Atmospheric Degradation of Volatile Methyl-Silicon Compounds

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The current widespread use of poly(dimethylsiloxane)s (PDMS) in a broad range of applications leads to their release into soil environments where they degrade to monomeric products, primarily dimethylsilanediol, most of which enter the atmosphere by volatilization. The major degradation pathway of volatile organosilicon compounds in the atmosphere is expected to be a reaction with hydroxyl (OH) radicals. In this work, the kinetics of the gas-phase reactions of dimethylsilanediol, trimethylsilanol, and tetramethylsilane with the OH radical were measured using a relative rate method which employed the N₂H₄ + 0₃ reaction as a nonphotolytic source of OH radicals, with analysis by Fourier transform infrared (FT-IR) spectroscopy in a 5870 L chamber. The measured values of the OH radical reaction rate constants (cm³ molecule⁻¹ s⁻¹) at 298 \pm 2 K are as follows: dimethylsilanediol, (8.1 \pm 1.0) \times 10⁻¹³; trimethylsilanol, (7.2 \pm 0.8) \times 10⁻¹³; and tetramethylsilane, (8.5 \pm 0.9) \times 10⁻¹³. These values lead to an estimate of tropospheric lifetimes with respect to reaction with the OH radical of ca. 15 days for these organosilicon compounds. FT-IR spectroscopy and atmospheric pressure ionization mass spectrometry (API-MS) were employed to analyze the products of OH radical- and Cl atominitiated photooxidations of dimethylsilanediol and trimethylsilanol. Infrared signatures of the probable formate ester intermediate products from both silanols were detected. API-MS analyses indicated the formation of methylsilanetriol from dimethylsilanediol, of both dimethylsilanediol and methylsilanetriol from trimethylsilanol, and of the corresponding intermediate formate esters. Possible reaction mechanisms are discussed.

Introduction

The rapid growth of the silicone industry and resulting widespread use of poly(dimethylsiloxane)s (PDMS) [(CH₃)₃-SiO[Si(CH₃)₂O]_nSi(CH₃)₃] in a broad range of industrial, healthcare, and consumer applications has resulted in the release of these substances into the environment. An overview of the scope of usage and relative environmental loadings of commercial silicon materials, including PDMS, and the possible pathways of their entry into the environment is given by the recent articles of Allen et al. (1) and Chandra et al. (2). Fendinger et al. (3) discuss the partitioning of PDMS

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between environmental compartments (air, soil, and water), the processes which influence their concentrations, and their ultimate fate. The predicted mass flow of PDMS in the United States is predominantly to the soil environment as a component of sludge (*3*), where they undergo soil-catalyzed hydrolysis to produce dimethylsilanediol as the major product (*3*). The major fraction of the dimethylsilanediol produced in soil is expected to migrate into the atmosphere, since in several types of soil its volatilization has been shown to dominate over biodegradation (*4*). Hence, a knowledge of the rate and mechanism by which dimethylsilanediol is transformed in the atmosphere is required for a complete assessment of the impact of PDMS release into the environment.

Reaction with the hydroxyl (OH) radical has been shown to be the main atmospheric degradation pathway for a number of volatile methyl siloxanes and silanols (*5*), and OH radical reaction rate constants for a number of organosilicon compounds, including $(CH_3)_3$ SiOH and $(CH_3)_3$ SiOSi- $(CH_3)_2$ OH, have been reported (*5*–*9*). However, no similar measurement has been carried out for dimethylsilanediol. Hence, in this work we have measured the rate constant for reaction of the OH radical with dimethylsilanediol and carried out similar measurements for tetramethylsilane (to test the experimental technique) and trimethylsilanol. The products of the atmospheric reactions of silylalkoxy radicals, formed after H-atom abstraction by OH radicals and/or Cl atoms from dimethylsilanediol and trimethylsilanol, were also investigated.

