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# Kinetics and Products of the Gas-phase Reactions of $(CH_3)_4Si$, $(CH_3)_3SiCH_2OH$, $(CH_3)_3SiOSi(CH_3)_3$ and $(CD_3)_3SiOSi(CD_3)_3$ with Cl Atoms and OH Radicals

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Direct air-sampling atmospheric-pressure ionisation tandem mass spectrometry and FTIR spectroscopy were used to analyse the products of the OH radical- and Cl atom-initiated reactions of hexamethyldisiloxane, $[^2H_{18}]$hexamethyldisiloxane, tetramethylsilane and trimethylsilylmethanol at room temperature and atmospheric pressure. The data obtained indicate the initial formation of $(CH_3)_3SiOSi(CH_3)_2OCHO$ and $(CD_3)_3SiOSi(CD_3)_2OCDO$ from hexamethyldisiloxane and $[^2H_{18}]$hexamethyldisiloxane, respectively, and $(CH_3)_3SiOCHO$ from both tetramethylsilane and trimethylsilylmethanol.

Volatile organosilicon compounds consisting of $—(CH_3)_2SiO—$ structural units in linear or cyclic arrangements are widely used as components of cosmetic and personal care product formulations, penetrating oils, speciality cleaners, and lubricants. The use of these compounds leads to their emission into the atmosphere, where they are subject to physical and chemical removal and/or transformation processes, including photolysis and chemical reaction with hydroxyl (OH) radicals, nitrate ($NO_3$) radicals and ozone ($O_3$).[1,2] The dominant tropospheric chemical loss process for tetramethylsilane, hexamethyldisiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane has been shown to be by reaction with the OH radical,[3,4] with calculated tropospheric lifetimes of *ca.* 10–30 days.[3]

Using gas chromatographic analyses, Carter *et al.*[5] observed $(CH_3)_3SiOSi(CH_3)_2OH$ as a product of the $NO_x$–air photooxidations of hexamethyldisiloxane, while Sommerlade *et al.*[4] reported heptamethylhydroxycyclotetrasiloxane to be the most abundant product from the OH radical reaction of octamethylcyclotetrasiloxane in the presence of $NO_x$, by analysing washings of the reaction vessel walls by combined gas chromatography–mass spectrometry.[4] In this work, we have investigated the products of the gas-phase reactions of the OH radical with tetramethylsilane $[(CH_3)_4Si]$, trimethylsilylmethanol $[(CH_3)_3SiCH_2OH]$, hexamethyldisiloxane $[(CH_3)_3SiOSi(CH_3)_3]$, and $[^2H_{18}]$hexamethyldisiloxane $[(CD_3)_3SiOSi(CD_3)_3]$ using *in situ* FTIR absorption spectroscopy and direct air sampling, atmospheric-pressure ionisation tandem mass spectrometry (API MS/MS). The OH radical reactions with organosilicon compounds are slow,[3,4] and hence reactions were initiated by Cl atoms as well as by OH radicals, and rate constants for the reactions of the Cl atom with these organosilicon compounds and for the OH radical with trimethylsilylmethanol were also determined.

## Experimental

### Kinetic Studies

Rate constants for the gas-phase reactions of the Cl atom with tetramethylsilane, trimethylsilylmethanol, hexamethyldisiloxane, and $[^2H_{18}]$hexamethyldisiloxane and for the OH radical with trimethylsilylmethanol were determined using relative rate methods,[3,6] in which the relative decays of the organosilicon compound and a reference organic compound (whose Cl atom or OH radical reaction rate constant is reliably known) were monitored in the presence of Cl atoms or OH radicals. *n*-Butane was used as the reference organic compound for both reaction systems and, provided that the organosilicon compound and *n*-butane were removed solely by reaction with Cl atoms or OH radicals, then

$$\ln\left\{\frac{[\text{organosilicon}]_{t_0}}{[\text{organosilicon}]_t}\right\} = \frac{k_1}{k_2}\ln\left\{\frac{[n\text{-butane}]_{t_0}}{[n\text{-butane}]_t}\right\} \quad (I)$$

where $[\text{organosilicon}]_{t_0}$ and $[n\text{-butane}]_{t_0}$ are the concentrations of the organosilicon compound and *n*-butane, respectively, at time $t_0$, $[\text{organosilicon}]_t$ and $[n\text{-butane}]_t$ are the corresponding concentrations at time $t$, and $k_1$ and $k_2$ are the rate constants for reactions (1) and (2), respectively.

$$\left.\begin{matrix}\text{Cl}\\ \text{OH}\end{matrix}\right\} + \text{organosilicon} \rightarrow \text{products} \quad (1)$$

$$\left.\begin{matrix}\text{Cl}\\ \text{OH}\end{matrix}\right\} + n\text{-butane} \rightarrow \text{products} \quad (2)$$

Experiments were carried out in a 7900 l all-Teflon chamber equipped with two parallel banks of blacklamps at 296 ± 2 K and 740 Torr total pressure of purified air at *ca.* 5% relative humidity. Chlorine atoms were generated by the photolysis of $Cl_2$ at wavelengths >300 nm,[6] and the initial reactant concentrations (in molecule $cm^{-3}$) were: $Cl_2$, $(4.8–7.2) \times 10^{13}$; organosilicon, $(2.5–4.8) \times 10^{13}$; and *n*-butane, $(2.4–4.8) \times 10^{13}$. Irradiations were carried out at 20% of the maximum light intensity for 1–33 min (hexamethyldisiloxane), 5–15 min ($[^2H_{18}]$hexamethyldisiloxane), or 4–15 min (tetramethylsilane and trimethylsilylmethanol).

