Investigations of the Reaction of Trimethylsilane with O(³P) Atoms

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The reaction $\text{O}(\text{}^3\text{P}_1) + (\text{CH}_3)_3\text{SiH} \rightarrow \text{products}$ (1) has been investigated by the discharge/fast-flow method with mass spectrometric detection (DF-MS) over 298–773 K and by the flash photolysis/resonance fluorescence (FP-RF) technique over 293–549 K. The rate constants from both methods are in close accord and may be summarized by $k_1(T) = 5.6 \times 10^{-11} \exp(-1005 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 290–770 K. There is reasonable agreement with previous room-temperature studies. k_1 is larger than k_2 for $\text{O} + \text{SiH}_4$ (2), similar to results for triethylsilane and triisopropylsilane [Buchta, Chr.; Stucken, D.-V.; Vollmer, J.-T.; Wagner, H. Gg. *Z. Phys. Chem. Neue Folge*, to be published], and tri-alkylation is seen to increase the reactivity of the Si–H bonds by similar amounts largely independent of the nature of the alkyl group. This silane activation occurs through lowering the energy barrier to abstraction to form $\text{OH} + (\text{CH}_3)_3\text{Si}^\bullet$. *Ab initio* analysis of this pathway at the MP2/6-31G*/HF/3-21G(*) level of theory gives relative energies for the transition states of reactions 1 and 2 that agree well with experiment.

1. Introduction

Initial discharge/fast-flow studies of the reaction of ground-state atomic oxygen, $\text{O}(2\text{p})^3\text{P}_1$, with trimethylsilane, using mass spectrometric detection (DF-MS),

by Hoffmeyer *et al.*¹ at room temperature yielded a rate constant k_1 greater than k_2 for²

The result that $k_1 > k_2$, although questioned by Park *et al.*,³ has been confirmed in further room-temperature DF-MS experiments by Horie *et al.*⁴ Several studies^{4–7} indicate that the major product channel for both reactions is H-atom abstraction to form OH. In the light of this similarity and the similar Si–H bond dissociation enthalpies D_{298} recommended by Walsh,⁸ reactions 1 and 2 might have been expected to show similar reactivities per Si–H bond, while $k_1 < k_2$ might have been expected from the suggestion that $D_{298}((\text{CH}_3)_3\text{Si–H}) > D_{298}(\text{SiH}_3\text{–H})$.^{9,10} Recent studies confirm the magnitude of k_2 ,^{6,11} here we present a check on the magnitude of k_1 at room temperature by two different techniques, DF-MS and flash photolysis/resonance fluorescence (FP-RF), and the first measurements of the temperature dependence of k_1 . The Arrhenius parameters of reactions 1 and 2 aid interpretation of the relative reactivity of silane and trimethylsilane, because the preexponential factor A separates primarily entropic properties of the transition state from the energetics, which mainly influence the activation energy E_a . The present data also extend the kinetic database for alkyl-substituted silanes and are discussed in the context of recent measurements on $\text{O}(\text{}^3\text{P})$ reactions with triethylsilane and triisopropylsilane.¹²

Recently it was shown that k_2 could be closely reproduced by combination of *ab initio* Gaussian-2 theory, which approximates QCISD(T)/6-311+G(3df,2p)/MP2/6-31G* energies,¹³ with a transition state theory (TST) analysis.⁶ Here the analogous transition state for k_1 is too large to analyze at the same level of theory, so we assess the relative energetics of the transition states

for reactions 1 and 2, TS1 and TS2, at lower levels of theory. As will be seen, MP2/6-31G* theory is sufficient to reproduce the relative reactivity of these silanes.

2. Experimental Techniques

2.1. Discharge-Flow/Mass Spectrometry Experiments. The experimental DF-MS set up at Göttingen has been described in detail previously.¹⁴ The kinetic measurements were performed in an isothermal discharge flow system with molecular beam sampling, and a quadrupole mass spectrometer was used for analysis with an ionization energy of only 20 eV. The flow system was about 70 cm long and the lower part of the flow reactor (50 cm) was heated to 773 K by three electric furnaces. The measurements were performed in the lowest 30 cm of the flow system at pressures between 2 and 5 mbar. The trimethylsilane entered the reactor through an axial movable injector probe, located at the center axis of the flow system, and was mixed with excess atomic oxygen at the end of the injector. The oxygen atoms were generated at room temperature by a chopped microwave discharge through an oxygen–helium mixture in the two side arms of the flow system. The power output of the microwave generator was between 50 and 75 W in each arm. The concentration of oxygen atoms produced was determined by the difference of the mass spectrometric signal at the O_2 mass with and without the microwave discharge. The chopping frequency and the power of the microwave discharge were computer controlled. The purities of the helium and oxygen were over 99.99% (Messer-Griesheim), and the purity of the trimethylsilane (from ABCR GmbH & Co.) was over 99%.