Experimental Section

Experiments were carried out in two reaction chambers: a 5870 L evacuable, Teflon-coated chamber containing an in situ multiple-reflection optical system interfaced to a Nicolet 7199 Fourier transform infrared (FT-IR) absorption spectrometer, with irradiation being provided by a 24 kW xenon arc lamp filtered through a 6.4 mm thick Pyrex pane to remove wavelengths <300 nm and a 7500 L Teflon chamber equipped with two parallel banks of blacklamps and interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS). Both chambers are fitted with Teflon-coated fans to ensure rapid mixing of reactants during their introduction to the chambers.

Kinetic Studies. Kinetic experiments were carried out in the 5870 L chamber at 298 ± 2 K and 740 Torr of dry synthetic air (80% N₂ + 20% O₂), with analysis by FT-IR absorption spectroscopy. The OH radical rate constants of dimethylsilanediol, trimethylsilanol, and tetramethylsilane were measured using a relative rate method which employed the reaction of hydrazine with ozone as the OH radical source (10) and dimethyl ether as the reference compound. The use of the fast $N_2H_4 + O_3$ reaction (10) to generate OH radicals enabled short-duration experiments to be carried out which allowed corrections for the autodecay of dimethylsilanediol to be reliably made (cf. later). For these experiments, aliquots of hydrazine were introduced (with mixing) to O₃-organosilicon-dimethyl ether-air mixtures, with the $N_2H_4 + O_3$ reaction at each stage being essentially complete during the 2-3 min mixing time. Typical initial concentrations (molecule cm^{-3}) were as follows: organosilicon compound, (1.2–1.8) \times 10¹⁴; dimethyl ether, 1.8 \times 10¹⁴; and O₃, 4.8 \times 10¹⁴; with each N₂H₄ aliquot corresponding to a concentration in the chamber of $(1.0-2.4) \times 10^{14}$ molecule cm⁻³. The decay rates of the organosilicon compounds in the O₃-organosilicondimethyl ether-air mixtures were monitored by FT-IR

absorption spectroscopy for 20-60 min prior to the introduction of N₂H₄. The kinetic experiments consisted of recording spectra of the initial mixture and of the reaction mixture after each N₂H₄ injection. In these experiments, and those for product studies, infrared spectra were recorded using a path length of 62.9 m, a full-width at half-maximum resolution of 0.7 cm⁻¹, and a 2-min averaging time (64 scans/ interferograms).

The applicability of the $N_2H_4 + O_3$ reaction as a nonphotolytic source of OH radicals for OH rate constant measurements has previously been validated (10, 11). Where the only loss processes for the organosilicon and the dimethyl ether reference compound are due to their reactions with OH radicals

organosilicon + OH
$$\rightarrow$$
 products (1)

$$(CH_3)_2O + OH \rightarrow \text{products}$$
 (2)

then

$$\begin{aligned} &\ln\{[\operatorname{organosilicon}]_{t0} / [\operatorname{organosilicon}]_t\} = \\ & (k_1 / k_2) \ln\{[(\operatorname{CH}_3)_2 \operatorname{O}]_{t0} / [(\operatorname{CH}_3)_2 \operatorname{O}]_t\} \ \ \text{(I)} \end{aligned}$$

where $[organosilicon]_{t0}$ and $[(CH_3)_2O]_{t0}$ are the organosilicon and dimethyl ether concentrations at time t_{0} , respectively; $[organosilicon]_t$ and $[(CH_3)_2O]_t$ are the corresponding concentrations at time t; and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

Product Studies. Chlorine atom-initiated photooxidations of dimethylsilanediol and trimethysilanol were conducted in both reaction chambers. The experiments in the 5870 L chamber with FT-IR analysis were carried out by photolyzing mixtures of the organosilicon compound and Cl₂ in dry synthetic air at 298 \pm 2 K and 740 Torr. The initial organosilicon and Cl₂ concentrations were $(1.2-1.8)\times10^{14}$ and $(2.4-5.1)\times10^{14}$ molecule cm⁻³, respectively. Irradiations were carried out continuously for 20–40 min, with spectra being recorded every 5 min. Prior to the above runs, an exploratory photolysis of an air mixture of dimethylsilanediol, CH₃ONO, and NO with initial concentrations (molecule cm⁻³) of 1.8 \times 10¹⁴, 2.4 \times 10¹⁴, and 1.8 \times 10¹⁴, respectively, was carried out.

