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Supplementary Material Available: Detailed differential equations and data for the computations of the behavior of the mechanism in Table II, leading to the results summarized in section IVB (2 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of the Reactions of $O(^{3}P)$ with SiH₄, CH₃SiH₃, (CH₃)₂SiH₂, and (CH₃)₃SIH

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The reactions of O(³P) atoms with the silanes Me_{4-n}SiH_n (n = 1-4) have been investigated at room temperature in a discharge flow system with mass spectrometric detection and also in stationary photolysis experiments. Analysis of the end products provided conclusive evidence that the only primary process occurring in each case was the abstraction of hydrogen from the Si-H bond by the O atom leading to the formation of the OH and silyl radicals. The values of the rate constants obtained are $k/10^{-13}$ cm³ s⁻¹): $k(O + SiH_4) = 3.5$, $k(O + SiD_4) = 1.4$, $k(O + MeSiH_3) = 8.9$; $k(O + Me_2SiH_2) = 18.0$, $k(O + Me_2SiH_3) = 18.0$, $k(O + MeSiH_3) =$ Me_3SiH = 30.6, and $k(O + Me_3SiD) = 16.0$. The marked increase in rate constant with methylation is unexpected in view of the known similarity of the Si-H bond dissociation energy in SiH_4 and the methylsilanes. A possible explanation is offered in terms of a reaction model involving partial charge transfer from Si to the attacking O, followed by proton transfer.

Introduction

Although the literature on the gas-phase reactions of atoms and free radicals with silanes has now reached voluminous proportions, few investigations involving O-atom attack are on record. In two previous contributions^{1,2} from this laboratory we presented results for the reactions of O atoms with Me₃SiH and Me₆Si₂, respectively. In the former, using a discharge-flow apparatus complemented by stationary photolysis experiments we showed that O atoms abstract hydrogen from the Si-H bond in Me₃SiH with the rate constant $k(298 \text{ K}) = (2.6 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Atkinson and Pitts³ have studied O-atom attack on SiH₄ by a flash photolysis chemiluminescence technique. They obtained the Arrhenius expression $k = 6.84 \times 10^{-12} \exp[-(794 \pm 151)/T]$ but did not establish the nature of the primary process. The rate constant at 298 K evaluated from their expression is lower than our value for $O + Me_3SiH$ by a factor of 5. An even lower value for O +SiH₄, deduced from experiments carried out in a flow reactor, has been reported by Mkryan et al.⁴

In view of the similarity in the bond dissociation energies of the Si-H bond in SiH₄ and Me₃SiH,⁵ we might reasonably expect the rate constants for attack on the two silanes to be similar on a per Si-H bond basis. The apparent difference between them is therefore difficult to reconcile, and it suggests that systematic errors may have distorted the results in one or more of the investigations or that the primary processes for O-atom attack on SiH_4 and Me_3SiH may be different.

According to Withnall and Andrews,⁶ on the basis of a matrix isolation study, the primary process for $O + SiH_4$ is not an abstraction reaction but an insertion reaction forming a vibrationally excited silanol, H_3SiOH^{v} (where the superscript v denotes vibrationally excited state), which subsequently decomposes. However, the credibility of their interpretation is in doubt following their subsequent claim that O-atom attack on the methylated silanes also proceeds via an insertion reaction.⁷

The suggestion that the primary process involved in these reactions is an insertion reaction disagrees not only with our earlier work, but also with recent studies concerned with the dynamics of the reaction. Agrawalla and Setser⁸ have investigated the chemiluminescence and laser-induced fluorescence of OH radicals formed in the reaction of O atoms with SiH₄. They came to the conclusion that the dominant reaction channel is

$$O(^{3}P) + SiH_{4} \rightarrow OH + SiH_{3}$$
(1)

and from the observed inverted vibrational distribution they inferred that it is a direct process. In a recent study of the vibrational and rotational distributions of the OH radical formed in the reactions of O atoms with SiH₄ and Me₃SiH, Wiesenfeld and co-workers^{9,10} argue that both reactions proceed via a linear collision complex. In the case of SiH₄, however, they found that a small proportion of the OH radicals were rotationally excited, which led them to suggest that there is a minor contribution from an insertion reaction which also results in the formation of OH radicals.

It can be seen from the results published thus far that the relative importance of the different primary processes is still a matter of debate and that the values of the rate constants reported are widely scattered, possibly as a result of the different experimental techniques employed in the various investigations.

The object of the present work was therefore to use the same techniques to explore the nature of the primary processes for O-atom attack on SiH₄ and the methylsilanes and to determine the effect of methyl substitution on the measured rate constant. Accordingly we have carried out fresh experiments on $O + SiH_4$ and $O + Me_3SiH$, and we have undertaken the first known study of $O + MeSiH_3$ and $O + Me_2SiH_2$. We have also determined kinetic isotope effects for $O + SiH_4/SiD_4$ and $O + Me_3SiH/$

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TABLE I:	Experimental	Conditions for	Kinetic Measurements
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	$O + H_2S$	$O + C_2H_4$	$O + 1 - C_4 H_8$	O + SiH ₄	O + SiH ₄	$O + SiD_4$
reactor	uncoated	uncoated	uncoated	coated ^a	uncoated	coated ^a
carrier gas	He	He	He	He, Ar	He	He
pressure/Pa	480700	290-480	230-300	240-550	380-669	300-550
temperature/K	302 ± 3	304 ± 1.5	305 ± 4	297 🌢 3	301 ± 2	297 ± 3
linear velocity/cm s ⁻¹	190-468	681-1151	1390-2599	540-920	527-1276	420-990
$[O]_0/10^{13} \text{ cm}^{-3}$	15-31	4.5-16	2.6-6.6	7.4-28.3	3.1-24.4	13.7-43.3
$[R_3SiH]_0/10^{11} \text{ cm}^{-3}$	18-55	14-62	3.2-20.9	5.5-26.3	7.5-137	15.4-28.2
[O] ₀ /[R ₃ SiH] ₀	34-119	27-62	19-128	64-400	11-122	76-197
47001 ARAY .	O + SiD ₄	O + MeSiH ₃	$O + Me_2SiH_2$	$O + Me_2SiH_2$	O + Me ₃ SiH	O + Me ₃ SiD
reactor	uncoated	uncoated	uncoated	coated ^a	uncoated	uncoated
carrier gas	He	He	He	He	He	He
pressure/Pa	354-500	400480	400	350-400	171-350	200-350
temperature/K	303 🌨 4	302 ± 2	303 ± 3	298 ± 1	302 单 3	303 🌨 3
linear velocity/cm s ⁻¹	512-1179	757-1085	916-1183	920-1324	1126-1917	1194-2339
$[O]_0/10^{13} \text{ cm}^{-3}$	4.4-22.8	2.8-15.1	3.8-13.2	2.3-8.6	2.5-10.0	2.7-9.0
$[R_3SiH]_0/10^{11} \text{ cm}^{-3}$	6.5-48.6	8.5-119.5	26-84	19.1-46.5	2.8-6.0	1.2-6.3
O]_/[R_SiH]_	39-172	9-61	11-25	10-27	84-236	111-383