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths >300 nm,[7] and NO was added to the reactant mixtures to suppress the formation of $O_3$ and hence of $NO_3$ radicals.[7] The initial reactant concentrations (in molecule $cm^{-3}$) were: $CH_3ONO$, $2.1 \times 10^{14}$, NO, $(1.9–2.1) \times 10^{14}$, $(CH_3)_3SiCH_2OH$ and *n*-butane, $(2.3–2.4) \times 10^{13}$ each. Irradiations were carried out at 20% of the maximum light intensity for 12–45 min.

*n*-Butane and the organosilicon compounds were analysed during the reactions by gas chromatography with flame ionisation detection (GC–FID). For the analyses of *n*-butane, tetramethylsilane, hexamethyldisiloxane, and $[^2H_{18}]$hexamethyldisiloxane, gas samples were collected from the chamber in 100 $cm^3$ all-glass, gas-tight syringes and transferred *via* a 1 ml gas sampling loop onto a 30 m DB-5 megabore column in a Hewlett Packard (HP) 5890 GC, initially held at −25 °C and then temperature programmed at 8 °C $min^{-1}$. For the analyses of trimethylsilylmethanol, 100 ml gas samples were collected onto Tenax-TA solid adsorbent, with subsequent thermal desorption at *ca.* 250 °C onto a 30 m DB-5.625 megabore column in an HP 5710 GC, initially held at 0 °C and then temperature programmed at 8 °C $min^{-1}$.

## Product Studies

Experiments were carried out in a 5800 l evacuable, Teflon-coated chamber equipped with an *in situ* multiple reflection optical system interfaced to a Nicolet 7199 FTIR absorption spectrometer, with irradiation being provided by a 24 kW xenon arc lamp filtered through a 0.25 in. Pyrex pane to remove wavelengths $\leqslant 300$ nm, and in a *ca.* 6500 l all-Teflon chamber equipped with two parallel banks of blacklamps and interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric-pressure ionisation tandem mass spectrometer. Reactions were initiated by either OH radicals or Cl atoms, as described above for the kinetic experiments.

### *Evacuable Chamber with FTIR Analysis*

In this chamber, reactants and products were analysed by long pathlength FTIR absorption spectroscopy, using a pathlength of 58 m and a full-width at half-maximum spectral resolution of 0.7 $cm^{-1}$. For all but one experiment with hexamethyldisiloxane, Cl atoms were used to initiate the reactions. The initial reactant concentrations (molecule $cm^{-3}$) were: organosilicon compound, (7–11) × $10^{13}$ and $Cl_2$, (6–8) × $10^{13}$ (or $CH_3ONO$, 3.0 × $10^{14}$ and NO, 7.4 × $10^{13}$). Dry synthetic air (80% $N_2$–20% $O_2$) was normally used as the diluent gas, with a relative humidity of $<3\%$, with three Cl atom-initiated reactions of hexamethyldisiloxane being conducted at 50% relative humidity. All experiments were carried out at 298 K and 740 Torr total pressure. Irradiations of the reactant mixtures were carried out for 30–60 min for the Cl-atom-initiated reactions, and for 54 min for the OH-radical-initiated reaction. FTIR spectra (each comprised of 64 averaged scans with 1.8 min total measurement time) were collected at various times during the irradiations.

For initial experiments with hexamethyldisiloxane carried out in this chamber, gas samples were collected onto Tenax-TA solid adsorbent with subsequent thermal desorption and analysis by GC–FID (HP 5710 GC system described above), combined gas chromatography–mass spectrometry (GC–MS) (HP 5890 GC interfaced to a HP 5970 mass selective detector operating in the scanning mode), and gas chromatography with FTIR detection (GC–FTIR) (HP 5890 GC interfaced to a HP 5965B FTIR detector with FID detection in series).

### *All-Teflon Chamber with API MS/MS Analysis*

The 6500 l chamber was interfaced directly to a PE SCIEX API III MS/MS *via* a 25 mm diameter × *ca.* 75 cm long Pyrex sampling tube, with a sampling rate from the chamber of 20–100 l $min^{-1}$ (typically *ca.* 30 l $min^{-1}$). The positive-ion mode was used throughout these experiments and the chemical ionisation reagents were mainly protonated hydrates ($H_3O^+[H_2O]_n$) produced by a corona discharge in the instrument's atmospheric pressure ionisation (API) chamber.

In the MS scanning mode, mass spectra (each the sum of 10 scans) of the reactants and the reacted mixtures were obtained by the first quadrupole (Q1), with the second and third quadrupoles (Q2 and Q3) being operated in the 'total-ion' rf-only mode. Each scan was acquired over the range 60–300 u using a step size of 0.2 u and a dwell time of 30 ms.

Two MS/MS modes of the API-MS were employed in this work. In the 'daughter'-ion scan mode, the precursor ion was selected by Q1 and the fragment ions were scanned by Q3 after collision-activated dissociation (CAD) in Q2. In the 'parent'-ion scan, the fragment ions were selected by Q3 and matched to their precursors by scanning Q1. Ultra-pure argon was used as the collision gas in the open rf-only Q2 collision cell, with the collision gas thickness of *ca.* 3 × $10^{14}$ molecule $cm^{-2}$. The CAD spectrum of an analyte (sum of 20 scans) was acquired using a step size of 0.2 u and a dwell time of 20 ms.

Experiments were carried out at 296 ± 2 K and 740 Torr total pressure of purified air at *ca.* 5% relative humidity, with the reactions being initiated by both OH radicals and Cl atoms. The initial reactant concentrations (in molecule $cm^{-3}$) were: for OH-radical-initiated reactions: organosilicon compound, (0.88–1.16) × $10^{13}$; $CH_3ONO$, 1.2 × $10^{13}$; and NO, 1.2 × $10^{13}$; for Cl-atom-initiated reactions: organosilicon compound, (0.93–1.23) × $10^{13}$; and $Cl_2$, 1.2 × $10^{13}$. Irradiations were carried out at the maximum light intensity for 2–10 min (OH radical reactions) or 0.5–2.0 min (Cl-atom-initiated reactions), corresponding to up to 9% reaction for the OH radical reactions with tetramethylsilane and hexamethyldisiloxane, up to 55% reaction for the OH radical reaction with trimethylsilylmethanol, up to 35% reaction for the Cl atom reactions with hexamethyldisiloxane and $[^2H_{18}]$hexamethyldisiloxane, and up to 65% reaction for the Cl atom reactions with tetramethylsilane and trimethylsilylmethanol. Since the API MS/MS was often insensitive to the organosilicon reactants, the organosilicon compounds were analysed by GC–FID, as described above.