The experiments conducted in the 7500 L Teflon chamber with API-MS analysis consisted of irradiations of each of dimethylsilanediol and trimethylsilanol with Cl_2 at 298 \pm 2 K and 740 Torr total pressure of purified air at ca. 5% relative humidity. The initial organosilicon and Cl₂ concentrations were $(2-4) \times 10^{13}$ and 1.2×10^{14} molecule cm⁻³, respectively. Prior to these experiments, an exploratory photolysis of a mixture of dimethylsilanediol with CH₃ONO and NO was also conducted with initial concentrations (molecule cm⁻³) of 4 \times 10¹³, 2.4 \times 10¹⁴, and 1.8 \times 10¹⁴, respectively. The mixtures were irradiated for periods of 0.5-1.0 min at 100% of the maximum light intensity. The chamber contents were sampled through a 25 mm diameter \times 75 cm length Pyrex tube at \sim 20 L min⁻¹ directly into the API mass spectrometer source. MS (scanning) and MS/MS [with collision activated dissociation (CAD)] analyses of the mixtures were performed prior to irradiation and after each illumination period (12). The instrument was operated in the positive ion mode, and details of the operation of the API-MS under these conditions have been described previously (12).

Chemicals. The chemicals used, and their stated purities, were as follows: tetramethylsilane (99.9+%), dimethoxy-dimethylsilane (95%), and methoxytrimethylsilane (99%), Aldrich Chemical Co.; Cl₂ (\geq 99.5%) and NO (\geq 99.0%), Matheson Gas Products. CH₃ONO was prepared as described by Taylor et al. (*13*) and stored under vacuum at liquid nitrogen temperature. O₃ was produced in a Welsbach T-408

generator at a precalibrated settings of voltage and input flow of high purity O₂ (Puritan-Bennett Corp., 99.994%).

Dimethylsilanediol was prepared by a procedure similar to that described by Kantor (14). All vessels employed in the preparation, handling, and storage of the product were acid-washed and rinsed thoroughly before use to minimize condensation reactions known to be catalyzed by traces of acids and bases (14). The infrared spectrum of the solid prepared as a Nujol mull agreed with that reported by Kantor (14), and API-MS analysis of a vapor sample showed the presence of the protonated $[M + H]^+$ ion at 93 u.

Trimethylsilanol was prepared by heating a mixture of methoxytrimethylsilane $[(CH_3)_3SiOCH_3]$ (15 g) and distilled water (50 mL) at ca. 320 K with vigorous stirring for 4 h in a similar reflux setup used to prepare dimethylsilanediol and with the same attention given to acid-washing the reaction and storage vessels. The organic phase was separated, and a top fraction, presumably containing mostly methanol, was distilled off and discarded. The remaining fraction was stored under vacuum at 77 K. The IR spectrum of trimethylsilanol vapor from this sample is presented below; an API-MS analysis showed the presence of a protonated $[M + H]^+$ ion at 91 u. Vapors obtained directly from this sample at room temperature typically showed a molar composition of 83% trimethylsilanol, 7% hexamethyldisiloxane, and 10% methanol as deduced from the IR calibrations of the latter two components and the measured total vapor pressure of the sample. The trimethylsilanol contents of these vapor samples were significantly higher than the 33-35% reported by Kantor (14) for the trimethylsilanol-hexamethyldisiloxane azeotrope which was obtained by ether extraction and distillation of the organic layer.

Except for dimethylsilanediol, the reactants were measured into calibrated 2 L- and 5 L-Pyrex bulbs with an MKS Baratron capacitance manometer (100 Torr sensor) and flushed with a stream of nitrogen with mixing into the chamber. Dimethylsilanediol was weighed into a stopcocked Pyrex vial (acid-washed prior to use) which was then connected to the chamber, and the sample was introduced with heating and flushing with nitrogen gas.

