Kinetic studies of the reactions of hydroxyl radicals with the methyl-substituted silanes $\text{SiH}_n(\text{CH}_3)_{4-n}$ ($n = 0$ to 4) at room temperature

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Abstract

The flash-photolysis resonance-fluorescence method has been employed at 293–297 K to measure rate constants for the reactions of OH with SiH_4 , $\text{Si}(\text{CH}_3)\text{H}_3$, $\text{Si}(\text{CH}_3)_2\text{H}_2$, $\text{Si}(\text{CH}_3)_3\text{H}$, and $\text{Si}(\text{CH}_3)_4$ of $(1.2 \pm 0.2) \times 10^{-11}$, $(3.3 \pm 0.4) \times 10^{-11}$, $(4.4 \pm 0.5) \times 10^{-11}$, $(3.1 \pm 0.4) \times 10^{-11}$, and $(1.2 \pm 0.2) \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$, respectively. The uncertainties are 95% confidence intervals (see text). The results reveal that the per Si–H bond reactivity towards OH increases with the degree of methylation, and that $\text{Si}(\text{CH}_3)_2\text{H}_2$ is the most reactive member of the series.

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1. Introduction

The use of volatile silicon compounds in semiconductor manufacturing and in silicon carbide CVD may lead to their emission into the atmosphere, where they can be removed by reactions with a variety of reactive species, such as hydroxyl and nitrate radicals. For most hydrocarbons, hydrogen abstraction by OH radicals is one of the major channels for their removal in the atmosphere, and the rate constants of these reactions have been measured or estimated reliably

[1–6]. However, the only silane compounds whose reactions with OH have been studied to date are silane itself, SiH_4 [7], tetraethylsilane [8], and tetramethylsilane [9–11]. The flammability of silanes makes them hazardous, and reaction with OH is a likely step in silane combustion, which will help determine the flame speed and explosion limits. In the present work, the flash-photolysis resonance-fluorescence (FP-RF) technique is applied to measure the rate constants $k_1 - k_5$ for the gas-phase reactions of hydroxyl with silane, and mono-, di-, tri-, and tetramethylsilane at room temperature:

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The results indicate that the atmospheric lifetimes of these silanes is short, less than a month. Our data are compared with previously published values of k_1 and k_5 , while $k_2 - k_4$ have not been reported previously. The new data reveal the effect of methyl-substitution on the reactivity of Si–H bonds toward OH, and allow a rough separation of the reactivity of C–H and Si–H bonds. The trend of Si–H reactivity is opposite to what might be expected on simple thermochemical grounds: stronger Si–H bonds react faster.

2. Experimental method

The application of the FP-RF technique in our laboratory to halogen atom reactions with silane has been described elsewhere [12]. Several modifications have been made for OH detection. In order to reduce scattered light, a Pyrex reactor with an 8-cm diameter region around the reaction zone was constructed, and the microwave-powered discharge flow lamp, the source of the resonance radiation, was placed 30 cm away from one arm of the reactor. A 2% $\text{H}_2\text{O}/\text{Ar}$ mixture flowed through the lamp at a pressure of about 0.9 mbar. The light path for photolysis radiation was flushed with nitrogen, and a quartz lens ($f = 5$ cm) was placed in one of the arms, orthogonal to both the discharge and the flash lamps, to collect the resonance fluorescence from the center of the reactor and focus it onto a photomultiplier tube (Thorn EMI Electron Tubes, 9813 QB). A band pass filter (FWHM = 15 nm) transmitting the $\lambda = 307$ nm band of OH ($\text{A}^2\Sigma, v' = 0 \rightarrow \text{X}^2\Pi, v'' = 0$) was fitted in the PMT housing.