"Halocarbon wax.

Me₃SiD. Rate constants were measured in a discharge flow apparatus with mass spectrometric detection, and end product analyses were carried out in these experiments and also in stationary photolyses by mass spectrometry and gas chromatography.

Experimental Section

The discharge flow system used for rate constant measurements has been described in detail previously.¹ A Pyrex reactor of 26 mm i.d., coated for some experiments with Halocarbon wax, was used throughout. Phase-sensitive detection was employed as before, but in addition the signal-to-noise ratio was improved by feeding the output of the lock-in amplifier to a signal averager (Nicolet 1074).

In order to reduce interference by O_2 , oxygen atoms were generated by the titration reaction $N + NO \rightarrow N_2 + O$. In the case of $O + SiH_4$ the NO concentration was kept slightly (~5%) lower than the initial N-atom concentration. This was necessary in order to eliminate the contribution of ¹⁵NO to the mass peak of SiH₃ (m/e = 31) in the detection of SiH₄, since very low concentrations of the substrate had to be used. The principal experimental conditions for the kinetic measurements are listed in Table I.

Only for O + SiH₄ were reaction products of flow experiments analyzed. The experiments were performed with either O atoms or SiH₄ in excess, the reactant ratios being [O]/[SiH₄] = 3-20 or [SiH₄]/[O] = 5-13, respectively. In some runs, O₂ was added to the reaction mixtures. Mass spectrometric calibrations for SiH₄, Si₂H₆, O₂, and H₂ were carried out in the usual way but the calibration for H₂O involved sampling laboratory air and determining its humidity with a precision hygrometer (Lambrecht). The detection limits at an electron energy of 50 eV were 5×10^9 cm⁻³ for SiH₄ and Si₂H₆, 1×10^{11} cm⁻³ for H₂, 1×10^{10} cm⁻³ for O₂, and about 1×10^{12} cm⁻³ for H₂O. The low sensitivity for H₂O was due to the high background signal, which also caused the calibration to be rather inaccurate, the relative error being as high as ±30%. For O and H atoms the detection limit at a nominal 15-eV electron energy was 5×10^{11} cm⁻³.

Stationary photolysis experiments were carried out in the same manner as described previously.¹ Condensable products which could be detected by flame ionization were analyzed by gas chromatography (Carlo Erba 2900, 50-m glass capillary column, OV1, FID); those which could not were analyzed by mass spectrometry (MAT 311A), except for H₂O, which was analyzed by gas chromatography with thermal conductivity detection (Hewlett Packard 5890, 50-m silica capillary column, CW 20 M, TCD). The pressure of the noncondensable products was measured by a capacitance manometer (MKS 310).

The purities of the gases as given by the manufacturers were He 99.996%, N₂ 99.99%, NO > 99.9%, N₂O > 99.0%, O₂ 99.995%, SiH₄ 99.9%. MeSiH₃, Me₂SiH₂, and Me₃SiH were used as supplied by the manufacturer (PCR). SiD₄ and Me₃SiD were prepared by the reaction of $LiAlD_4$ with $SiCl_4$ and Me_3SiCl_5 , respectively. Mass spectrometric analysis showed that in each case the isotopic purity was greater than 99%. NO was passed over Ascarite (Fluka) to remove higher oxides.

Results

Kinetic Measurements. Since wall reactions are often important in discharge-flow studies the condition of the surface of the reactor was monitored throughout the experimental program. The reactor showed low activity toward O atoms, whether coated with Halocarbon wax or not. The wall constant which was measured regularly, never exceeded 5 s⁻¹, and therefore the O-atom concentration could be taken to be constant along the reactor.

In use the reactor became coated with a thin film of metallic appearance. This phenomenon was more marked in the case of the uncoated reactor, especially during experiments on the O/SiH_4 system.

After numerous exploratory experiments it became clear that in order to obtain accurate rate constants the ratio $[O]/[R_3SiH]$ had to be as large as possible. This was especially true of the O/SiH_4 system, where it was found that when the concentration of SiH₄ was too high there was a disproportionately large decrease in the O-atom concentration, resulting in an incorrect value for the rate constant. For the methylsilanes the ratio of reactants turned out to be much less crucial.

When O atoms are generated by titrating N atoms with NO, under- or overtitration always leaves a small concentration of one or the other reactant in excess. In addition there is always residual O_2 present. Hence, the different influences of N, NO, and O_2 on the value of the rate constant were investigated in separate experiments. When N atoms were generated in the presence of the various silanes there was no consumption of the substrate provided that a critical value of the ratio [N]/[R₃SiH] was exceeded. Again the value of this ratio depended on the number of methyl groups in the silane. The effect of excess NO was tested by adding NO to the O/SiD₄ system beyond the end point of titration. The measured rate constant was not affected by the presence of NO. The effect of O_2 , whose concentration was typically <10% of [O], was examined in the system O/SiH₄ by adding O₂ to give a concentration of up to 1×10^{15} cm⁻³. As can be seen from Figure 2, no effect on the rate constant was observed.

Under the experimental conditions listed in Table I, all of the silanes studied showed simple exponential decays (Figure 1). The plots of the first-order rate constants, k^1 , versus [O] gave straight lines with small intercepts (Figure 2). From these the values of the corresponding second-order rate constants listed in Table II were obtained.