Results

Infrared Spectra and Dark Decay in the 5870 L Chamber. Dimethylsilanediol. Vapor samples of (CH₃)₂Si(OH)₂ introduced into the 5870 L chamber showed the initial presence and growth of another component with time. Figure 1A is the spectrum of a mixture of this product and (CH₃)₂Si(OH)₂ which was recorded 61 min after introduction of a vapor sample (total concentration of 1.3×10^{14} molecule cm⁻³) into the evacuated chamber (<5 Torr N₂ diluent) maintained at room temperature. From the known amount of the sample and the differences between the spectra with time, the spectrum of the "decay" product(s) at t = 61 min and of dimethylsilanediol at t = 0 were derived and are shown in Figure 1B,C, respectively. (The concentration shown for dimethylsilanediol in Figure 1C was derived assuming that all components remained in the gas phase.) The OH stretch frequency of $(CH_3)_2Si(OH)_2$ is at 3735 cm⁻¹ (not included in Figure 1). The Q-branch feature at 1265.1 cm⁻¹ allowed accurate monitoring of the (CH₃)₂Si(OH)₂ concentration despite its overlap with a broader absorption band by the "decay" product(s). Figure 1D shows the spectrum of the solid in Nujol mull (Nujol bands subtracted), and, as noted above, the band positions agree with those reported by Kantor (14).

The disappearance of $(CH_3)_2Si(OH)_2$ was faster in the evacuated chamber than in the presence of one atmosphere of air. In both cases, however, the decays could be described as first order in $(CH_3)_2Si(OH)_2$, with observed decay rates of



FIGURE 1. Vapor-phase IR spectra of (A) (CH₃)₂Si(OH)₂ sample after 61 min in evacuated chamber, (B) "decay" product(s), and (C) "pure" (CH₃)₂Si(OH)₂ derived from the dark decay experiment. (D) Spectrum of solid (CH₃)₂Si(OH)₂ sample in Nujol mull (Nujol bands subtracted). Number in parentheses is concentration in molecule cm⁻³.



FIGURE 2. (A) IR spectrum of vapor from a trimethylsilanol sample showing the presence of methanol and hexamethyldisiloxane (HMDS) as impurities. (B) $(CH_3)_3SiOH$ spectrum from (A) after subtraction of the impurity absorptions. (C) $Si(CH_3)_4$ spectrum. Numbers in parentheses are concentrations in 10^{13} molecule cm⁻³.

0.015 min⁻¹ at reduced pressure (<5 Torr N₂ diluent) and 0.0022 min⁻¹ for the next experiment which was carried out in 1 atm of air. During the prereaction stages of the kinetic experiments described below, however, varying (and higher) dark decay rates of (CH₃)₂Si(OH)₂ in 1 atm of diluent air were obtained.

Trimethylsilanol and Tetramethylsilane. The spectrum of a vapor sample from the $(CH_3)_3SiOH$ preparation with a molar composition of 83% $(CH_3)_3SiOH$, 7% $(CH_3)_3SiOSi(CH_3)_3$, and 10% CH_3OH is shown in Figure 2A. The spectrum of $(CH_3)_3SiOH$ with the absorption bands of impurities subtracted is shown in Figure 2B. The OH stretch frequency is found at 3735 cm⁻¹ (not illustrated). The sharp Q-branch at 1258.4 cm⁻¹ was employed for FT-IR analysis. Trimethylsilanol samples in the chamber at atmospheric pressure of



FIGURE 3. Least-squares plot of eq I for the gas-phase reaction of OH radicals with dimethylsilanediol, with dimethyl ether as reference compound. The measured (CH₃)₂Si(OH)₂ concentrations have been corrected to account for the (CH₃)₂Si(OH)₂ "prereaction" losses using the (CH₃)₂Si(OH)₂ decay rates measured prior to addition of N₂H₄ (see text).

air and 298 K showed no measurable dark decay as monitored by FT-IR spectroscopy over periods of 30-40 min.

No measurable dark decay of $Si(CH_3)_4$ in 1 atm of air diluent at 298 K was observed. The sharp Q-branch feature of its spectrum at 1255.0 cm⁻¹ (Figure 2C) was employed for FT-IR analysis.