Liquid water was degassed via freeze–pump–thaw cycles at 77 K. Ar (Big Three, 99.998%) and N_2 (Air Products, Industrial Grade) were used as supplied. Silane (Matheson), and mono-, di-, tri-, and tetramethylsilane (Hüls) were degassed by several freeze–pump–thaw cycles at 77 K and were stored in glass bulbs before use. Stock mixtures of silanes were prepared by first diluting around 5–20 mbar of the pure reagent with Ar to about

900 mbar total pressure in a glass bulb, and then a portion of the order of 10 mbar of this mixture was diluted a second time. Similarly, around 15 mbar of water vapor was made up to 900 mbar with Ar in another glass bulb. A known flow (set via a calibrated MKS Instruments 1159B mass-flow controller) of the diluted silane was mixed with controlled flows of pure Ar and of diluted water vapor, prior to entering the reaction cell. The concentration of silane was derived from these flows, the total pressure and the mixing ratios. In order to avoid the accumulation of photolysis and reaction products, experiments were performed under slow flow conditions so that the gas mixture in the reaction zone was replenished between every flash.

OH radicals were generated by flash lamp photolysis of H_2O vapor through MgF_2 optics, with a repetition rate of 1 Hz, in the presence of a second reactant. Provided $[\text{reactant}] \gg [\text{OH}]$, these conditions yield pseudo-first-order loss of OH:

$$\begin{aligned} d[\text{OH}]/dt &= -k[\text{OH}][\text{reactant}] - k_{\text{diff}}[\text{OH}] \\ &= -k_{\text{ps1}}[\text{OH}], \end{aligned} \quad (6)$$

k_{diff} approximately accounts for diffusion out of the reaction zone, k is the bimolecular rate constant, and k_{ps1} is the pseudo-first-order decay coefficient for [OH]. OH radicals are detected via resonance fluorescence, excited by the microwave powered flow lamp.

Photon counts from typically 50–1000 shots were accumulated in a multichannel scaler. An example of a fluorescence decay is shown in Fig. 1, and the k_{ps1} value is derived from a non-linear least-squares exponential fit. The lower trace is a plot of the residuals from this fit. The desired k value is then obtained as the slope of a linear plot of k_{ps1} vs. silane concentration such as Fig. 2, weighted according to the uncertainties in both concentration and k_{ps1} [13]. Typically 4–6 concentrations of silane, ranging from 0 to $[\text{silane}]_{\text{max}}$, were used to derive k under a given set of conditions. Aside from zero, the lowest reactant concentration was typically about 0.25 of the maximum value. The photolysis flash energy F was varied by a factor of two, the total pressure P by a

Fig. 1. Plot of fluorescence intensity (photon counts) vs. time obtained with $[\text{H}_2\text{O}] = 1.45 \times 10^{15} \text{ molecule cm}^{-3}$ and $[\text{Si}(\text{CH}_3)_2\text{H}_2] = 8.1 \times 10^{12} \text{ molecule cm}^{-3}$. The solid line is an exponential fit to the upper trace, and the lower trace shows a plot of the residuals together with zero drawn in as a dashed line.

Fig. 2. Plot of six pseudo-first-order decay coefficients of OH vs $[\text{Si}(\text{CH}_3)_2\text{H}_2]$ at 295 K and 73 mbar. The solid circle is the result derived from the data shown in Fig. 1. The error bars show $\pm 1\sigma$ for reactant concentration and k_{ps1} . The slope of the weighted linear fit is the bimolecular rate constant.

factor of three, $[\text{H}_2\text{O}]$ by a factor of two, and the average residence time for reagents inside the reactor before photolysis τ_{res} , by a factor of two, to

check for any dependence of the derived rate constants on these parameters.