The larger scatter of values for the rate constant for $O + SiH_4$ reported by different groups led a referee to suggest that a measurement of k(1) should be immediately followed by a measurement of the rate constant of a calibration reaction. In



Figure 1. First-order plot of SiH₄ and SiD₄ decay. O + SiH₄: $[O]_0 = 2.12 \times 10^{14} \text{ cm}^{-3}$, $[SiH_4]_0 = 2.66 \times 10^{12} \text{ cm}^{-3}$, p = 360 Pa, Ar carrier gas. O + SiD₄: $[O]_0 = 2.27 \times 10^{14} \text{ cm}^{-3}$, $[SiD_4]_0 = 2.82 \times 10^{12} \text{ cm}^{-3}$, p = 330 Pa, He carrier gas.

TABLE II: Rate Constants for O(³P) + R₃SiH

	$k/10^{-13}$ cm ³ s ⁻¹							
R₃SiH	experimental	corrected	per SiH(D)					
SiH4	2.1 ± 0.4^{a}							
	2.3 ± 0.2^{b}	3.5	0.9					
SiD	0.74 单 0.12 ^a							
•	0.79 🏚 0.10 ^b	1.4	0.36					
MeSiH ₃	6.0 单 0.6 ^a	8.9	3.0					
Me ₂ SiH ₂	16.6 ± 2.1ª							
	12.4 ± 1.6^{b}	18.0	9.0					
MeaSiH	21.2 ± 1.2°	30.6	30.6					
Me ₃ SiD	11.0 ± 0.8^{b}	16.0	16.0					

^aReactor coated with Halocarbon wax. ^bReactor uncoated.

TABLE III: Rate Constants for the Calibration Reactions

	$k/10^{-13}$ cm ³ s ⁻¹				
reaction	measured	literature value ^a			
0 + H ₂ S	0.26 0.06	0.25 • 0.075			
$O + C_2 H_4$	4.6 ± 0.4	7.3 ± 1.1			
$O + 1 - C_4 H_8$	28.9 🛳 3.7	41.5 ± 8.3			

"All values taken from refs 11 and 12.

the event we used three reference reactions, $O + H_2S$, $O + C_2H_4$, and $O + 1-C_4H_8$, whose rate constants^{11,12} cover the span of values given in Table II. It turned out that our measured values for the rate constants of the reference reactions were unaffected by the history of the reactor, i.e., which of the silanes had been used in the previous experiment, but showed a systematic deviation from the published values of about 40% at medium and high values (Table III). The reason for this discrepancy could not be elucidated. A linear regression gives the following relation between the experimental and corrected rate constants: $k_{corr} = 1.42k_{exp}$ + (2.9 × 10⁻¹⁴). The corrected rate constants are also given in Table II.

Reaction Products in Flow Experiments. The investigation of the products of the $O + SiH_4$ reaction carried out in flow experiments involved much larger concentrations of SiH₄ than



Figure 2. Plot of the first-order rate constant k^1 vs $[O]_0$. Open symbols: uncoated reactor; closed symbols: Halocarbon wax coated reactor. (O) He carrier gas, (\diamond) Ar carrier gas, (\triangle) O₂ added, He carrier gas, (\Box) NO added, He carrier gas.

were used in the kinetic measurements. The only stable species detected in the mass spectra of the reaction products were H_2O , Si_2H_6 , H_2 , and O_2 . In addition, three peaks at m/e values of 44, 46, and 47 were also recorded when the uncoated reactor was used. The ratio of intensities of the last two peaks varied little with changes in experimental conditions $(I(47)/I(46) = 2.3 \pm 0.2)$, suggesting that both peaks belonged to a single reaction product. When O_2 was added to the system the intensities of the two peaks increased almost by an order of magnitude. It is conceivable that these two peaks belong to SiH₃OH. Whenever O atoms were present in the system a very large peak appeared at mass 44, corresponding to SiO⁺, irrespective of whether SiH₄ was present or not. Because of this, whether SiO itself was also a product could not be established with certainty, but its presence was indicated by a weak chemiluminescence due to SiO ($A^{1}\Pi \rightarrow X$ ${}^{1}\Sigma^{+}$), which we observed using a modified discharge flow arrangement similar to that employed in our study of the chemiluminescence of SiN.13

During the product analysis experiments the walls of the reactor became gradually covered with a thin metallic film, the phenomenon being more marked in the case of the uncoated reactor. We took this to be an indication that Si atoms were being formed in the reaction, and although we were unable to verify their presence directly, we found strong evidence for their formation. When the reactor coated with Halocarbon wax was used, three peaks at m/e = 47, 66, and 85, which could not be directly associated with the O/SiH₄ system, appeared in the mass spectra of the products. This is consistent with the successive abstraction of F atoms from the Halocarbon wax by Si atoms.

Concentration-time profiles for the reactants and products of the O + SiH₄ reaction are shown in Figure 3a. The observed rate of silane disappearance agrees well with that calculated on the basis of reaction 1 and a pseudo-first-order rate constant derived for each experimental point by combining $k(1) = 2.3 \times 10^{-13}$ cm³ s⁻¹ (Table II) with the mean values of [O] for the corresponding time interval. This implies that under the Oatom-rich conditions obtaining in these experiments SiH₄ is consumed predominantly by reaction with O atoms.

By comparison with the loss of SiH₄, however, the consumption of O atoms is disproportionately large. Even if it is assumed that SiH₄ is totally converted into SiO₂ and H₂O, indicated by the dashed line in Figure 3a, the O-atom depletion observed cannot be accounted for. Similar behavior was noticed during the kinetic measurements, as mentioned above, although the initial concentrations of SiH₄ used there were much smaller than in the product analysis experiments. When the products were analyzed with SiH₄ in large excess, for example $[SiH_4]_0/[O]_0 = 3.78 \times 10^{14} \text{ cm}^{-3}/3.0$

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Figure 3. Concentration profiles for $O + SiH_4$: (a) $[O]_0 = 2.32 \times 10^{14}$ cm⁻³, $[SiH_4]_0 = 4.15 \times 10^{13}$ cm⁻³, p = 405 Pa; (b) same as for (a) with $[O_2]_0 = 1.43 \times 10^{15}$ cm⁻³ added. Ordinate scales for both (a) and (b): $[O]/10^{14}$ cm⁻³, $[SiH_4]/10^{13}$ cm⁻³, $[H_2O]/10^{13}$ cm⁻³, $[H_2]/10^{13}$ cm⁻³, $[Si_2H_6]/10^{11}$ cm⁻³.