Kinetic Studies. Initial experiments with $(CH_3)_2Si(OH)_2$ using the photolysis of CH_3ONO as the source of OH radicals resulted in acutely nonlinear plots of eq I, with the curvature indicating a marked acceleration of the $(CH_3)_2Si(OH)_2$ loss rate as the irradiations progressed. It is likely that the acid products of this reaction system (i.e., HNO_3 , HONO) catalyzed the decay and/or self-condensation of $(CH_3)_2Si(OH)_2$, as discussed later. Hence, the relative rate technique involving the use of the $N_2H_4 + O_3$ reaction as the OH radical source was employed to measure the rate constants for the reactions of the OH radical with dimethylsilanediol, trimethylsilanol, and tetramethylsilane.

The observed decay rates of (CH₃)₂Si(OH)₂ in its mixtures with (CH₃)₂O and O₃ prior to injection of N₂H₄ were in the range $(0.6-1.3) \times 10^{-2}$ min⁻¹, and these decay losses (due to self-reaction and/or wall losses) were significant fractions (48–62%) of the total losses after introduction of $N_2H_4.$ Hence, only one injection of N₂H₄ per experiment was made, with the last spectral record of the "prereaction" decay measurement being used to establish the initial concentrations of $(CH_3)_2Si(OH)_2$ and $(CH_3)_2O$ and the final concentrations being determined from the next spectrum recorded after N₂H₄ injection and the mixing time of ca. 3 min duration. The elapsed time between these two spectra was 6-8 min. No measurable decays of the reference compound (CH₃)₂O in the reaction chamber prior to N₂H₄ injection were observed. The data from four separate experiments, corrected for the 'prereaction" decay losses, are plotted according to eq I in Figure 3, resulting in a slope = (k_1/k_2) of 0.285 \pm 0.020, with the indicated error being two least-squares standard deviations.

The negligible decay rates of $(CH_3)_3SiOH$ and $Si(CH_3)_4$ in their respective mixtures in air with $(CH_3)_2O$ and excess O_3 allowed more than one N_2H_4 injection to be made during an experiment and, hence, to obtain more data points per experiment. Plots of eq I for the combined data from three experiments for $(CH_3)_3SiOH$ and from two experiments for

TABLE 1. Summary of Rate Constant Ratios, k_1/k_2 , and Rate Constants, k_1 , for the Gas-Phase Reactions of OH Radicals with Organosilicon Compounds and Other Selected Organic Compounds at 298 \pm 2 K

		$10^{12} \times k_1$ (cm ³ molecule ⁻¹ s ⁻¹)		
compound	<i>k</i> ₁ / <i>k</i> ₂ ^a	this work ^b	literature	ref
(CH ₃) ₂ Si(OH) ₂ (CH ₃) ₃ SiOH Si(CH ₃) ₄ (CH ₃) ₃ SiOSi(CH ₃) ₃ (CH ₃) ₃ SiOSi(CH ₃) ₂ OH C(CH ₃) ₄ (CH ₃) ₃ COH	$\begin{array}{c} 0.285 \pm 0.020 \\ 0.253 \pm 0.011 \\ 0.301 \pm 0.008 \end{array}$	$\begin{array}{c} 0.81 \pm 0.10 \\ 0.72 \pm 0.08 \\ 0.85 \pm 0.09 \end{array}$	$\begin{array}{c} 3.95 \pm 0.65 \\ 1.00 \pm 0.27 \\ 1.28 \pm 0.55 \\ 1.38 \pm 0.36 \\ 1.19 \pm 0.30 \\ 1.89 \pm 0.60 \\ 0.85 \pm 0.10 \\ 1.08 \pm 0.10 \\ 0.99 \pm 0.266 \end{array}$	(7) (6) (7) (6) (7) (9) (16) (17)

^a Reference organic is dimethyl ether; indicated errors are two least-squares standard deviations. ^b Placed on an absolute basis using k_2 (OH + dimethyl ether) = 2.84 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (ca. ± 10%) (*15*). The indicated errors include the ± 10% uncertainty in the rate constant k_2 . ^c Average of literature values summarized in ref *17*.