3. Results

Ten measurements of k_1 are summarized in Table 1. Typically the 1σ statistical uncertainty in k_1 arising from the uncertainty in the slope of plots such as Fig. 2 is small, in the range 1–10%. The scatter between the determinations is considerably greater than this, for reasons that are unclear. Speculation might involve surface adsorption of silanes, or decomposition [7]. We report the mean value in Table 6. Uncertainty is first assessed through the standard deviation (s.d.) of the mean, i.e., the sample s.d. of the n measurements divided by $\sqrt{n}$. In this way repeated measurements tend to smooth random scatter. To obtain the 95% confidence interval given in Table 6 we multiply the s.d. of the mean by Student's t for $n - 1$ degrees of freedom (5%, two-tailed), and combine this in quadrature with a 10% allowance for possible systematic errors arising from propagated instrumental errors. A similar treatment is applied to the rate constants $k_2 - k_5$ detailed in Tables 2–5, and summarized in Table 6 for the temperature range of $295 \pm 2 \text{ K}$.

An alternative treatment of the scattered data for a single reaction is to plot all the runs on the same axes, which is done for the worst case (reaction (1)) in Fig. 3. Here, $k_{\text{ps1}} - k_{\text{diff}}$ is plotted against $[\text{SiH}_4]$. The overall weighted fit gives $k_1 = 1.15 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$, with a purely statistical 1σ uncertainty of 3%. The rate constant is similar to that obtained via the former treatment, which we prefer because the larger statistical uncertainty seems more plausible.

The initial hydroxyl concentration is not known absolutely, but is expected to be roughly dependent on the product of F and $[\text{H}_2\text{O}]$. We made the null hypothesis that the k values do not change consistently with this product. This hypothesis was tested for each reaction by ranking the k values in order of increasing $F \cdot [\text{H}_2\text{O}]$, dividing the values into two groups at the median, and applying Student's t test to find the probability that the two samples of k were drawn from populations with

Table 1

Rate constant measurements for OH + SiH₄

<i>T</i> K	<i>F</i> J	τ_{res} s	<i>P</i> mbar	[H ₂ O] $\times 10^{15}$ molecule cm ⁻³	[SiH ₄] _{max} $\times 10^{13}$ molecule cm ⁻³	<i>k</i> ₁ ^a $\times 10^{-11}$ molecule ⁻¹ cm ³ s ⁻¹
294	4.05	1.3	42.0	3.41	6.14	1.08 ± 0.05
294	5.00	1.2	49.9	2.93	6.14	1.15 ± 0.04
294	2.50	1.2	49.9	2.93	6.14	1.17 ± 0.02
294	4.05	1.6	102.4	2.88	4.45	1.20 ± 0.02
294	4.05	0.9	53.7	1.58	4.29	1.28 ± 0.07
295	5.00	1.0	55.7	1.60	5.79	1.44 ± 0.05
295	2.50	1.0	55.7	1.60	5.79	1.44 ± 0.05
296	4.05	0.9	49.5	1.29	6.23	1.64 ± 0.08
297	4.05	1.6	69.4	2.67	4.87	0.86 ± 0.06
297	4.05	1.2	31.2	2.05	4.23	0.93 ± 0.04

^a Uncertainty represents 1 σ statistical error only.

Table 2

Rate constant measurements for OH + Si(CH₃)H₃

<i>T</i> K	<i>F</i> J	τ_{res} s	<i>P</i> mbar	[H ₂ O] $\times 10^{15}$ molecule cm ⁻³	[Si(CH ₃)H ₃] _{max} $\times 10^{13}$ molecule cm ⁻³	<i>k</i> ₂ ^a $\times 10^{-11}$ molecule ⁻¹ cm ³ s ⁻¹
294	4.05	0.8	40.3	1.31	2.33	3.20 ± 0.10
295	5.00	1.5	72.9	2.49	2.34	3.57 ± 0.14
295	2.50	1.5	72.9	2.49	2.33	3.73 ± 0.04
295	4.05	0.9	68.9	1.40	1.14	3.29 ± 0.22
292	4.05	1.2	52.7	1.93	1.92	3.29 ± 0.22
292	5.00	0.9	63.2	1.35	0.60	4.18 ± 0.13
292	2.50	0.9	63.2	1.35	0.48	3.47 ± 0.27
293	4.05	1.6	82.5	2.65	1.13	3.17 ± 0.11
293	4.05	0.9	45.6	1.82	1.01	2.98 ± 0.07
296	4.05	1.7	86.5	2.69	0.95	2.96 ± 0.11
296	4.05	1.0	45.0	1.69	0.97	3.22 ± 0.11
295	5.00	1.4	76.9	2.27	0.97	3.25 ± 0.16
295	2.50	1.4	76.9	2.24	0.97	3.10 ± 0.10