2.2. Flash Photolysis/Resonance Fluorescence Experiments. The FP-RF apparatus at Denton has also been described elsewhere.^{15–17} Briefly, atomic O was generated by flashlamp photolysis of SO_2 through MgF_2 optics in the presence of excess trimethylsilane, and the transient concentration was monitored by means of resonance fluorescence ($\lambda \approx 130 \text{ nm}$, $1^8\text{O}(3\text{s})^3\text{S} \rightarrow (2\text{p})^3\text{P}_1$) excited by a microwave discharge lamp. The vacuum UV fluorescence, which is proportional to $[\text{O}]$, was detected with a solar-blind photomultiplier tube employed with pulse counting, and signals from typically 100 decays were averaged in a multichannel scaler before analysis on a microcomputer. The

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repetition rate was 1 Hz, and a slow flow of reactant gas was passed through the reaction zone so that no sample of gas was exposed to more than one photolysis pulse, to avoid accumulation of products. The residence time within the central reaction zone was, however, long compared to the time scale for chemical reaction, typically 1–10 ms, so the apparatus was kinetically equivalent to a static system. Experiments were carried out in a large excess of Ar bath gas which maintained thermal equilibrium of the reactants and reduced diffusive loss of O, described by k_{diff} , to the reactor walls. The gas temperature T in the reaction zone was monitored with a thermocouple corrected for radiation errors ($\sigma_T/T \approx 2\%$).¹⁹ (CH₃)₃SiH was synthesized as described earlier;⁹ the other reagents were SO₂ (J.T. Baker, 99.96%, purified further by freeze–pump–thaw cycles), O₂ (MG Industries, UHP 99.99%), and Ar (Big Three Industries, 99.998%).

3. Results

3.1. Discharge-Flow/Mass Spectrometry Experiments. The temperature T was varied between 298 and 773 K, and further system parameters were also changed. The pressure was varied between about 2.5 and 5 mbar, and [O] was between 1.0 and 3.4 $\times 10^{14}$ molecule cm⁻³. The flow speed v was varied between 2400 and 3400 cm s⁻¹, and the reaction time was between 4 and 20 ms. The measurements were performed in an excess of O(³P) atoms over trimethylsilane with excess ratios between 110 and 380. Because of the high excess [O], the investigations took place under pseudo-first-order conditions (PFO), so that

$$\frac{-d[(\text{CH}_3)_3\text{SiH}]}{dt} = k_{\text{PFO}} [(\text{CH}_3)_3\text{SiH}] \quad (3)$$

The decay of trimethylsilane was followed via two fragment peaks ($m/e = 59$ as well as $m/e = 73$). In both cases the kinetic data were equal within the error limits. The regression lines of different plots of $\ln([\text{trimethylsilane}]_-/[\text{trimethylsilane}]_+)$ as a function of time (the subscript “+” refers to the presence of oxygen atoms and “-” refers to the absence of oxygen atoms) gave generally straight lines through the origin.

A correction to the oxygen atom concentration was performed as outlined earlier.²⁰ The values obtained can be used to calculate the initial concentration [O]₀ for each set of measurements with the same O₂/He ratio. Typical correction factors ranged from 1.030 (low temperatures and low pressures) to 1.13 (high temperatures and high pressures). The measured rate constants were also corrected for diffusion effects using the expressions given by Taylor²¹ and Aries;²² here the maximum diffusion correction was by a factor of 1.30. The plots of k_{PFO} versus [O] gave fairly straight lines through the origin, which suggests that any additional wall reactions of trimethylsilane were negligible.

The DF-MS data for reaction 1 are listed in Table 1 and are plotted in Figure 1. It may be seen that the regression line of this Arrhenius plot is linear up to 773 K, and the rate constant k_1 for the reaction of trimethylsilane with oxygen atoms is given by

$$k_1(T) = (4.5 \pm 0.8) \times 10^{-11} \times \exp(-980 \pm 100 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

The uncertainties represent estimated error limits for each parameter, and the corresponding activation energy E_a is 8.1 ± 0.8 kJ mol⁻¹.