FIGURE 4. Least-squares plot of eq I for the gas-phase reactions of OH radicals with trimethylsilanol and tetramethylsilane, with dimethyl ether as reference compound. The ordinates of the tetramethylsilane plot are offset for clarity.

Si(CH₃)₄ are shown in Figure 4, with good straight-line plots being observed. The k_1/k_2 values for the three organosilicon compounds studied are given in Table 1. These rate constant ratios are placed on an absolute basis with the use of a value of k_2 , the rate constant for the (CH₃)₂O + OH reaction, of 2.84 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (ca. ± 10%) (15). The resulting rate constants, k_1 , are also presented in Table 1.

Product Studies. Dimethylsilanediol. FT-IR Measure*ments*. The reaction of (CH₃)₂Si(OH)₂ with OH radicals was examined by photolysis of a mixture of (CH₃)₂Si(OH)₂ with CH₃ONO and NO in air. The qualitative results are presented in Figure 5, where only the infrared spectra of the products arising from (CH₃)₂Si(OH)₂ itself are depicted, i.e., absorptions by remaining reactants and by the photooxidation products from CH₃ONO and NO have been subtracted. The sequence of spectra presented in Figure 5 (parts A and B) shows that the product formed in the early stage of photolysis is the same one observed during the dark decay of (CH₃)₂Si(OH)₂ (see Figure 1B), indicating that the reaction with OH radicals probably did not occur to a significant extent. A different major product is formed later in the photolysis (Figure 5C). However, this latter product has a spectrum that is similar to the product or mixture of products obtained (see Figure 5D) during our first attempts to prepare (CH₃)₂Si(OH)₂. In those earlier attempts the reaction vessels were not acidwashed, and the literature warns of the transformation



FIGURE 5. IR spectra of products from the photolysis of a dimethylsilanediol— $CH_3ONO-NO$ —air mixture (with absorptions of products from the photooxidation of CH_3ONO and NO subtracted) after irradiation times of (A) 13 min, (B) 31 min, and (C) 71 min. (D) Vapor-phase spectrum of product obtained from reacting dimethoxy-dimethylsilane with water (to prepare dimethylsilanediol) without acid-washing of the reaction vessels (see text).

that $(CH_3)_2Si(OH)_2$ can undergo during preparation in the presence of traces of alkali or acid (see ref *14*). It is possible that the significant amounts of HNO₃ formed during the CH₃ONO–NO–air photolysis catalyzed the transformation of $(CH_3)_2Si(OH)_2$ and its intermediate decay product(s) to the product(s) represented by Figure 5D.

The results of a Cl-atom initiated photooxidation of $(CH_3)_2$ -Si(OH)₂, with a mixture containing initial concentrations of 1.3×10^{14} molecule cm⁻³ of $(CH_3)_2$ Si(OH)₂ and 3.0×10^{14} molecule cm⁻³ of Cl₂ in 1 atm of dry air, are presented in Figure 6. Figure 6A is the spectrum of the reaction mixture prior to irradiation. Figure 6 (parts B and D) corresponds to 2 min (41% consumption of $(CH_3)_2$ Si(OH)₂) and 12 min (~100% consumption of $(CH_3)_2$ Si(OH)₂) of photolysis, respectively. Figure 6 (parts C and E) is corresponding spectra where the absorptions of H₂O, HC(O)OH, and unreacted $(CH_3)_2$ Si(OH)₂ have been subtracted. An intermediate product is indicated in Figure 6 (parts B and C) by absorption bands at 1721 and 1213 cm⁻¹, most likely the characteristic pair of C=O stretch and C-C stretch frequencies of an ester group (*18, 19*) and attributed to (HO)₂Si(CH₃)OCHO, which dis-