## Chemicals

The chemicals used, and their stated purities, were: hexamethyldisiloxane (99.5+%) and tetramethylsilane (99.9+%), Aldrich Chemical Company; $[^2H_{18}]$hexamethyldisiloxane (99.8%D), C/D/N isotopes; trimethylsilylmethanol ($\geqslant 97\%$), TCI America; $(CH_3)_3SiOSi(CH_3)_2OH$, Dow-Corning Corporation; and $Cl_2$ ($\geqslant 99.5\%$), NO ($\geqslant 99.0\%$), and *n*-butane ($\geqslant 99.5\%$), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously.[7]

# Results

## Kinetic Studies

The data obtained from the irradiations of $Cl_2$–organosilicon–*n*-butane–air mixtures are plotted in accordance with eqn. (I) in Fig. 1, and the rate constant ratios $k_1/k_2$ for the Cl-atom and OH-radical reactions, obtained from least-squares analyses of the experimental data, are given in Table 1. These rate constant ratios $k_1/k_2$ can be placed on an absolute basis by use of rate constants, $k_2$, for the reactions of *n*-butane with Cl atoms and OH radicals of 1.94 × $10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (±*ca.* 20%)[8] and 2.51 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (±20%), respectively.[2,9] The resulting rate constants, $k_1$, are also given in Table 1 together with the literature rate constants for the Cl atom reaction with tetramethylsilane[10] and for the OH-radical reactions with tetramethylsilane and hexamethyldisiloxane.[3,4]

The isotope effect observed for the Cl-atom reactions with hexamethyldisiloxane and $[^2H_{18}]$hexamethyldisiloxane, of $k_H/k_D = 3.41 \pm 0.25$ (where the error is two least-squares standard deviations), shows that the Cl atom reactions with these organosilicon compounds proceed by H- (or D-) atom abstraction, as expected. This deuterium isotope effect is similar to that for the Cl atom reactions with ethane and

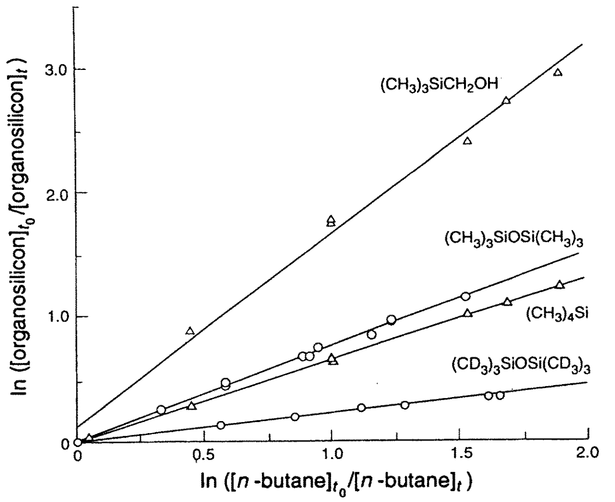


**Fig. 1** Plots of eqn. (I) for the gas-phase reactions of the Cl atom with hexamethyldisiloxane, [$^2H_{18}$]hexamethyldisiloxane, tetramethylsilane and trimethylsilylmethanol, with *n*-butane as the reference compound

[$^2H_6$]ethane,[11–13] consistent with the rate constant per —CH$_3$ group in hexamethyldisiloxane and ethane being similar to within 30%. Our relative rate constant for tetramethylsilane is in good agreement with the absolute rate of Lazarou and Papagiannakapoulos.[10] The significantly higher rate constant for trimethylsilylmethanol than for tetramethylsilane (by a factor of 2.4) indicates that the Cl-atom reaction with trimethylsilylmethanol proceeds mainly ($\gtrsim$ 65%) by H-atom abstraction for the —CH$_2$OH group, and the OH radical reaction rate constants given in Table 1 show that this is also the case for the OH radical reaction with trimethylsilylmethanol, with H-atom abstraction from the —CH$_2$OH group accounting for $\gtrsim$95% of the overall OH radical reaction.

## Product Studies

Unless noted otherwise, the product studies discussed below were carried out at low relative humidities ($\lesssim$5%). Initial experiments on the Cl atom reaction with hexamethyldisiloxane in the 5800 l chamber with GC–FID, GC–MS and GC–FTIR analyses all gave a major product peak identified as (CH$_3$)$_3$SiOSi(CH$_3$)$_2$OH by matching the retention times and spectra with those of an authentic standard. However, the *in situ* FTIR analyses showed that (CH$_3$)$_3$SiOSi(CH$_3$)$_2$OH was not the major product formed from the Cl atom reaction with hexamethyldisiloxane (see below), indicating that (CH$_3$)$_3$SiOSi(CH$_3$)$_2$OH was formed during the Tenax sampling/thermal desorption procedure, and hence that the observations of this product are artifactual. Accordingly, all subsequent experiments were carried out with *in situ* FTIR spectroscopy and API MS/MS detection of reactants and products.