 $\times 10^{13}$ cm⁻³ = 12.6, or 2.18 $\times 10^{14}$ cm⁻³/4.6 $\times 10^{13}$ cm⁻³ = 4.7, O atoms were observed to disappear completely within the first 5 and 8 ms, respectively.

Summation of the products analyzed in these experiments reveals that the material balance for O and Si is extremely poor: about 93% and 98%, respectively, of these two elements could not be accounted for by the products observed. On the other hand, the material balance for H is reasonably good ($85 \pm 10\%$), especially if one takes into account the large errors in the H₂O calibration. Under the reaction conditions corresponding to Figure 3a, the results can be summarized formally by the stoichiometric equation (neglecting the small quantities of Si₂H₆ formed)

$$SiH_4 + 7.4O \rightarrow (SiO_{6.8}H_{0.6}) + 1.1H_2 + 0.6H_2O$$

The effect of adding O_2 to the reaction mixture is shown in Figure 3b. It is apparent that the addition of O_2 has little influence on O and SiH₄ depletion, but the relative importance of the products H₂ and H₂O is inverted. It was also found that the material balance for H improves to almost 100%

$$SiH_4 + 8.1O \rightarrow (SiO_{6.8}) + 0.75H_2 + 1.25H_2O$$

and that the formation of Si_2H_6 is much reduced.

The effect on the reaction products of varying the initial concentration of SiH₄ is shown in Figure 4. As can be seen, the three different products H₂, H₂O, and Si₂H₆ behave very differently: while the concentration of H₂ increases linearly with [SiH₄]₀, the concentrations of H₂O and Si₂H₆ show a quadratic dependence. If the H₂ formed is taken as a measure of the SiH₄ reacted, it can be shown that at low SiH₄ concentrations one molecule of O₂ is formed per SiH₄ reacted, and that the number of O atoms consumed per reacted SiH₄ increases from about 8 at the highest SiH₄ concentration ([O]₀/[SiH₄]₀ = 4.5) to more than 20 at the lowest concentration.

In order to throw further light on the nature of the primary process we explored the possibility that the observed quadratic dependence of H_2O formation on $[SiH_4]$ conceals a linear contribution:

$$[H_2O] = k_1[SiH_4]^2 + k_2[SiH_4]$$

When the results from Figure 4 are plotted in the form $[H_2O]/[SiH_4]$ versus $[SiH_4]$, a straight line is obtained, which



Figure 4. Effect of $[SiH_4]_0$ on the product distribution for O + SiH₄. [O]₀ = 2.17 × 10¹⁴ cm⁻³, p = 405 Pa, t = 24 ms. Ordinate scales are the same as for Figure 3, with in addition $[O_2]/10^{13}$ cm⁻³, $[H_2O]^{0.5}/$ arbitrary units.



Figure 5. Dependence of HD, D₂, and HDO, D₂O on $[SiH_4 + SiD_4]_0$. (a) HD, D₂: $[O]_0 = 2.05 \times 10^{14} \text{ cm}^{-3}$, p = 400 Pa, Ar carrier gas, t = 46 ms. (b) HDO, D₂O: $[O]_0 = 1.96 \times 10^{14} \text{ cm}^{-3}$, p = 400 Pa, Ar carrier gas, t = 40 ms.

yields $k_1 = (1.53 \pm 0.17) \times 10^{-14}$ cm³ and $k_2 = 0.031 \pm 0.0020$. Under these conditions corresponding to Figure 3a, these values lead to the conclusion that less than 5% of the H₂O measured is formed by a process linear in SiH₄.

Another important piece of information needed to unravel the nature of the primary process is the knowledge of whether H₂ and H₂O are formed in radical or molecular processes. To examine this problem, measurements with a SiH_4/SiD_4 mixture were made. The composition of the mixture, 26.6% SiH₄ and 73.4% SiD₄, was determined by the kinetic isotope effect found in our rate measurements (Table II), k(1,H)/k(1,D) = 2.8. The results are shown in Figure 5, in which the magnitude of the mass ion current is taken to be proportional to concentration, it being assumed that similar isotopic species have similar ionization cross sections. Because of high noise levels at m/e = 2 and 18, we were unable to measure H₂ and H₂O in these experiments. However, since HD and HDO can be formed only in free-radical processes, measurements of the ratios $[D_2]/[HD]$ and $[D_2O]/[HDO]$ allow the contribution of molecular processes to be ascertained. If only free-radical reactions were involved we would expect the values

TABLE IV: Product Yields in the Stationary, Hg-Sensitized Photolysis of N_2O/SiH_4 Mixtures

	reacta	ints								
SiH ₄ / N ₂ O/ NO/ O ₂ /			0,/	products/quantum yield						
Pa	kPa	Pa	Pa	$\phi(H_2 + N_2)$	$ N_2 / H_2 $	$\phi(H_2)$	φ(N ₂)			
185	3.3			1.55 ± 0.15	2.06 ± 0.17	0.51	1.04			
185	27			1.6 ± 0.1	3.0 ± 0.2	0.4	1.2			
190	43			1.9 ± 0.1	3.0 ± 0.2	0.5	1.4			
185	86			1.8 ± 0.1						
185	3.4	133			19					
185	3.6	160			16.4					
185	3.4	266			25					
93	17.3	32			22					
80	16.6	22			36					
190	43		40	6.1	0.3	4.7	1.4			
1300						1.04				
1300			27			8.0				

"Assumed.

 $[D_2]/[HD] \approx 0.5$ and $[D_2O]/[HDO] \approx 0.5$. The experimental values obtained were $[D_2]/[HD] = 2.2 \pm 0.5$ and $[D_2O]/[HDO] = 0.5 \pm 0.05$, which indicate clearly that hydrogen formation has a substantial molecular component, while H₂O formation proceeds mainly by a radical process.