3.2. Flash Photolysis/Resonance Fluorescence Experiments. Pseudo-first-order conditions with excess (CH₃)₃SiH over O were employed, so that

$$\frac{-d[\text{O}]}{dt} = k_1[(\text{CH}_3)_3\text{SiH}][\text{O}] + k_{\text{diff}}[\text{O}] = k_{\text{PFO}}[\text{O}] \quad (5)$$

TABLE 1: DF-MS Data for the Reaction of Trimethylsilane with O(³P) Atoms

T, K	p, mbar	$v, \text{cm s}^{-1}$	$[\text{O}]_0, 10^{14} \text{ molecule cm}^{-3}$	$[\text{O}]_0/[(\text{CH}_3)_3\text{SiH}]$	$k_1, 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
298	3.0	2500	2.5	280	1.5
298	2.6	2800	2.2	250	2.0
298	3.4	3200	2.3	255	2.0
298	2.6	2800	2.2	240	1.7
298					1.78 ^a
323	4.2	3400	2.5	280	1.8
323	3.5	3100	3.3	360	2.2
323	3.5	3100	3.3	370	2.2
323	3.1	2900	3.4	380	2.3
323					2.12 ^a
373	2.7	2700	1.8	200	3.2
373	3.5	3100	2.0	230	3.2
373	3.5	3100	2.1	240	3.0
373	4.1	3400	2.2	250	3.2
373					3.11 ^a
423	2.9	2500	2.2	240	4.3
423	4.4	3300	2.2	240	4.5
423	3.7	2900	2.4	270	4.0
423					4.26 ^a
473	4.3	3300	1.8	210	5.8
473	2.9	2600	1.9	220	4.8
473	4.4	3300	1.7	200	5.8
473	3.7	2900	1.8	200	5.6
473					5.52 ^a
573	4.5	3100	1.6	190	7.3
573	3.0	2400	1.4	170	10.3
573	3.8	2800	1.6	170	7.0
573	3.8	2900	1.7	190	9.3
573					8.47 ^a
673	4.7	3000	1.4	160	10.8
673	4.0	2700	1.4	160	9.8
673	3.5	2600	1.3	140	10.0
673	4.7	3000	1.3	140	11.5
673					10.5 ^a
773	4.9	2900	1.2	130	13.0
773	5.0	2900	1.0	110	13.4
773	4.1	2600	1.1	120	12.3
773	4.5	2400	1.1	130	11.5
773					12.5 ^a

^a Mean value: data carried to three decimal places before being averaged.

Figure 1. Arrhenius plot for the reaction of O(³P) with trimethylsilane. The hollow circles represent individual DF-MS measurements, and the filled circles represent the averaged DF-MS rate constant for each temperature. The filled squares represent averaged FP-RF data. The lines represent $k_1(T)$ fits for the FP-RF (upper) and DF-MS (lower) experiments.

k_{PFO} is the exponential decay constant for the loss of O, obtained from nonlinear least-squares fits²³ to the fluorescence signals. Because the time for diffusion of O to the walls of the reactor was long compared to the chemical lifetime, the reactor is effectively wall-less. O-atom consumption by recombination with SO₂ is included in k_{diff} , and k_1 is obtained as the slope²⁴ of a linear plot of k_{PFO} against typically six values of [(CH₃)₃SiH] from 0 to [(CH₃)₃SiH]_{max}, with [SO₂] and the total pressure, P , held constant.

Nineteen measurements of k_1 were carried out at six temperatures from 293 to 550 K, and these are summarized in Table 2. σ_{k_1} represents the statistical precision of k_1 . The initial O atom concentration [O]₀ was varied by changing the flashlamp