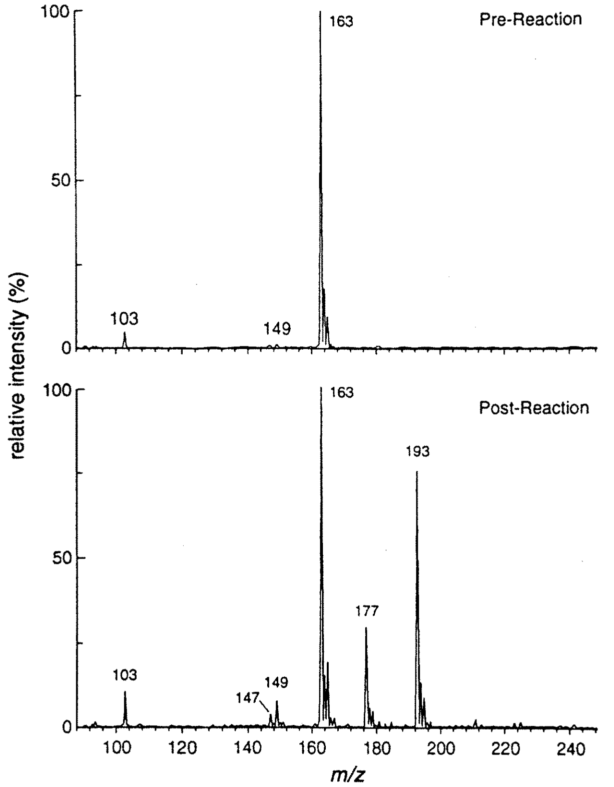


**Fig. 2** API MS spectra before and after irradiation of a Cl$_2$–hexamethyldisiloxane–air mixture for 2.0 min

### *Hexamethyldisiloxane and* [$^2H_{18}$]*Hexamethyldisiloxane*

*API MS/MS Measurements* Fig. 2 compares the API mass spectra before and after reaction of hexamethyldisiloxane with Cl atoms. API MS detection of hexamethyldisiloxane yields a protonated molecular ion [M + H]$^+$ at 163 u [the

**Table 1** Rate constant ratios, $k_1/k_2$, and rate constants, $k_1$, for the gas-phase reactions of Cl atoms and OH radicals with organosilicon compounds at 296 ± 2 K

| | | $k_1/10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | | |
|---|---|---|---|---|
| organosilicon | $k_1/k_2$[a] | this work[b] | literature | ref. |
| | | Cl atom reaction | | |
| (CH$_3$)$_4$Si | 0.644 ± 0.012 | 125 ± 26 | 156[c] | 10 |
| (CH$_3$)$_3$SiCH$_2$OH | 1.52 ± 0.12 | 295 ± 64 | | |
| (CH$_3$)$_3$SiOSi(CH$_3$)$_3$ | 0.753 ± 0.026 | 146 ± 30 | | |
| (CD$_3$)$_3$SiOSi(CD$_3$)$_3$ | 0.221 ± 0.014 | 43 ± 9 | | |
| | | OH radical reaction | | |
| (CH$_3$)$_4$Si | | | 1.00 ± 0.27[d] | 3 |
| | | | 1.28 ± 0.55[d] | 4 |
| (CH$_3$)$_3$SiCH$_2$OH | 8.9 ± 1.5 | 22 ± 6 | | |
| (CH$_3$)$_3$SiOSi(CH$_3$)$_3$ | | | 1.38 ± 0.36[d] | 3 |
| | | | 1.19 ± 0.30[d] | 4 |

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis using rate constants $k_2$ of $k_2$(Cl + *n*-butane) = 1.94 × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (±20%)[8] and $k_2$(OH + *n*-butane) = 2.51 × 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (±20%).[2,9] The indicated errors include the estimated overall uncertainties in the rate constants $k_2$. [c] Calculated at 296 K from the cited Arrhenius expression. [d] At 297 ± 2 K.

isotope peaks due to $^{29}Si$ (5.1% natural abundance) and $^{30}Si$ (3.4% natural abundance) are clearly apparent at 164 and 165 u, respectively]. The product spectrum from the OH radical and Cl atom reactions with hexamethyldisiloxane both showed mass peaks at 177 u and 193 u {the ion peak at 103 u present before and after reaction is due to $[(N_2)_3(H_3O)]^+$ clusters formed from the diluent air}.

A number of API operating parameters were varied during these experiments, including, for example, the orifice (OR) voltage which affects the degree of fragmentation of the analyte prior to entering the quadrupole assembly. While the relative intensities of the 177 and 193 u reaction product peaks changed significantly, both ion peaks were always present. However, parent-ion spectra of the 177 u peak and daughter-ion spectra of the 193 u peak showed that some, if not all, of the 177 u peak arose from fragmentation of the 193 u ion. As discussed below, the data from the $[^2H_{18}]$hexamethyldisiloxane reactions suggest that only one product is observed and that the 177 u peak is entirely due to fragmentation of the product prior to entering Q1.

The API MS spectrum of an authentic sample of $(CH_3)_3SiOSi(CH_3)_2OH$ displayed ion peaks at 163 u ($[M - H]^+$) and 165 u ($[M + H]^+$). The peak at 165 u in the post-reaction spectrum (Fig. 2) is slightly more intense than expected if it were due entirely to the $^{30}Si$ isotope abundance from hexamethyldisiloxane, and may indicate the formation of a small amount of $(CH_3)_3SiOSi(CH_3)_2OH$.

Experiments with $[^2H_{18}]$hexamethyldisiloxane gave analogous results to the hexamethyldisiloxane experiments, with a product ion at 209 u being observed for the Cl-atom-initiated reaction (Fig. 3). Parent-ion spectra of the 190 u peak and daughter-ion spectra of the 209 u peak indicated that the ion peak at 190 u was a fragment ion of the 209 u ion.