FIGURE 6. IR spectra from a CI atom-initiated photooxidation of dimethylsilanediol: (A) initial dimethylsilanediol, (B) reaction mixture after 2 min of irradiation and 41% consumption of reactant, (C) from (B) after subtraction of absorptions by HC(O)OH, H₂O, and remaining dimethylsilanediol, (D) reaction mixture after 12 min of irradiation and 100% loss of reactant, and (E) from (D) after subtraction of absorptions by HC(O)OH and H₂O.

appeared in the later stage of the photolysis with formation of an unidentified major product(s) which was accompanied by an increase in the production of HC(O)OH. Since HCl is a product of the Cl atom-initiated photooxidation of organic compounds, it was possible that HCl also catalyzed the selfcondensation of $(CH_3)_2Si(OH)_2$ in this experiment but to a much lesser degree than the acid catalysis observed in the $CH_3ONO-NO$ systems because of the much shorter reaction times involved.

API-MS Measurements. A preirradiation API-MS spectrum of a mixture of (CH₃)₂Si(OH)₂ and Cl₂ in air is presented in Figure 7A, which shows the presence of (CH₃)₂Si(OH)₂ along with its dark decay products. Product ion peaks were identified based on the observation of the protonated homoor heterodimer ions (for example, $[(M_{P1})_2 + H]^+$, $[(M_{P2})_2 +$ H]⁺, and $[M_{P1} + M_{P2} + H]$ ⁺, where P_1 and P_2 are a product or a reactant) in the API-MS/MS "parent ion" spectra and consistency of the API-MS/MS "daughter ion" spectrum of a homo- or heterodimer ion with the "parent ion" spectra of the various $[M_P + H]^+$ peaks (12). Water cluster ion peaks of the product ions, $[M + H + H_2O]^+$, were often observed. Thus, in Figure 7A, the ion peaks at 93 (weak), 167, 223, and 241 u are assigned to the $[M + H]^+$ ions of $(CH_3)_2Si(OH)_2$ (molecular weight (MW) = 92) and its known condensation products $(CH_3)_2Si(OH)OSi(OH)(CH_3)_2$ (MW = 166),

(MW = 222) and $(CH_3)_2Si(OH)OSi(CH_3)_2OSi(OH)(CH_3)_2$ (MW = 240) (20). All of the other ion peaks shown in Figure 7A can be assigned to homo- or heterodimers of these MW 92, 166, 222, and 240 species, including 111 ([92 + H + H_2O]), 185 ([92 + 92 + H] and/or [166 + H + H_2O]), 203 ([92 + 92 + H + H_2O])]), 241 ([222 + H + H_2O] and/or [240 + H]), 259 ([92 + 166 + H], [222 + H + 2H_2O] and/or [240 + H + H_2O]), 277 ([92 + 166 + H + H_2O] and/or [240 + H + 2H_2O]), 315



FIGURE 7. API-MS spectra (A) before and (B) after irradiation of a mixture of dimethylsilanediol and Cl₂ in air.

(222 + 92 + H]), and 333 ([166 + 166 + H] and/or [240 + 92 + H]). Other ion peaks observed (not shown) and their assignments are 407 ((222 + 92 + 92 + H]), 481 ([240 + 240 + H] and/or [240 + 222 + H + H₂O]), and 555 u ([240 + 222 + 92 + H] and/or [222 + 222 + 92 + H + H₂O]).

After 1.5 min irradiation of this $Cl_2-(CH_3)_2Si(OH)_2$ -air mixture, the API-MS spectrum in Figure 7B was obtained. Most of the ion peaks associated with the condensation products of $(CH_3)_2Si(OH)_2$ have disappeared, and the spectrum shows the presence of fewer dimer ions than is the case in Figure 7A. Of special interest in Figure 7B are the presence of ion peaks at 95, 113, and 131 u, which are attributed to the $[M + H]^+$, $[M + H + H_2O]^+$, and $[M + H + 2H_2O]^+$ ions of a MW 94 product. Additional ion peaks associated with this MW 94 product are those at 187 ([94 + 92 + H]) and 189 ([94 + 94 + H]), and we attribute this MW 94 product to CH₃Si(OH)₃. An ion peak at 141 u may be the $[M + H + H_2O]^+$ ion of a MW 122 product which could then be the intermediate formate ester CH₃Si(OH)₂OCHO.