The dependence of the product yields on the O_2 scavenger concentration is shown in Figure 6 for two $[O]/[SiH_4]$ ratios. With O atoms in excess ($[O]/[SiH_4] = 4.16$), as O_2 is added, the sum of $[H_2O]$ and $[H_2]$, which is equivalent to the SiH₄ consumed, remains virtually unchanged. With SiH₄ in excess ($[O]/[SiH_4]$ = 0.21), however, the production of H₂ and H₂O, and therefore the consumption of SiH₄, increases by a factor of 5 at high O_2 concentration. In both cases the amount of Si₂H₆ formed decreases with the addition of O_2 . Furthermore, it can be deduced from Figure 6 that, in the absence of O_2 , H₂O and Si₂H₆ become increasingly important as the ratio $[SiH_4]/[O]$ increases.

Reaction Products in Stationary Photolysis Experiments. In these experiments O atoms were generated by the Hg-sensitized photolysis of N₂O, first in the presence of SiH₄ alone, and then with either O₂ or NO added to the reaction mixture. From the results, given in Table IV, we see that, with only SiH₄ present, H₂ is an important product even when [O] is very much less than [SiH₄], and that within our experimental error limits, $\phi(H_2)$, the quantum yield of H₂, is independent of the pressure of N₂O. The slightly higher yield of H₂ at low N₂O pressure can be explained by additional H₂ being formed by the direct Hg-sensitized decomposition of SiH₄. The quantum yield of N₂ increases from about 1 to 1.4 with increasing N₂O pressure. The same behavior has been observed in the O/Me₃SiH system and was accounted for by the abstraction of O from N₂O by silyl radicals yielding more N₂.¹

The possibility must be considered that the H₂ observed in this reaction is formed in either the primary $O + SiH_4$ reaction or secondary reactions involving silyl radicals or both. If H₂ is formed in radical reactions it should be suppressed by the introduction of a radical scavenger. O₂, our first choice, turned out not to be a suitable scavenger for silyl radicals, as $\phi(H_2)$ increased by a factor of 10 (see Table IV) and the O₂ was completely used up. It was subsequently shown that silyl radicals generated by Hgsensitized photolysis of SiH₄ behaved in exactly the same manner.

Replacement of O₂ by NO led to a substantial decrease in $\phi(H_2)$ and the complete disappearance of Si₂H₆. If the formation of H₂



Figure 6. Effect of the addition of O_2 on the reaction products. Open symbols: $[O]_0 = 4.6 \times 10^{13} \text{ cm}^{-3}$, $[SiH_4]_0 = 2.18 \times 10^{14} \text{ cm}^{-3}$, p = 405Pa, t = 24 ms. Closed symbols: $[O]_0 = 2.57 \times 10^{14} \text{ cm}^{-3}$, $[SiH_4]_0 = 5.61 \times 10^{13} \text{ cm}^{-3}$, p = 405 Pa, t = 24 ms.

by the direct Hg-sensitized photolysis of SiH_4 is taken into account, it is found that H_2 production is completely suppressed by the addition of NO, from which we conclude that the H_2 generated in the scavenger-free O/SiH₄ system derives solely from secondary radical processes.

Since the condensable products of the $O + SiH_4$ reaction could not be analyzed by gas chromatography due to the lack of a suitable detector, we undertook a similar end-product study of the $O + MeSiH_3$ reaction, for which flame ionization detection could be used.

The product yields obtained, with and without added NO, are given in Table V. We see that $\phi(H_2)$ in the absence of a scavenger is only 0.25, a factor of around 2 lower than for $O + SiH_4$. In the presence of NO this figure is reduced further, and after correction for H_2 formation directly from the photolysis of the silane, $\phi(H_2)$ is again found to be negligible.

Because authentic samples of the products were not available for $O + MeSiH_3$, we had to be content with comparing the results with the $H + MeSiH_3$ reaction and with expressing our results only in terms of peak areas.

Discussion

The Primary Processes. Two different channels for the reaction of O atoms with silanes can be envisaged: direct abstraction leading to the formation of an OH radical and a silyl radical

$$O(^{3}P) + R_{3}SiH \rightarrow OH + R_{3}Si \qquad (I)$$

and an insertion reaction in which the triplet collision complex formed initially undergoes intersystem crossing to yield a vibrationally hot ground-state silanol:

$$O(^{3}P) + R_{3}SiH \rightarrow {}^{3}(R_{3}SiHO) \rightarrow R_{3}SiOH^{v}$$
(II)

TABLE V: Product Yields in the Stationary, Hg-Sensitized Photolysis of N2O/MeSiH3 Mixtures

						products					
		quantum yi	eld		area/%						
reactants/Pa	$\phi(H_2+N_2)$	N ₂ / H ₂	$\phi(H_2)$	φ(N ₂)	Me ₂ SiH ₂	(MeH ₂ Si) ₂ O	Me ₂ Si ₂ H ₄	UP1ª	UP2ª	UP3ª	Si ₃ C ₃ H ₁₄
183 MeSiH ₃ , 3.3×10^3 N ₂ O 188 MeSiH ₃ , 3.3×10^3 N ₂ O, 83 NO	1.25 ± 0.05	4.1 ± 0.9 10.5	0.25	1.0							
183 MeSiH ₃ , 3.3×10^3 N ₂ O, 127 NO 180 MeSiH ₃ , 3.3×10^3 N ₂ O		13			6 ± 2	7 ± 3	72 ± 7	1 ± 0.3	3 ± 1	4 ± 3	7 ± 2
180 MeSiH ₃ , 3.3×10^3 N ₂ O, 127 NO 182 MeSiH ₃ , 3.5×10^3 H ₂						79	5 91 ± 2				9 ± 2
"Unidentified product.											