The major products from the OH-radical and Cl-atom reactions with hexamethyldisiloxane and from the Cl atom reaction with $[^2H_{18}]$hexamethyldisiloxane are then those yielding 193 and 209 u ions, respectively. If the 193 u ion from hexamethyldisiloxane is the $[M + H]^+$ ion, then this product has a molecular weight of 192 and a formula of $C_6H_{16}Si_2O_3$. The 209 u peak from $[^2H_{18}]$hexamethyldisiloxane then corresponds to the $[M + H]^+$ ion and a reaction product of molecular formula $C_6D_{16}Si_2O_3$. Since we observed, in agreement with previous studies,[14,15] that D atoms on —OD groups readily and rapidly undergo D/H exchange with the water vapour present in the chamber (at *ca.* 5% relative humidity), these formulae suggest that an —OH (or —OD) group is not present in the major product of the hexamethyldisiloxane and $[^2H_{18}]$hexamethyldisiloxane reactions. These observations indicate that the products giving rise to the 193 and 209 u ions from the hexamethyldisiloxane and $[^2H_{18}]$hexamethyldisiloxane reactions are $(CH_3)_3SiOSi(CH_3)_2OCHO$ and $(CD_3)_3SiOSi(CD_3)_2OCDO$, respectively.

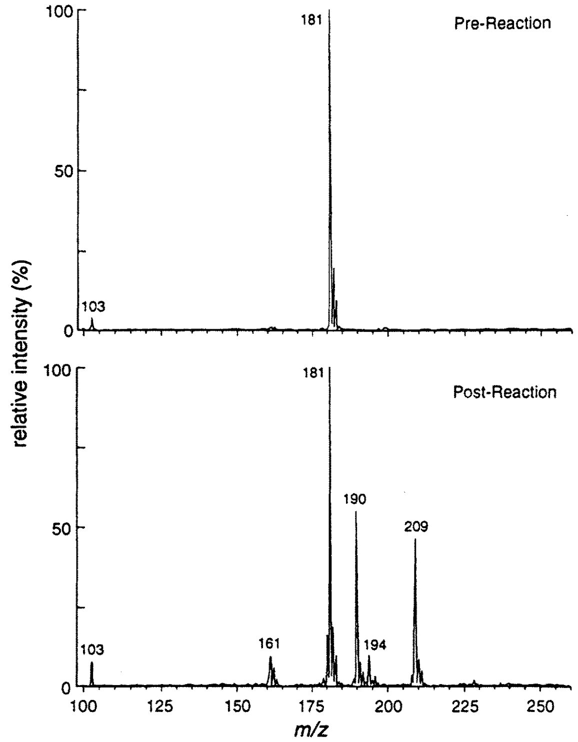


**Fig. 3** API MS spectra before and after irradiation of a $Cl_2$–$[^2H_{18}]$hexamethyldisiloxane–air mixture

If the 177 u ion peak from hexamethyldisiloxane is interpreted as a protonated molecular ion, the product would have a molecular weight of 176 and a formula of $C_6H_{16}Si_2O_2$, most likely the aldehyde $(CH_3)_3SiOSi(CH_3)_2CHO$. The corresponding deuteriated analogue from the reaction of $[^2H_{18}]$hexamethyldisiloxane would be $(CD_3)_3SiOSi(CD_3)_2CDO$ giving an $[M + H]^+$ ion peak at 193 u. The lack of a significant ion peak at 193 u indicates that only one product, and not the aldehyde $(CD_3)_3SiOSi(CD_3)_2CDO$, is being observed. Therefore, the 177 u peak from hexamethyldisiloxane and the 190 u peak from $[^2H_{18}]$hexamethyldisiloxane are best interpreted as a loss of $CH_4$ from the 193 u ion formed from hexamethyldisiloxane and a loss of $CD_3H$ from the 209 u ion formed from $[^2H_{18}]$hexamethyldisiloxane, in agreement with the daughter-ion and parent-ion spectra.

The deuteriated analogue to $(CH_3)_3SiOSi(CH_3)_2OH$ is expected to be $(CD_3)_3SiOSi(CD_3)_2OH$, where the alcohol —OD group has exchanged with water in the chamber, with an $[M + H]^+$ ion peak at 180 u. The post-reaction spectrum (Fig. 3) again does not rule out the formation of a small amount of the silanol product (see also below).

*FTIR Measurements* Fig. 4A shows the IR spectrum of initial concentrations of hexamethyldisiloxane and $Cl_2$ of $7.2 \times 10^{13}$ molecule cm$^{-3}$ and $8.2 \times 10^{13}$ molecule cm$^{-3}$, respectively, during a photolysis experiment in the 5800 l evacuable chamber. Fig. 4B is the spectrum recorded after 6

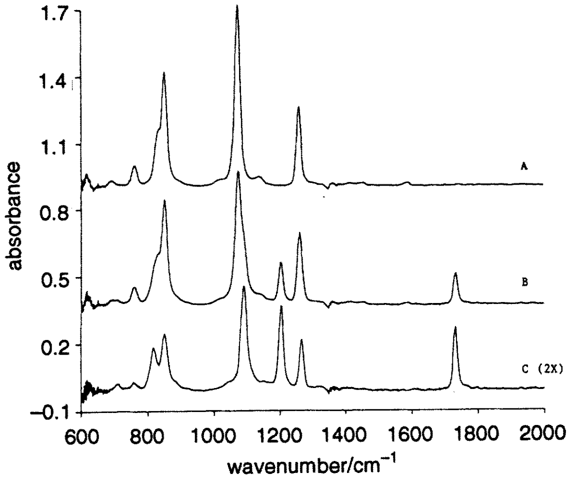


**Fig. 4** IR absorption spectrum from the photolysis of a $Cl_2$–hexamethyldisiloxane–air mixture. A, Initial hexamethyldisiloxane, $7.2 \times 10^{13}$ molecule cm$^{-3}$. B, Reaction mixture after 6 min of irradiation (33% reaction). C, From B after subtraction of unreacted hexamethyldisiloxane. The ordinates of the upper plots are offset for clarity.