TABLE 2: FP-RF Data for the Reaction of Trimethylsilane with O(³P) Atoms

<i>T</i> , K	<i>p</i> , mbar	<i>τ</i> _{res} , s	<i>F</i> , J	[SO ₂], 10 ¹⁵ molecule cm ⁻³	[(CH ₃) ₃ SiH] _{max} , 10 ¹³ molecule cm ⁻³	<i>k</i> ₁ ± σ <i>k</i> ₁ , 10 ⁻¹² molecule ⁻¹ cm ³ s ⁻¹
293	66.7	2.0	5.00	7.3	10.0	2.71 ± 0.08
293	66.7	2.0	3.20	7.3	10.0	2.41 ± 0.16
293	66.7	2.0	1.25	7.3	10.0	2.09 ± 0.06
293						1.88 ± 0.04 ^a
294	66.7	1.0	5.00	7.5	15.3	2.88 ± 0.10
294	66.7	1.0	3.20	7.5	15.3	2.58 ± 0.06
294	66.7	1.0	1.25	7.5	15.3	2.20 ± 0.15
294						2.00 ± 0.04 ^a
332	66.7	1.0	5.00	6.5	7.1	3.74 ± 0.14
332	66.7	1.0	3.20	6.5	7.1	3.40 ± 0.09
332	66.7	1.0	1.25	6.5	7.1	3.04 ± 0.16
332						2.81 ± 0.06 ^a
379	66.7	1.0	5.00	5.7	4.4	4.83 ± 0.15
379	66.7	1.0	3.20	5.7	4.4	4.38 ± 0.17
379	66.7	1.0	1.25	5.7	4.4	4.88 ± 0.12
379						4.70 ± 0.16 ^b
458	66.7	1.0	5.00	4.8	2.2	7.45 ± 0.39
458	66.7	1.0	3.20	4.8	2.2	6.89 ± 0.28
458	66.7	1.0	1.25	4.8	2.2	8.31 ± 1.64
458						7.10 ± 0.52 ^b
549	133	1.0	4.05	4.0	1.1	9.15 ± 0.79
550	66.7	1.0	4.05	3.9	1.1	11.6 ± 0.9
546	101	0.5	4.05	4.0	1.2	9.04 ± 0.18
550	40	0.5	4.05	4.0	1.2	10.7 ± 0.3
548						9.53 ± 0.71 ^b

^a Linear extrapolation of *k*₁ to *F* = 0. ^b Mean value of *k*₁.

discharge energy, *F*, by a factor of 4 (1.25–5.0 J). Below 350 K there was a modest but consistent increase of the measured *k*₁ values with increasing [O]₀, by 30% over the range of *F*, which perhaps reflects chemistry that competes with reaction 1, such as consumption of O by photolytic or reaction products, e.g. (CH₃)₃Si. Accordingly, best estimates of *k*₁ were obtained by linear extrapolation to *F* = 0. Above 350 K no systematic variation of *k*₁ with *F* was observed, probably because reaction 1 was then fast enough to dominate any secondary chemistry, and the sets of *k*₁ values at each temperature were averaged. At the highest temperature studied, the average residence time of gas within the heated reactor before photolysis, *τ*_{res}, was varied to check for possible thermal decomposition of the reagents: a variation of a factor of 2 gave no consistent effect. The six best estimates of *k*₁ from Table 2 are plotted in Arrhenius form in Figure 1. A linear fit, where each point was weighted by the inverse variance, yields

$$k_1(T) = (6.7 \pm 2.0) \times 10^{-11} \times \exp(-1030 \pm 100 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

with *E*_a = 8.6 ± 0.8 kJ mol⁻¹. The quoted uncertainties represent ±2σ for *A* and *E*_a.

An expression that combines the DF-MS and FP-RF results was obtained by averaging the similar Arrhenius parameters from both sets of experiments, and for *T* = 290–770 K we recommend

$$k_1(T) = 5.6 \times 10^{-11} \times \exp(-1005 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

The corresponding *E*_a is 8.4 kJ mol⁻¹, and our approximate 95% accuracy estimate for this *k*₁(*T*) is ±15%.

4. Theoretical Analysis

Reactions 1 and 2 were investigated using quantitative molecular orbital theory, employing standard *ab initio* methods described, e.g., by Hehre *et al.*²⁵ Geometries and scaled vibrational frequencies for (CH₃)₃SiH and SiH₄ and the transition states TS1 and TS2, for H-atom abstraction from the Si–H bonds in (CH₃)₃SiH and SiH₄, respectively, were calculated at the HF/3-21G(*) level using the GAMESS program.²⁶ Then single-

Figure 2. HF/3-21G(*) geometries for the transition states for H-atom abstraction by O from (CH₃)₃SiH and SiH₄.