The excited silanol may then be stabilized by collision or may decompose by several pathways:

$$R_{3}SiOH^{v} + M \rightarrow R_{3}SiOH + M \qquad \Delta H \approx -650 \text{ kJ mol}^{-1}$$
(IIa)

$$R_3SiOH^{\nu} \rightarrow R_3Si + OH \qquad \Delta H \approx -50 \text{ kJ mol}^{-1} \text{ (IIb)}$$

$$R_3SiOH^v \rightarrow R_2Si + ROH \qquad \Delta H \approx -250 \text{ kJ mol}^{-1} \qquad (IIc)$$

$$R_3 \text{SiOH}^v \rightarrow R_2 \text{SiOH} + R \qquad \Delta H \approx -260 \text{ kJ mol}^{-1} \qquad (\text{IId})$$

$$R_3 SiOH^{\nu} \rightarrow RSiOH + R_2 \qquad \Delta H \approx -400 \text{ kJ mol}^{-1} \qquad (IIe)$$

where in the present work R represents H and/or Me, and the values of ΔH , given for R = H, serve as a coarse guide to the energy requirements of the various pathways.

In the event that the insertion reaction is important the R₃SiOH^v formed would only be stabilized at high pressures and when the substrate has a large number of internal degrees of freedom. If the large amount of reaction energy is distributed statistically over the whole molecule we would expect the lowest energy decomposition pathway (IIe) to be favored, resulting in the formation of R_2 . The R_2 (H_2 for SiH_4, H_2 and CH₄ for MeSiH₃, and CH₄ for Me₂SiH₂) formed in the stationary photolysis experiments therefore provides a means of probing the contribution of the insertion reaction to the primary process.

The end products formed in the reaction of O atoms with R₃SiH will depend strongly on the reactant ratio $[O]/[R_3SiH]$, which, in turn, depends on the experimental approach adopted. In the flow experiments, $[O] \approx [R_3SiH]$, and the product pattern is complex because O acts as a radical scavenger. In the stationary photolysis experiments, $[O] \ll [R_3SiH]$, and a simpler spectrum of products is usually obtained. Because of this, the results obtained in these experiments form the foundation of the following examination of the nature of the primary process.

 $O + SiH_4$. On the basis of the above discussion of the primary processes most likely to occur in the attack of O atoms on silanes, and taking into account our present knowledge of similar systems, 1,14,15 the mechanism in eqs 1-8 can be considered as pro-

$$O(^{3}P) + SiH_{4} \rightarrow OH + SiH_{3}$$
(1)

$$\rightarrow$$
 H₃SiOH^v (2)

$$H_3SiOH^v + M \rightarrow H_3SiOH + M$$
 (2a)

$$H_3SiOH^v \rightarrow HSiOH + H_2$$
 (2e)

$$OH + SiH_4 \rightarrow H_2O + SiH_3$$
(3)

$$2\mathrm{SiH}_3 \to \mathrm{Si}_2\mathrm{H}_6^{\mathrm{v}} \tag{4}$$

$$\rightarrow$$
 SiH₂ + SiH₄ (5)

$$Si_2H_6^{\nu} + M \rightarrow Si_2H_6 + M$$
 (6)

$$Si_2H_6^{\nu} \rightarrow SiH_2 + SiH_4$$
 (7)

$$\rightarrow$$
 Si₂H₄ + H₂ (8)

viding an adequate foundation for the discussion of the $O + SiH_4$ reaction. If primary process 2 occurred in our system, the H₃SiOH^v formed, because of its relatively few internal degrees of freedom, would in all likelihood not be stabilized. The H₃SiOH found in our flow experiments must therefore be attributed to a surface reaction similar to that responsible for silanol formation in the closely related $O + Me_3SiH$ reaction.¹

Fragmentation of H₃SiOH^v via the lowest energy reaction path, (2e), would lead to the appearance of H_2 in the products. Since the other source of H_2 , reaction 8, constitutes only a few percent of the total $Si_2H_6^{v}$ decomposition,¹⁴ the rather large quantum yield of H₂ observed in our stationary photolysis experiments therefore appears to corroborate the view that an insertion reaction contributes to the primary process. However, as described in the previous section, all of the H₂ formed was suppressed by the

The absence of the most energetically favored decomposition channel implies the absence of all the other decomposition channels, (2b)-(2d). That the decomposition reaction

$$H_3SiOH^v \rightarrow SiH_2 + H_2O$$
 (2c)

does indeed not take place can be shown to follow from the observation that Si₂H₆ completely disappears on the addition of small amounts of NO. SiH_4 is known to be a better scavenger than NO for SiH_2^{16} and therefore if the latter were formed in (2c) it would be removed by SiH₄ to give Si₂H₆ irrespective of the presence of NO.

Support for the conclusion that (1) is the preeminent primary process can also be obtained from the results of the flow experiments, although they are more ambiguous to interpret. Almost all the hydrogen from SiH₄ appears in the products as H_2 and H_2O , but it is not easy to decide what fraction of each results from primary as against secondary processes. Both the isotopic composition of the H₂O and its quadratic dependence on SiH₄ concentration are, however, consistent with (1), as is the formation of one molecule of O_2 for every SiH₄ reacted at high $[O]/[SiH_4]$ ratios. All these results can be understood in terms of the reaction sequence (1), (3), and (9) but, as can be seen below, secondary reactions also play a role.

$$O + OH \rightarrow O_2 + H$$
 (9)

 $O + MeSiH_3$, Me_2SiH_2 , and Me_3SiH . Previous studies on the kinetics¹ and dynamics¹⁰ of $O + Me_3SiH$ came to the conclusion that it proceeds by direct H-atom abstraction. If the primary process II were also taking place, we would expect, because of the high pressures used in the stationary photolysis experiments, together with the large number of internal degrees of freedom of the insertion product, Me₃SiOH^v, that the latter would be at least partially stabilized. Me₃SiOH was indeed detected in our earlier work,¹ but its formation could be completely attributed to the occurrence of a heterogeneous wall reaction. In addition, no products have been found, which could be associated with the decomposition of Me₃SiOH^v.

The presence of a methyl group reduces the quantum yield of H_2 in the stationary photolysis of MeSiH₃ by a factor of about 2 in comparison with SiH₄, without the compensating formation of CH₄. This trend is continued with increasing methylation. Again the H₂ found disappeared almost completely with the addition of NO. We therefore draw the same conclusion for MeSiH₃ as for SiH₄ that (II) contributes at most 5% to the primary process.