min of irradiation, which resulted in 33% conversion of the initial hexamethyldisiloxane. After subtraction of the absorptions by the remaining hexamethyldisiloxane from Fig. 4B, the absorption bands of the major products are shown in Fig. 4C. Fig. 4C clearly shows the presence of a carbonyl group, with the C=O stretch frequency at 1733 $cm^{-1}$. It is most likely that at this stage of the reaction (*i.e.* $\leqslant$33% conversion) the residual spectrum shown in Fig. 4C is due largely to one product, since residual spectra from earlier reaction times appear similar and the intensity of the 1733 $cm^{-1}$ band during this period is linear with respect to the amount of hexamethyldisiloxane consumed. A comparison of the product spectrum with a calibrated vapour-phase spectrum of $(CH_3)_3SiOSi(CH_3)_2OH$ (Fig. 5) indicates that $(CH_3)_3SiOSi(CH_3)_2OH$ could be, at most, only a very minor product, and based on its weak but distinct absorption band at 918 $cm^{-1}$ its upper limit yield from the photolysis of the $Cl_2$–hexamethyldisiloxane–air mixture was determined as $\leqslant$4%.

The C=O-group-containing product which is most consistent with the product of molecular weight 192 u indicated by the API MS/MS results and with the functional group frequencies evident in Fig. 4C is the formate ester $(CH_3)_3SiOSi(CH_3)_2OCHO$. The strong identifying features in the IR spectrum of Fig. 4C are the pair of bands at 1733 $cm^{-1}$ (C=O stretch) and 1204 $cm^{-1}$ (C—O stretch).[16,17] An increase in the intensities of peaks at 818 and 1206 $cm^{-1}$ in the later stages of the photolysis was observed, indicating the formation of additional, unknown, product(s). The formation of these unknown product(s) was accompanied by the formation of formic acid [HC(O)OH] with formation yields of 3.3% and 11% at $t = 12$ and 26 min, respectively.

In parallel experiments conducted in synthetic air with 50% relative humidity, the Cl-atom-initiated reaction of hexamethyldisiloxane formed the same ester product, $(CH_3)_3SiOSi(CH_3)_2OCHO$, as in dry air, but with a yield *ca.* 80% of that in dry air. As in dry air, the yield of HC(O)OH in humidified air was non-linear with respect to hexamethyldisiloxane consumption. However, in air at 50% relative humidity the HC(O)OH yield was much higher than in dry air, rising to *ca.* 30% at 50% hexamethyldisiloxane consumed compared with a *ca.* 3% yield in dry air for the same amount of hexamethyldisiloxane reacted. The other (minor) product formed directly from the Cl atom reaction was not $(CH_3)_3SiOSi(CH_3)_2OH$.

In the dark at *ca.* 50% relative humidity, the ester $(CH_3)_3SiOSi(CH_3)_2OCHO$ reacted to form $(CH_3)_3SiOSi(CH_3)_2OH$, with 48% conversion over a 1 h time period. This dark reaction of the ester to form the silanol $(CH_3)_3SiOSi(CH_3)_2OH$ in humid air is in contrast to the situation in dry air where negligible conversion (<3%) was observed over the same period (1 h). The conversion of the ester to the silanol was accompanied by HC(O)OH formation, with the yield of HC(O)OH being *ca.* 1 : 1 with respect to ester consumption during the early part of the dark reaction but with the HC(O)OH yield being much reduced at later stages of the reaction, presumably due to HC(O)OH decay to the chamber walls. The formation of gas-phase HC(O)OH indicates that the hydrolysis is a homogeneous gas-phase reaction.

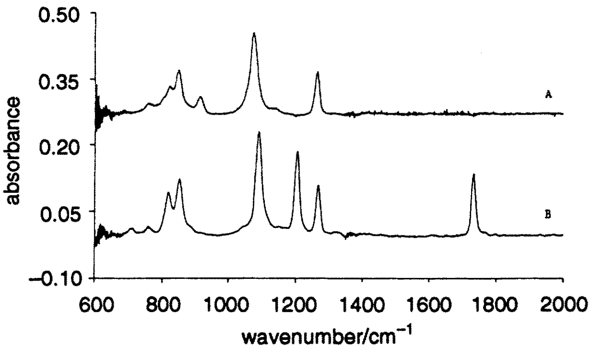


**Fig. 5** Comparison of A, the IR spectrum of an authentic sample of $(CH_3)_3SiOSi(CH_3)_2OH$ ($2.4 \times 10^{13}$ molecule $cm^{-3}$) with B, the IR spectrum of $(CH_3)_3SiOSi(CH_3)_2OCHO$ (the same spectrum as in Fig. 4C). The ordinates of the upper plots are offset for clarity.

$$(CH_3)_3SiOSi(CH_3)_2OCHO + H_2O \rightarrow (CH_3)_3SiOSi(CH_3)_2OH + HC(O)OH$$

Using the same reaction conditions as employed for hexamethyldisiloxane, a mixture of $7.2 \times 10^{13}$ molecule $cm^{-3}$ of $[^2H_{18}]$hexamethyldisiloxane and $8.2 \times 10^{13}$ molecule $cm^{-3}$ of $Cl_2$ in air was irradiated in the 5800 l chamber. The analogous formation of the corresponding product ester from $[^2H_{18}]$hexamethyldisiloxane was observed, with the pair of bands for the postulated main product $(CD_3)_3SiOSi(CD_3)_2OCDO$ occurring at 1701 and 1198 $cm^{-1}$. Minor changes in the product spectra that could be attributed to formation of additional product(s) were seen during the course of the reaction. Analogous to the formation of HC(O)OH from hexamethyldisiloxane, the formation of DC(O)OH from $[^2H_{18}]$hexamethyldisiloxane as a minor product was indicated by the occurrence and development of a band at 1760 $cm^{-1}$ (C=O stretch), this being intermediate between the corresponding absorption of HC(O)OH at 1770 $cm^{-1}$ and that of DC(O)OD at 1742 $cm^{-1}$.[18] It is possible that DC(O)OD was initially formed followed by rapid —OD to —OH exchange.