^a Uncertainty represents 1 σ statistical error only.

the same mean. With one exception (reaction (1)), we do not reject the null hypothesis with 95% confidence and thereby we deduce that *k* is independent of [OH]₀. In the case of reaction (1), we focus on two pairs of experiments specially designed to test for this dependence, the second and third entries in Table 1 and the sixth and seventh entries. These were interleaved sets of runs where for each [SiH₄] the photolysis energy *F* was changed by a factor of 2, with constant [H₂O]. It may be seen that *k*₁ changed by less than 2%. We conclude that in this case too, *k* was independent of [OH]₀. This indicates that pseudo-first-order conditions were attained, which is consistent with the first-order fits obtained (see Fig. 1).

4. Discussion

4.1. Comparison with previous measurements

Our measurements are summarized in Table 6. A room temperature study of OH + Si(CH₃)₄ has been reported previously by Atkinson [9], who employed photolysis in a 6.4 m³ chamber combined with gas-chromatographic analysis to determine *k*₅ = (1.00 ± 0.27) × 10⁻¹² cm³ molecule⁻¹ s⁻¹, in good accord with our FP-RF value of (1.1 ± 0.2) × 10⁻¹² cm³ molecule⁻¹ s⁻¹. A somewhat lower value of (8.5 ± 0.9) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ was obtained by Tuazon et al. using a relative rate method in a 5.87 m³ chamber [11].

Table 3

Rate constant measurements for OH + Si(CH₃)₂H₂

<i>T</i> K	<i>F</i> J	τ_{res} s	<i>P</i> mbar	[H ₂ O] $\times 10^{15}$ molecule cm ⁻³	[Si(CH ₃) ₂ H ₂] _{max} $\times 10^{13}$ molecule cm ⁻³	<i>k</i> ₃ ^a $\times 10^{-11}$ molecule ⁻¹ cm ³ s ⁻¹
294	4.05	1.7	72.4	2.88	3.29	4.93 ± 0.08
294	4.05	0.9	43.2	1.71	1.74	4.35 ± 0.19
294	5.00	2.1	89.0	3.35	1.68	4.73 ± 0.11
294	2.50	2.1	89.0	3.35	1.68	4.18 ± 0.19
294	4.05	1.2	53.5	2.00	1.41	4.73 ± 0.07
293	4.05	1.8	77.6	3.17	0.97	4.32 ± 0.17
294	4.05	0.9	64.1	1.66	0.62	4.45 ± 0.10
294	5.00	0.9	61.9	1.61	0.69	4.06 ± 0.08
294	2.50	0.9	61.9	1.61	0.69	3.83 ± 0.17
295	4.05	1.6	72.7	2.73	1.45	4.31 ± 0.20
295	4.05	1.0	73.6	1.77	0.89	4.39 ± 0.11
295	4.05	0.8	34.7	1.44	0.78	4.99 ± 0.15
295	4.05	1.6	59.4	3.74	0.96	4.38 ± 0.05
295	4.05	1.6	80.1	3.30	0.78	4.55 ± 0.17

^a Uncertainty represents 1 σ statistical error only.