The silicon-containing products observed in the reaction O + MeSiH₃ (see Table V) provide further confirmation of the importance of the abstraction process. They are similar to those found in the reaction of H atoms with MeSiH₃, in which the initial reaction is known to be H abstraction.^{17,18} The difference between the two sets of products can be traced back to the interaction between silvl radicals and N₂O.

Our results relating to the nature of the primary process are at variance with the interpretation offered by Withnall and Andrews^{6,7} of their matrix experiments. In our opinion it is likely that the silanols observed in their work were formed in secondary reactions in the cage.

Secondary Processes. Our investigations also give some insight into the reactions following the primary abstraction process. Under the experimental conditions of the flow experiments the O atoms interact to a greater or lesser extent with both products of the

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abstraction reaction, the OH and the silyl radical. The OH radicals are involved in two competing pathways, (3) and (9) leading to H_2O , O_2 , and H_2 by radical processes. The silyl radicals are likely to react with O atoms in two ways:

$$O + SiH_3 \rightarrow OH + SiH_2 \tag{10}$$

$$O + SiH_3 \rightarrow SiH_3O^{v}$$
 (11)

Because of the strong Si–O bond the SiH₃O^v will decompose by splitting off either H or H₂:

$$SiH_3O^v \rightarrow H + H_2SiO(HSiOH)$$
 (12)

$$SiH_3O^{\nu} \rightarrow H_2 + HSiO(SiOH)$$
 (13)

 H_2SiO and HSiO will suffer a further loss of their hydrogens by the attack of O atoms. Silylene may undergo, besides the wellcharacterized fast insertion reaction into SiH₄, similar reactions with O atoms to those of SiH₃. This mechanism explains the dominant formation of H₂ by mixed radical and molecular processes, and the formation of H₂O by pure radical reactions.

Addition of O_2 opens up a further pathway for the disappearance of SiH₃:

$$O_2 + SiH_3 \rightarrow H_3SiO_2^{\nu}$$
 (14)

From the experiments shown in Figure 6, and in agreement with chemical intuition, one has to conclude that the peroxy radical decomposes mainly by splitting off OH or H_2O ; H-atom loss is also reported in the literature:¹⁹

$$H_3SiO_2^{\nu} \rightarrow H_2SiO(HSiOH) + OH$$
 (15)

$$H_3SiO_2^{\nu} \rightarrow HSiO(SiOH) + H_2O$$
 (16)

$$H_3SiO_2^{v} \rightarrow H(OH)SiO + H$$
 (17)

When $[O] > [SiH_4]$, and in the presence of a large concentration of O₂, reactions 11, 12, and 13 are replaced by reactions 14-17, leading to the formation of H₂O at the expense of H₂. When $[O] < [SiH_4]$, radical combination also takes place. These processes die out when O₂ is added, and H₂O as well as H₂ formation gain in importance due to the reactions given above.

Reactions 14-17 also explain the occurrence of chain processes in the stationary photolysis of N₂O/SiH₄ or H₂/SiH₄ systems in the presence of O₂. Similar reactions have been proposed by O'Neal and co-workers²⁰ for the SiH₄-O₂ explosion.

The Rate Constant. The rate data reported here were collected under the experimental condition $[O] \gg [R_3SiH]$, and therefore possible errors due to the fast reaction of OH with R_3SiH have to be considered. The very large excess of O atoms over R_3SiH used in the kinetic measurements ensures, however, that practically all OH are converted to H atoms, whose rate of disappearance by reaction with R_3SiH is negligible due both to the very small concentration of R_3SiH , and, less directly, through its influence on the concentration of H atoms produced from it via (I) and (9).

Of the rate constants given in Table II, only $k(O + SiH_4)$ and $k(O + Me_3SiH)$ have been reported before. The value determined in this work for $O + Me_3SiH_3$, $k = 2.1 \times 10^{-12}$ cm³ s⁻¹, is in satisfactory agreement with our previous value, $k = 2.6 \times 10^{-12}$ cm³ s⁻¹. There is disagreement, however, in the values obtained for the kinetic isotope effect, k_H/k_D . Our present value, k_H/k_D = 1.9, is much larger than our earlier value, $k_H/k_D = 1.16$, and similar to that found in the present work for the O + SiH₄/SiD₄ system, $k_H/k_D = 2.5$. Our rate constant for O + SiH₄, $k = 3.5 \times 10^{-13}$ cm³ s⁻¹, is somewhat smaller than the value at room temperature calculated from the Arrhenius parameters of Atkinson and Pitts, $^3 k = 4.8 \times 10^{-13}$ cm³ s⁻¹. Taking the different experimental techniques into account we consider the agreement to be acceptable. In any case the experimental scatter does not conceal the dramatic increase of the rate constant with methylation.



Figure 7. Reduced rate constants for reaction I, k/n vs ionization potential of Me_{4-n}SiH_n.

TABLE VI: Arrhenius Parameters for $O + R_3SiH$ Calculated by the BEBO Method

	E _A /kJ mol ⁻¹		A/1 cm ²	0 ⁻¹¹ s ⁻¹	$k/10^{-1}$ cm ³ s ⁻¹	3 a
reaction	expt	calc	expt	calc	expt	calc
O + SiH ₄	6.6 ^b	10.9	0.70	3.6	4.7, ^b 3.5 ^c	4.6
$O + SiD_4$		12.1		3.6	1.4°	2.7
O + Me ₃ SiH		7.9		6.6 ^d	31°	28
O + Me ₃ SiD		8.5		6.6 ^d	16 ^c	21

^a298 K. ^bReference 3. ^cThis work. ^dCalculated on the assumption that the methyl rotors are free in the activated complex.

The strong dependence of the rate constant on the number of the methyl groups present has also been observed in other systems, e.g., the alkanes²¹ and sulfides,^{22,23} but in the case of the silanes seemingly contradictory facts have to be reconciled: in all cases O-atom attack is a direct abstraction reaction, but the Si-H bond dissociation energy is constant in the series SiH₄-Me₃SiH within the presently known error limits.