### *Tetramethylsilane and Trimethylsilylmethanol*

*API MS/MS Measurements* The pre-reaction spectrum of tetramethylsilane is shown in the upper portion of Fig. 6, showing no 89 u $[M + H]^+$ parent ion prior to reaction. The ion peak at 73 u is a water cluster ion and the 75 and 103 u ions are nitrogen cluster ions formed from the diluent air. The post-reaction spectra of the Cl-atom- (Fig. 6) and OH-radical-initiated reactions of tetramethylsilane showed the same product ions. The 119 u ion is attributed to the $[M + H]^+$ ion of $(CH_3)_3SiOCHO$, the proposed product of the Cl-atom and OH-radical-initiated reactions of tetramethylsilane. The daughter-ion spectrum of the 119 u ion showed fragments at 73, 75 (minor), and 103 u. The 75 u peak was also a mass fragment of the 103 u $[(CH_3)_2SiOCHO]^+$ ion {possibly due to loss of CO and with the 75 u ion being $[(CH_3)_2SiOH]^+$}. The only significant ion peak not a potential fragment of the 119 u $[M + H]^+$ ion of $(CH_3)_3SiOCHO$ is that at 91 u, which could be the $[M + H]^+$ ion of $(CH_3)_3SiOH$.

The pre-reaction spectrum of trimethylsilylmethanol is shown in the upper portion of Fig. 7, exhibiting, in addition to the nitrogen and water cluster ions at 75 and 73 u, respectively, the $[M + H]^+$, $[M + H - H_2O]^+$, and $[M + H - CH_4]^+$ ions of trimethylsilylmethanol at 105, 87 and 89 u, respectively. The post-reaction spectrum of the Cl-atom-initiated reaction of $(CH_3)_3SiCH_2OH$ (Fig. 7) shows the same product-ion peaks as the tetramethylsilane reaction, suggesting that the Cl-atom- and OH-radical-initiated reactions of tetramethylsilane and $(CH_3)_3SiCH_2OH$ lead to an identical product.

*FTIR Measurements* The photolysis of tetramethylsilane ($7.2 \times 10^{13}$ molecule $cm^{-3}$) and $Cl_2$ ($8.2 \times 10^{13}$ molecule $cm^{-3}$) in air is illustrated in Fig. 8. The only major product

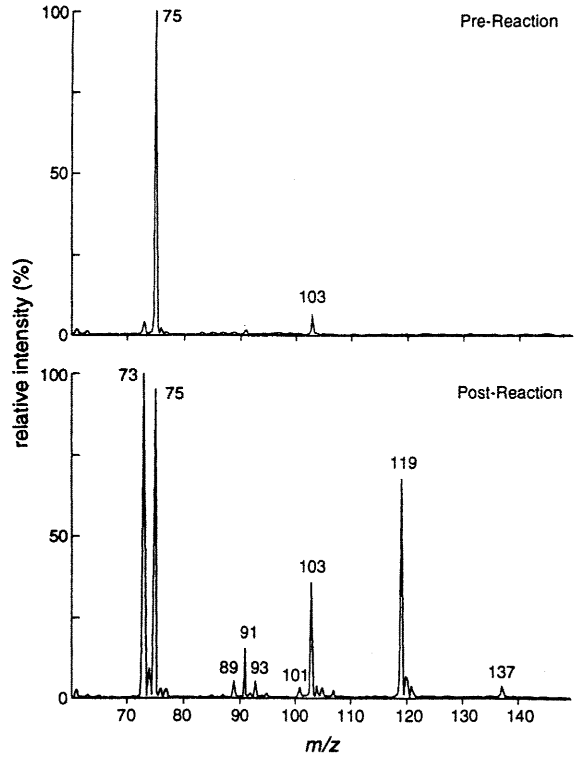


**Fig. 6** API MS spectra of a $Cl_2$–tetramethylsilane–air mixture before (top) and after (bottom) irradiation for 2.0 min

observed has a pair of distinct absorption bands at 1730 and 1204 $cm^{-1}$ (Fig. 8C) which are characteristic of esters.[16,17] Thus, consistent with the observation by API MS/MS of the dominant 119 u ion peak of the product, and consistent with the analogous observations for hexamethyldisiloxane, the IR spectrum of Fig. 8C is assigned to the formate ester $(CH_3)_3SiOCHO$.

An irradiation experiment with a mixture of trimethylsilylmethanol and $Cl_2$ in air was conducted with the same initial concentrations as employed for the experiment with tetramethylsilane. The IR spectrum of the product of this reaction was identical to that shown in Fig. 8C for the tetramethylsilane reaction. These data show that $(CH_3)_3SiOCHO$ is the major product formed from both tetramethylsilane and trimethylsilylmethanol. It was also observed that for the same amounts of organosilicon compound reacted, the yield of $(CH_3)_3SiOCHO$ from trimethylsilylmethanol was only 85–90% of the yield (assumed to be *ca.* 100%) from tetramethylsilane. HC(O)OH was formed from trimethylsilylmethanol, but was not detected in the experiment with tetramethylsilane.