TABLE 3: Calculated Total Energies at the HF/3-21G(*) Geometries^a

species	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*
O(³ P)	-74.393 66	-74.783 93	-74.880 04
(CH ₃) ₃ SiH	-406.291 93	-408.366 63	-408.842 98
(CH ₃) ₃ SiHO* (TS1)	-480.631 68	-483.105 19	-483.714 83
SiH ₄	-289.777 38	-291.225 11	-291.307 10
SiH ₄ O* (TS2)	-364.114 56	-365.961 81	-366.173 47

^a In au: 1 au ≈ 2625 kJ mol⁻¹.

point energies were obtained with the Gaussian 92 program²⁷ at these geometries using the 6-31G* basis set with MP2 (frozen core electrons) theory to make a partial correction for electron correlation. The results are summarized in Figure 2 and Table 3. The HF/3-21G(*) data for (CH₃)₃SiH, SiH₄, and TS2 are similar to those obtained earlier at the HF/6-31G* level.^{6,9} The *ab initio* geometry and frequency results²⁸ were then employed with conventional transition state theory (TST) to obtain *E*₀[‡], the enthalpy of the TS relative to reactants at 0 K or, equivalently, the barrier height.^{29,30}

$$k = \ell^* \frac{k_B T}{h} \frac{Q^*}{Q_O Q_{\text{silane}}} \exp\left[-\frac{E_0^*}{RT}\right] \quad (8)$$

Rotational symmetry factors were set equal to 1, and symmetry was taken into account via *ℓ*^{*}, the reaction path degeneracy, which is 1 for reaction 1 and 4 for reaction 2. The *Q*s are the

Figure 3. Comparison of the recommended $k_1(T)$ expression (solid line) with a transition state theory fit (dashed line).

partition functions calculated from the HF/3-21G(*) data with the usual assumption of the separability of rotational and harmonic vibrational motions. The experimental electronic partition function Q_{el} for O is $5 + 3 \exp(-228 \text{ K}/T) + \exp(-326 \text{ K}/T)$,³¹ Q_{el} for the silanes is 1, and a value of 6 was assumed for Q_{el} for the TS.³⁰

Equation 8 was fitted to the measured $k_1(T)$ (eq 7) over 290–770 K with E_0^* as the only adjustable parameter, to obtain $E_{0,1}^* = 2.8 \text{ kJ mol}^{-1}$. The TST results fit the experimental data with a root-mean-square deviation of 15% and are shown as the dashed line in Figure 3. $k_1(\text{TST})$ is summarized by $1.87 \times 10^{-17} (T/\text{K})^{2.13} \exp(-180 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It may be seen that E_0^* is significantly smaller than the empirical quantity E_a , which reflects the contribution of low-frequency vibrational modes in TS1 to the temperature dependence of $k_1(\text{TST})$. Not all these low-frequency modes may be well-approximated as harmonic oscillators, so that their contribution may be overestimated. This is perhaps why the TST curve in Figure 3 is more curved than the experimental line. Data for reaction 2⁶ were analyzed in the same way, to yield $E_{0,2}^* = 13.3 \text{ kJ mol}^{-1}$.³²

5. Discussion

Figure 1 shows that the two techniques, which employed different radical generation and detection methods and, further, widely differing conditions ($[\text{O}] \gg [(\text{CH}_3)_3\text{SiH}]$ and fast-flow conditions for DF-MS; $[\text{O}] \ll [(\text{CH}_3)_3\text{SiH}]$ and pseudostatic conditions for FP-RF), are in very good agreement. This applies both to the k_1 values, which lie within a factor of 1.3, and to the derived Arrhenius parameters, which are equal within the error limits. Thus the averaged $k_1(T)$ expression (eq 7) is probably free from significant systematic errors.

It is interesting to compare our results with the data of three other groups. Wörsdorfer³³ measured the rate constant at room temperature in a flow system with mass spectrometric analysis and obtained $1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Hoffmeyer *et al.*¹ obtained $k_1 = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature using the DF-MS technique. Horie *et al.*⁴ investigated this reaction also in a discharge flow system. They obtained a rate constant at room temperature of $3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. They also calculated $E_a = 7.9 \text{ kJ mol}^{-1}$ by the BEBO method, which is in excellent accord with our measured E_a . However, this accord may be fortuitous, as Horie *et al.* note that the BEBO method “fails completely” for O + silanes.⁴ Comparison of our result, $k_1(298) = 1.9 \times 10^{-12}$, with the kinetic data of other groups shows good agreement and is displayed in Table 4. This indicates that different experimental setups do not strongly influence the measured rate constants of the reaction of trimethylsilane with oxygen atoms.