Table 4

Rate constant measurements for OH + Si(CH₃)₃H

<i>T</i> K	<i>F</i> J	τ_{res} s	<i>P</i> mbar	[H ₂ O] $\times 10^{15}$ molecule cm ⁻³	[Si(CH ₃) ₃ H] _{max} $\times 10^{13}$ molecule cm ⁻³	<i>k</i> ₄ ^a $\times 10^{-11}$ molecule ⁻¹ cm ³ s ⁻¹
294	4.5	0.9	58.1	1.44	1.11	3.54 ± 0.15
294	4.5	2.2	117.6	2.07	2.47	3.54 ± 0.18
294	5.0	1.1	39.3	0.97	0.95	3.49 ± 0.13
294	2.5	1.1	39.3	0.97	0.95	3.36 ± 0.18
295	5.0	1.5	71.9	2.28	3.45	2.82 ± 0.11
295	2.5	1.5	71.9	2.28	3.45	2.78 ± 0.06
295	4.5	1.1	41.7	1.63	3.23	2.60 ± 0.02
295	4.5	1.3	39.3	1.03	3.28	3.32 ± 0.10
295	4.5	1.8	58.6	2.00	3.58	3.15 ± 0.14
294	4.5	2.1	40.6	2.00	3.45	3.30 ± 0.16
294	4.5	1.7	112.9	2.09	4.78	2.50 ± 0.04

^a Uncertainty represents 1 σ statistical error only.

Table 5

Rate constant measurements for OH + Si(CH₃)₄

<i>T</i> K	<i>F</i> J	τ_{res} s	<i>P</i> mbar	[H ₂ O] $\times 10^{15}$ molecule cm ⁻³	[Si(CH ₃) ₄] _{max} $\times 10^{14}$ molecule cm ⁻³	<i>k</i> ₅ ^a $\times 10^{-12}$ molecule ⁻¹ cm ³ s ⁻¹
295	4.5	0.9	57.4	1.37	3.26	1.31 ± 0.03
295	4.5	1.0	44.3	1.65	2.52	1.33 ± 0.09
294	5.0	1.0	46.8	1.58	2.96	0.97 ± 0.02
294	2.5	1.0	46.8	1.58	2.96	0.92 ± 0.02
295	4.5	1.2	83.1	1.99	2.98	1.11 ± 0.05
294	4.5	1.4	63.5	2.21	4.86	1.35 ± 0.06
294	2.5	1.4	63.5	2.21	4.87	1.18 ± 0.03
295	2.5	1.6	69.6	2.48	4.34	0.91 ± 0.06
295	5.0	1.6	69.6	2.48	4.34	1.03 ± 0.09
293	4.5	2.4	60.0	1.89	3.37	1.57 ± 0.07
293	4.5	2.4	108.7	3.56	7.96	1.07 ± 0.09

^a Uncertainty represents 1 σ statistical error only.

Table 6
Summary of OH rate constant measurements

Reactant	This work molecule ⁻¹ cm ³ s ⁻¹	Literature molecule ⁻¹ cm ³ s ⁻¹
SiH ₄	$(1.2 \pm 0.2) \times 10^{-11}$	$(1.24 \pm 0.19) \times 10^{-11}$ Ref. [7]
Si(CH ₃)H ₃	$(3.3 \pm 0.4) \times 10^{-11}$	–
Si(CH ₃) ₂ H ₂	$(4.4 \pm 0.5) \times 10^{-11}$	–
Si(CH ₃) ₃ H	$(3.1 \pm 0.4) \times 10^{-11}$	–
Si(CH ₃) ₄	$(1.2 \pm 0.2) \times 10^{-12}$	$(1.00 \pm 0.27) \times 10^{-12}$ Ref. [9], ^a $(1.28 \pm 0.46) \times 10^{-12}$ Ref. [10], ^b $(8.5 \pm 0.9) \times 10^{-13}$ Ref. [11] ^c

^a Measured relative to $k(\text{OH} + \text{cyclohexane}) = 7.47 \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹.

^b Measured relative to $k(\text{OH} + n\text{-hexane}) = 5.55 \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹.

^c Measured relative to $k(\text{OH} + (\text{CH}_3)_2\text{O}) = 2.84 \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹.