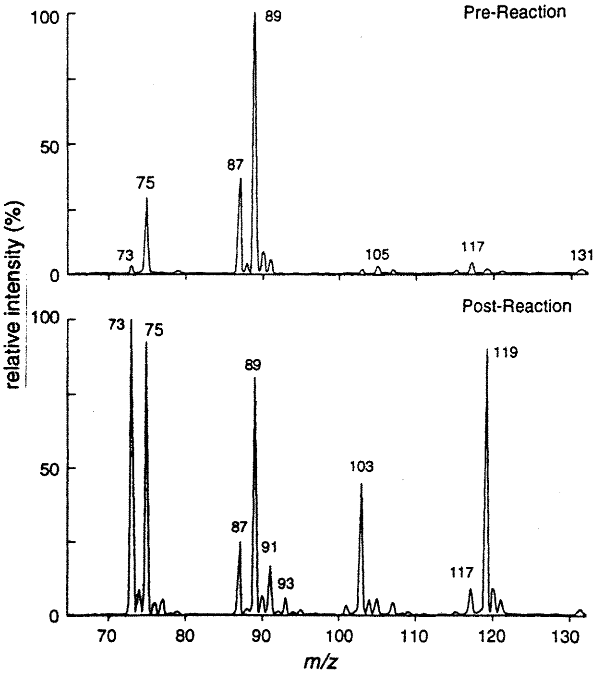


**Fig. 7** API MS spectra of a $Cl_2$–trimethylsilylmethanol–air mixture before (top) and after (bottom) irradiation

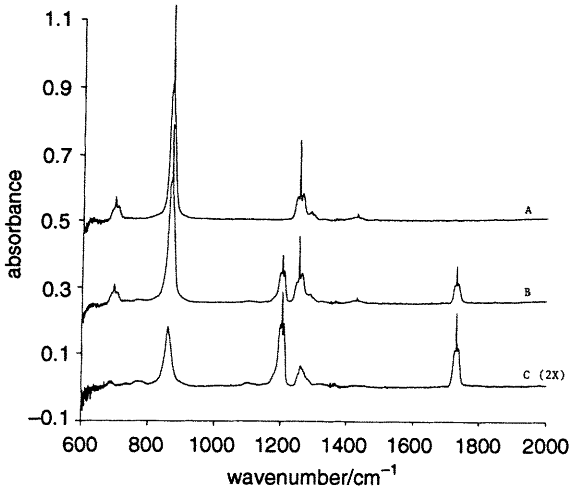


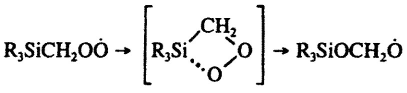
**Fig. 8** IR spectra from the photolysis of a $Cl_2$–tetramethylsilane–air mixture. A, Initial tetramethylsilane ($7.2 \times 10^{13}$ molecule $cm^{-3}$). B, Reaction mixture after 7 min of irradiation (25% reaction). C, From B after subtraction of unreacted tetramethylsilane. The ordinates of the upper plots are offset for clarity.

## Discussion

Our *in situ* product data are consistent with the formation of the formate esters as the major products initially formed from the four organosilicon compounds studied, with $(CH_3)_3SiOSi(CH_3)_2OCHO$ and $(CD_3)_3SiOSi(CD_3)_2OCDO$ being formed from hexamethyldisiloxane and $[^2H_{18}]$hexamethyldisiloxane, respectively, and $(CH_3)_3SiOCHO$ being formed from both tetramethylsilane and trimethylsilylmethanol. The initial Cl-atom or OH-radical reaction proceeds by H- (or D-) atom abstraction from the C—H or C—D bonds.

$$Cl + R_3SiCH_3 \rightarrow HCl + R_3Si\dot{C}H_2$$

By analogy with the reactions of $O_2$ with the $SiH_3$ radical[19–24] and alkyl and substituted-alkyl radicals,[2] it is expected that the $R_3Si\dot{C}H_2$ radical rapidly adds $O_2$ to form the $R_3SiCH_2O\dot{O}$ peroxy radical. It is possible that the $R_3SiCH_2O\dot{O}$ radical then undergoes a rearrangement to form the $R_3SiOCH_2\dot{O}$ radical,

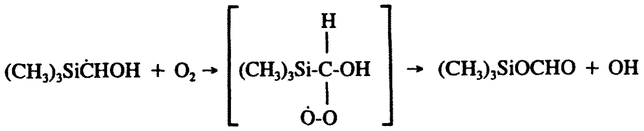


$$R_3SiCH_2O\dot{O} \rightarrow [R_3Si(CH_2)(O)O] \rightarrow R_3SiOCH_2\dot{O}$$

which then reacts with $O_2$ to form the observed formate ester product.

$$R_3SiOCH_2\dot{O} + O_2 \rightarrow R_3SiOCHO + HO_2$$

Our kinetic data (Table 1 and text) show that trimethylsilylmethanol reacts *via* H-atom abstraction from the $-CH_2OH$ group (and presumably from the C—H bonds rather than the O—H bond) to form the $(CH_3)_3Si\dot{C}HOH$ α-hydroxy radical, which is then expected to react with $O_2$.[2] Our product data show that this reaction gives rise to the same product as formed from tetramethylsilane, possibly *via*



$$(CH_3)_3Si\dot{C}HOH + O_2 \rightarrow \left[(CH_3)_3Si\text{-}\overset{H}{\underset{\dot{O}\text{-}O}{C}}\text{-}OH\right] \rightarrow (CH_3)_3SiOCHO + OH$$

While the silanols [for example, $(CH_3)_3SiOSi(CH_3)_2OH$ from hexamethyldisiloxane] are not the initially formed products, the observed homogeneous gas-phase hydrolysis of the initially formed formate esters [with a hydrolysis lifetime of $(CH_3)_3SiOSi(CH_3)_2OCHO$ of *ca.* 1.5 h at 298 K and 50% relative humidity] means that in the atmosphere the 'second-generation' and chemically longer-lived silanols (with calculated tropospheric lifetimes of $(CH_3)_3SiOH$ and $(CH_3)_3SiOSi(CH_3)_2OH$ with respect to reaction with the OH radical[2,4] of *ca.* 4 and *ca.* 8 days, respectively) may well be the important products.

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