The kinetic data for the reaction of trimethylsilane with oxygen atoms, reaction 1, may be compared with those for the reaction of monosilane with oxygen atoms, reaction 2. A DF-MS measurement of $k_2(298)$ ¹¹ is about a factor of 5 smaller than $k_1(298)$, and FP-RF results^{6,17} show similar behavior with $k_1 \approx 6k_2$ at 298 K. Over the whole investigated temperature range,

TABLE 4: Comparison of Kinetic Data for the Reaction of Trimethylsilane with O(³P)

$k_1(298)$, $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	E_a , kJ mol^{-1}	A , $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	method ^a	ref
2.1	8.6	6.7	FP-RF	this work
1.7	8.1	4.5	DF-MS	this work
1.3			DF-MS	33
2.7			DF-MS	1
3.1			DF-MS	4
	7.9	6.6	BEBO	4
1.9	8.4	5.6		recommended

^a DF-MS = discharge-flow system with mass spectrometric analysis; FP-RF = flash photolysis with resonance fluorescence analysis; BEBO = calculated using the bond-energy-bond-order method.

TABLE 5: Kinetic Data for the Reactions of Trialkylsilanes with Oxygen Atoms

silane	k_{298} , $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	E_a , kJ mol^{-1}	A , $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
trimethylsilane	1.9	8.4	5.6	this work
triethylsilane	2.0	7.4	4.0	12
triisopropylsilane	1.8	7.1	3.3	12

O(³P) reacts faster with trimethylsilane than monosilane, indicating that the three methyl groups have an activating influence on the reactivity of these silanes.

Reaction 1 may also be compared with the reactions of atomic oxygen with triethylsilane and triisopropylsilane.¹² Table 5 shows kinetic data for these three processes. The three reactions have similar rate constants over the observed temperature range. One small difference is that the preexponential factor decreases with increasing size of the alkyl groups, which might reflect steric hindrance of attack by O atoms. This is not, however, a very strong effect and is smaller than the uncertainties in the preexponential factors. The similar behavior of the reactions of the trialkylsilanes with oxygen atoms on the one hand and the fact that the reaction of trimethylsilane with oxygen atoms is significantly faster than the reaction of monosilane leads to the following conclusion: the number of alkyl groups has an important influence on the rate constant, but the kind of alkyl group has a less important influence. This idea is consistent with investigations of the reactions of O atoms with the series $(\text{C}_2\text{H}_5)_x\text{SiH}_{4-x}$ ¹² and $(\text{CH}_3)_x\text{SiH}_{4-x}$ ($x = 1-3$), that indicated increasing the number of alkyl groups increased the reactivity toward O(³P).

Several investigations of the reaction of monosilane with oxygen atoms in the gas phase³⁻⁶ suggest that the main channel for reaction 2 is the direct (simple) abstraction of an H atom from a Si–H bond. This is also the case for reaction 1.^{4,5,7} It is interesting to note that while alkylation lowers the activation energy for O-atom abstraction in silanes, it raises the Si–H bond dissociation enthalpy.^{9,10} The O + silane reactions therefore violate the Polanyi–Semenov relation.^{34,35}

A possible minor channel for reaction 1, abstraction of an H-atom from a methyl group, is also exothermic:^{10,31}

The thermochemistry for reaction 1b is assumed to be similar to that known^{8,31} for

on the basis of the similar theoretical C–H bond strengths calculated for trimethylsilane and tetramethylsilane by Allendorf and Melius.³⁶ We can estimate the contribution of channel 1b to the overall kinetics of reaction 1 in two ways. The first is based on consideration of reaction 9. FP-RF³⁷ and DF-MS³⁸ experiments yielded $k_9(T) = (5.1 \pm 0.7) \times 10^{-11} \exp(-2900 \pm 70 \text{ K}/T)$ and $(4.0 \pm 0.3) \times 10^{-11} \exp(-2640 \pm 260 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. A reasonable assumption is $k_{1b} \approx k_9$, so that

$$k_{1b}(T) \approx 4.6 \times 10^{-11} \times \exp(-2770 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (10)$$

