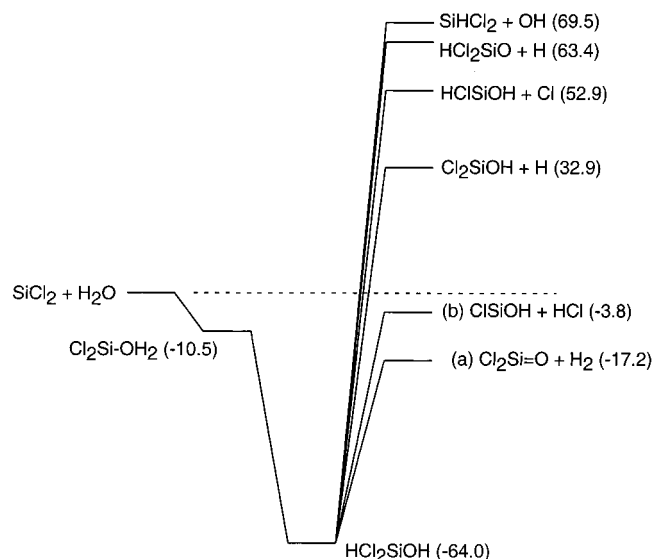


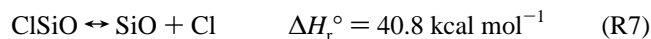
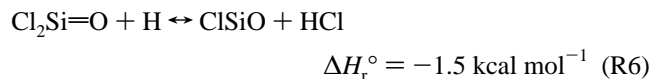
Figure 7. Energy diagram for $\text{SiCl}_2 + \text{H}_2\text{O}$. Energies (kcal mol^{-1}) are relative to those of the reactants.

measurements indicate that insertion barriers for halogenated silylenes are higher than those of SiH_2 . Nevertheless, the product molecule HSiCl_2OH will likely be formed hot and would have to be quenched by bath-gas collisions to be stabilized. If collisional energy transfer is insufficient, several subsequent channels may open, the one with the lowest energy being path a shown in Figure 7, forming $\text{Cl}_2\text{Si}=\text{O}$. A second, thermodynamically less favorable channel is the formation of another silylene, ClSiOH (path b, Figure 7). Unimolecular bond-breaking pathways for HSiCl_2OH decomposition are all considerably more endothermic. The BDE of the weakest bond in the molecule, $\text{Si}-\text{H}$, is $96.9 \text{ kcal mol}^{-1}$ (see Table 5). Thus, these reactions are unlikely to contribute significantly until very high temperatures.

If formation of $\text{Cl}_2\text{Si}=\text{O}$ via path a occurs, routes exist for the formation of SiO . Unlike the analogous reactions involving SiH_2 ,⁴³ however, formation of SiO is not thermoneutral:

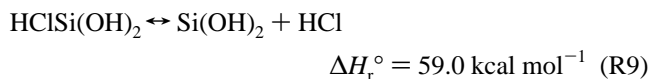
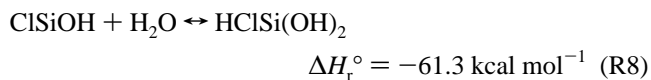


In fact, $\text{Cl}_2\text{Si}=\text{O}$ is thermodynamically quite stable and has few exothermic or even modestly endothermic decomposition pathways available to it. Unimolecular $\text{Si}-\text{Cl}$ bond breaking is endothermic by $101.7 \text{ kcal mol}^{-1}$ (Table 5). Reaction with H atoms is slightly exothermic and could lead to SiO formation by loss of the relatively weakly bound Cl in ClSiO :

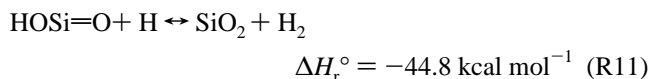
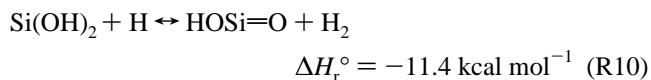


Given these energetics, it is little wonder that very high temperatures are required to oxidize SiCl_4 , in contrast with silane (SiH_4) oxidation, which can ignite at room temperature.

Assuming sufficient thermal energy is available for path b to proceed, a number of additional reactions could occur that lead to either SiO or SiO_2 . We did not attempt to catalog these exhaustively; however, some plausible reactions include the following:



$\text{Si}(\text{OH})_2$ can react via a number of endothermic unimolecular pathways to ultimately form SiO and SiO_2 ; these have been discussed previously.⁴³ Alternatively, two exothermic reactions with H atoms can also occur:



These may be effective at high temperatures where H radicals are more abundant. Given sufficient thermal energy for reaction R9 to proceed, reaction R12 should also occur at combustion temperatures, providing a potentially rapid unimolecular pathway to SiO_2 formation.

IV. Summary and Conclusions

The BAC-MP4 method has been applied to a series of silicon oxychloride compounds, allowing heats of formation and other thermodynamic data to be derived. Although there are almost no experimental data available for comparison with the predictions, the method appears to be working well, on the basis of linear trends in the heats of formation for homologous series and comparisons with previous BAC-MP4 results for $\text{Si}-\text{O}-\text{H}$ compounds. The data obtained from the calculations provide a basis for developing models of the gas-phase chemistry occurring during the combustion of chlorinated silanes. A preliminary analysis of this chemistry is presented here, using heats of reactions derived from the BAC-MP4 heats of formation, and indicates that the immediate products of SiCl_4 decomposition, SiCl_3 and SiCl_2 , can react with both O_2 and H_2O . A key intermediate product appears to be $\text{Cl}_2\text{Si}=\text{O}$, the silicon analogue of phosgene, whose $\text{Si}-\text{Cl}$ and $\text{Si}-\text{O}$ bonds are quite strong. Transition-state calculations are not a part of this investigation, so a logical next step toward full understanding of chlorinated silane oxidation is to determine transition-state geometries and energies for the reactions discussed above, as well as for other pathways not considered here.

Acknowledgment. We are grateful to the U.S. Department of Energy Office of Industrial Technologies Industrial Materials of the Future Program (Dr. Charles Sorrell, program manager) for supporting this research.

Supporting Information Available: Tables 7–11 of Cartesian coordinates, electronic energies, scaled frequencies, moments of inertia, and polynomial fits of thermodynamic data (Chemkin format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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