Fig. 3. Plot of all pseudo-first-order decay coefficients for OH + SiH₄, showing the run-to-run scatter. The runs, in the order of listing in Table 1, are given the symbols ■, ●, ▽, ▼, ◆, ▲, ◇, ○, ★, □ respectively. The line is a weighted least-squares fit.

This value agrees with ours within the combined error limits. Sommerlade et al. [10] used a 20 L chamber to obtain $(1.28 \pm 0.46) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for OH + Si(CH₃)₄, also in accord with our measurement. In addition, one FP-RF study of OH + SiH₄ was conducted over the range 297–438 K by Atkinson and Pitts [7], who reported k_1 at room temperature to be $(1.24 \pm 0.19) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, in good agreement with our FP-RF value of $(1.2 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. We therefore believe our other results to be free from systematic errors.

4.2. Atmospheric lifetimes

In order to help assess the environmental influence of these silane compounds if emitted into the atmosphere, the lifetimes of these compounds need to be determined. The atmospheric lifetimes were estimated on the basis that scavenging by OH is the dominant removal process in the troposphere, with the assumption that [OH] is of the order of 10⁶ molecule cm⁻³ [14]. The derived lifetime, $(k[\text{OH}])^{-1}$, of the species containing Si–H bonds is around a day or less. The precise lifetime will therefore be determined by local conditions. Tetramethylsilane is less reactive but still has a short lifetime of the order of 10 days. These values are rough upper limits, because other possible removal pathways (such as possible reaction with NO₃) will lead to still shorter lifetimes.

4.3. Reactivity trends and likely products

Reaction (1) is thought to proceed via H abstraction from an Si–H bond [7], and the general magnitudes of reactions (2)–(4) are also consistent with this mechanism. Abstraction from the stronger C–H bonds is in principle possible but the much lower reactivity of tetramethylsilane, where this is the only pathway, implies this is a minor channel for the other compounds. On the assumption of a similar reactivity of the methyl groups in all the compounds, the contribution of H abstraction from a C–H group is around 3% for trimethylsilane and less for mono- and dimethylsilane.

Fig. 4. Variation of the OH + silane rate constant with the extent of methyl substitution. Solid columns show total rate constants, and the open columns indicate rate constants per Si-H bond.

Fig. 4 indicates the variation of the rate constants with the degree of methyl-substitution, and reveals a maximum at dimethylsilane. The rate constants per Si-H bond were also calculated and are shown in Fig. 4. This latter quantity shows a monotonic trend of increasing Si-H bond reactivity with increasing number of methyl groups. While an obvious interpretation is that methylation has slightly weakened the remaining Si-H bonds, and hence made them more labile, it has been demonstrated that the bond dissociation enthalpy instead *increases* somewhat [15].

A similar paradox and a possible interpretation in frontier orbital terms was presented earlier for the reactions of silanes with $\text{O}(^3\text{P})$ atoms [16]. In that case it was argued that as the degree of methylation increases, electron withdrawal by the methyl groups makes the Si atom more positive. The σ bonding Si-H molecular orbital therefore has a greater amplitude at the more electronegative H atom, than at Si. The corresponding anti-bonding σ^* orbital thus has a greater amplitude at the Si atom. The attacking species donates electron density into this σ^* orbital, which is partially occupied at the transition state, and this orbital is increasingly stabilized as more electron-withdrawing methyl groups are included in the reactant.

5. Conclusions

Rate constants for the reactions of OH with the series of methylsilanes SiH_4 – $\text{Si}(\text{CH}_3)_4$ have been measured at room temperature by the FP-RF method, and are in good accord with literature data for the first and last species. Except in the case of tetramethylsilane, H_2O and a silyl radical appear to be the most likely products. Dimethylsilane is the most reactive molecule, and there is a monotonic trend of Si-H bond reactivity. All the molecules are shown to have short atmospheric lifetimes, of less than a month.

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