A second way to analyze channel 1b is via investigation of the reaction of oxygen atoms with trimethylchlorosilane. H-atom abstraction from an Si–H bond is blocked because the Si–H bond of trimethylsilane is replaced by an Si–Cl bond in trimethylchlorosilane. An investigation of the reaction of SiCl₄ with O(³P) showed that there is no attack by oxygen atoms at the Si–Cl bond.¹¹ Therefore the only sensible channel for the reaction of trimethylchlorosilane with atomic O is

for which $k_{11}(T) = (3.2 \pm 0.3) \times 10^{-11} \exp(-2840 \pm 280 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³⁸ This is also a plausible estimate of k_{1b} and gives similar values to eq 10. Comparison of our measured $k_1 = k_{1a} + k_{1b}$ with our estimates of k_{1b} shows that abstraction of an H-atom from the methyl group of trimethylsilane is negligible over the observed temperature range, because that process has an activation energy 15 kJ mol⁻¹ higher than H-atom abstraction from the Si–H bond. At the lowest temperature $k_1 \approx 600k_{1b}$, and at the highest temperature $k_1 \approx 15 k_{1b}$. Thus the more exothermic channel is favored, but at temperatures over 1000 K one would expect the reaction channel 1b to become more important.

We now analyze the relative reactivities of monosilane and trimethylsilane in more detail. SiH₄ has four sites for H-atom abstraction whereas (CH₃)₃SiH has only one; nevertheless, (CH₃)₃SiH is more reactive because the fundamental energy barrier to reaction is lower, i.e. $E_{0,1}^* < E_{0,2}^*$, as described in section 4. CH₃ is more electronegative than H,^{39,40} so that the central Si is expected to be more positive in (CH₃)₃SiH than in SiH₄. This qualitative argument is consistent with the Mulliken charges calculated from the *ab initio* HF/6-31G* wave function: the charges on Si and H in SiH₄ are +0.41 and -0.10, respectively, and change to +1.16 and -0.15 in (CH₃)₃SiH. The more polarized Si–H bond is seen to be more labile. C₂H₅ has a similar electronegativity^{39,40} to CH₃, and there is a similar lowering of E_a in going from monosilane to triethylsilane (Table 5). This effect can be qualitatively rationalized in terms of the HOMO and LUMO of the silane. For reaction 2 the σ bonding MO between Si and H has greater amplitude at the H-atom, reflecting the greater electronegativity of H. Thus the antibonding σ^* MO, into which the O atom donates electron density as the Si–H bond is broken, has greater amplitude at the Si atom. This antibonding MO, which is partially occupied in the TS, is stabilized by electronegative groups on Si such as alkyl groups, and therefore the barrier to reaction is decreased for reaction 1.

The TS for reaction 1, TS1, is too large to apply the Gaussian-2 theoretical methodology, which for TS2 gave an *ab initio* $E_{0,2}^*$ within 0.5 kJ mol⁻¹ of experiment, and at the same time direct calculation of E_0^* from MP2/6-31G* energies will be highly inaccurate (for reaction 2 the error was 39 kJ mol⁻¹, which corresponds to a factor of more than 10⁶ in k_2 at room temperature).⁶ Instead, the E_0^* values obtained from TST fits (section 4) can be tested by consideration of the isodesmic process

for which $\Delta H_0 = E_{0,1}^* - E_{0,2}^*$. In this way much of the error in the individual barrier heights, due to the modest basis set and correlation correction, is likely to cancel. The MP2/6-31G* energies in Table 3, combined with vibrational zero-point energies for each species, yield $\Delta H_0 = -13 \text{ kJ mol}^{-1}$. This is close to $\Delta H_0 = -10.5 \text{ kJ mol}^{-1}$ derived from the TST E_0^* values, and thus usefully accurate barrier heights are obtainable via isodesmic reactions such as 12.

6. Conclusions

The rate constant for O(³P) + (CH₃)₃SiH has been measured over 300–770 K by the discharge-flow/mass spectrometry method and over 290–550 K by the flash photolysis/resonance fluorescence method. The results are in excellent accord, and the dominant product channel is to OH + (CH₃)₃Si. Trialkylsilanes are seen to be more labile than SiH₄, mainly because alkylation lowers the activation energy, an effect which is largely independent of the nature of the alkyl groups. The transition states for direct H-atom abstraction from monosilane and trimethylsilane were characterized by *ab initio* methods, and the relative energies are found to be in accord with energy barriers derived from TST fits to the experimental measurements.

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