Presumably factors other than the dissociation energies of the bonds to be broken and formed play an important role in determining the energetic and entropic position of the transition state.

In a recent publication Streitwieser and co-workers²⁴ showed that the bonds between Si and H, C, O, and F are extensively polarized and that the bond to oxygen is dominated by an ionic interaction. Streitwieser²⁵ has therefore suggested that R₃Si⁺-H...O⁻ is an important resonance structure of the transition state in the reaction of O atoms with silanes. Such a structure reminds one of the classical harpoon model,²⁶ which predicts a dependence of the rate constant on the difference between the ionization potential of the silane and the electron affinity of the oxygen atom. As can be seen from Figure 7, a good correlation is indeed obtained for log k versus IP, and we therefore surmise that some aspects of this model are relevant to the reaction of oxygen atoms with silanes. The electrophilic attack of the oxygen atom leads to a partial charge transfer from silicon to oxygen followed by the transfer of the proton. Thus, the smaller the ionization potential of the silane, the earlier the charge transfer will take place along the reaction coordinate, and the faster the reaction.

The BEBO model together with activated complex theory²⁷ has been used successfully to provide an understanding of the reactions of O atoms with alkanes.²¹ For O + silanes on the other hand

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we find that it fails completely, emphasizing once again the difficulties one encounters in explaining the experimental results. One possibility for extending the scope of the BEBO model to embrace these reactions is to assume that the two parameters of the Sato triplet function, the Morse parameter β , and Si-O electronic dissociation energy, $E_{\rm is}$, which are interconnected, are dependent on methylation. Taking $E_{\rm is} = 540$ kJ/mol and $\beta =$ 2.1 Å⁻¹ for O + SiH₄, and $E_{15} = 520 \text{ kJ/mol}$ and $\beta = 2.25 \text{ Å}^{-1}$ for O + Me₃SiH, (for other parameters see ref 1) one obtains the results presented in Table VI. The trend in the rate constants with methylation can be satisfactorily reproduced but the Arrhenius parameters and kinetic isotope effects are in much worse agreement with the corresponding experimental values than is the

case for the O + alkane system.²¹

Finally, it should be mentioned that the peculiar behavior of silanes is not limited toward oxygen atoms; it has also been observed in a diminished form in reactions with H,¹⁷ OH,²⁸ SiH₂,²⁹ and Me₂Si.³⁰

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Kinetics of the Reaction of $CCl_3 + Br_2$ and Thermochemistry of CCl_3 Radical and Cation

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The rate constant of the $CCl_3 + Br_2 \rightarrow CCl_3Br + Br$ reaction was determined as a function of temperature between 300 and 532 K and fit to an Arrhenius expression: k_1 (L mol⁻¹ s⁻¹) = (1.8 ± 0.4) × 10⁸ exp[(-1.43 ± 0.29) kcal mol⁻¹/RT]. The reaction was studied in a tubular flow reactor by using laser photolysis to produce the CCl₃ reactant and photoionization mass spectrometry to monitor CCl₃ in time-resolved experiments. Previously published kinetic data were reevaluated to obtain k_{-1} , the rate constant for the reverse reaction, and recent spectroscopic data were used to calculate accurate entropies and heat capacities. The values of k_{-1} , k_1 , and these calculated thermodynamic properties were used in a third law determination to obtain $\Delta H^{\circ}_{f,298,15}(CCl_3) = 17.0 \pm 0.6$ kcal mol⁻¹ and $\Delta H^{\circ}_{f,0}(CCl_3) = 16.7 \pm 0.6$ kcal mol⁻¹. This information was combined with spectroscopic data on CCl_3^+ to obtain $\Delta H^{\circ}_{f,298,15}(CCl_3^+) = 205.2 \pm 0.6$ kcal mol⁻¹ and $\Delta H^{\circ}_{f,0}(CCl_3^+) = 203.7 \pm 0.6$ kcal mol⁻¹. Bond energies of several relevant compounds and tables of thermodynamic functions for CCl_3 and CCl_3^+ are presented. An improved heat of formation for the CCl₃O₂ radical, $\Delta H^{\circ}_{1,298,15}$ (CCl₃O₂) = 2.7 ± 1.1 kcal mol⁻¹, is also reported.

Introduction

The kinetic and thermochemical properties of chlorine-containing free radicals are receiving renewed interest because of their roles in chemical processes of environmental and commercial importance. The trichloromethyl (CCl₃) radical is particularly important. The production of CCl₃ radicals during the burning of industrial waste can account for the CHCl₃ that evolves from incinerators.¹ In the upper atmosphere, CCl₃ radicals formed by photolysis of freons eventually degrade yielding chlorine atoms that accelerate ozone depletion.² The etching of gallium arsenide (GaAs) microelectronic chips with RF discharges in CCl₄ gas may involve reactions of CCl₃ radicals with the semiconductor surface.^{3,4} Accordingly, reliable kinetic and thermochemical information on the CCl₁ radical is needed to accurately model these chemical processes.

During our recent experimental and theoretical investigations of CCl₃ species,^{5,6} we found that published thermochemical values for CCl₃ and CCl₃⁺ are inconsistent with the observed properties for these species. For example, the differences between the reported heats of formation of CCl₃ and CCl₃⁺ do not predict the adiabatic ionization potential of the CCl₃ radical. Furthermore, although it is now well-established that the CCl₃ radical has a pyramidal structure,^{5,7} the existing tabulations, such as the JANAF tables,⁸ were calculated by presuming that the CCl₃ radical is planar, similar to BCl₃, and has a harmonic ν_2 umbrella vibration.

The most commonly cited heat of formation for CCl₃ radical,^{8,9} $\Delta H^{\circ}_{f,298,15}(CCl_3) = 19.0 \pm 1 \text{ kcal mol}^{-1}$, is a thermochemical determination by Benson,^{10,11} which is based, in part, on estimated A factors for the reaction

$$\operatorname{CCl}_{3} + \operatorname{Br}_{2} \xleftarrow{k_{1}}_{k_{-1}} \operatorname{CCl}_{3} \operatorname{Br} + \operatorname{Br}$$
(1)

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As will be shown, this presumption has introduced significant errors into calculated thermochemical properties.

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