This experiment therefore provides evidence for the Clatom initiated reaction of $(CH_3)_2Si(OH)_2$ leading to the formation of $CH_3Si(OH)_3$, possibly via the intermediate formation of the formate ester $CH_3Si(OH)_2OCHO$.

The API-MS spectra obtained during the photolysis of a mixture of dimethysilanediol with CH_3ONO and NO showed no products except the dark decay/condensation species enumerated above which were already present prior to irradiation, in agreement with the results of the experiment conducted with FT-IR analysis.

Trimethylsilanol. The Cl atom-initiated photooxidation of trimethylsilanol carried out with FT-IR analysis showed the formation of an ester-like product, as indicated by a pair of absorption bands at 1720 cm⁻¹ (C=O stretch) and 1206 cm⁻¹ (C-C stretch) (*18, 19*). These absorptions overlapped with the corresponding absorptions of the formate ester product from the more reactive hexamethyldisiloxane (*8*), the latter being an impurity in the trimethylsilanol sample. However, the 1720 cm⁻¹ band of the trimethylsilanol product has a sharp Q branch that distinguishes it from the C=O stretch absorption of the hexamethyldisiloxane product. Similar to the Cl atom-initiated photooxidation of hexamethyldisiloxane (*8*), formic acid was also observed during the course of the irradiation. Dimethylsilanediol was not observed by



FIGURE 8. API-MS spectra (A) before and after (B) 0.5 min, (C) 1.0 min, and (D) 2.0 min irradiation of a mixture of trimethylsilanol and CI_2 in air.

FT-IR spectroscopy as a product from trimethylsilanol in this experiment. However, during the kinetic experiments described above which employed $N_2H_4 + O_3$ as a source of OH radicals, a weak but distinct Q-branch absorption at 1265.1 cm⁻¹ was observed in the spectrum of the reaction mixture, indicating the formation of (CH₃)₂Si(OH)₂ from (CH₃)₃SiOH via OH radical-initiated reaction in this nonphotolytic system. It should be noted that, due to H₂O production in the $N_2H_4 + O_3$ reaction systems, the prevailing H₂O concentrations in these experiments were significantly higher than in the photolysis of (CH₃)₃SiOH-Cl₂-air mixtures, which favors hydrolysis of an organosilicon ester to a silanol (8). Addition of significant amounts of H₂O to a Cl₂ photolysis mixture in the 5870 L chamber was not attempted, because a previous, similar experiment resulted in the destruction of the gold coatings of the multiple-reflection mirrors.

Photolysis of a Cl₂–(CH₃)₃SiOH–air mixture was carried out in the 7500 L Teflon chamber with analyses by API-MS and API-MS/MS. Figure 8A shows the API-MS spectrum (80–140 u region) of the reactants before irradiation, and Figure 8B–D shows the corresponding API-MS spectra after 0.5, 1.0, and 2.0 min of irradiation, respectively. Before irradiation, ion peaks are observed at 91 ([90 + H]), 109 ([90 + H + H₂O]), and 127 u ([90 + H + 2H₂O]) with the MW 90 species being (CH₃)₃SiOH and at 105 ([104 + H]) and 123 u ([104 + H + H₂O]), with the MW 104 species being an (CH₃)₃SiOCH₃ impurity in the (CH₃)₃SiOH sample (presumably from reaction of methanol with (CH₃)₃SiOH during the preparation of the trimethylsilanol).

The API-MS spectra after irradiation show the gradual disappearance of the 91 u ion peak (and its associated water cluster peaks at 109 and 127 u) [and of the 105 u ion peak of the (CH₃)₃SiOCH₃ impurity] and the appearance of a number of product ion peaks. The API-MS spectra after 0.5 and 1.0 min irradiation (Figure 8 (parts B and C) show the

formation of ion peaks at 93, 111, and 129 u (attributed to the $[M + H]^+$, $[M + H + H_2O]^+$, and $[M + H + 2H_2O]^+$ ions of a MW 92 product) and at 121 and 139 u (attributed to the $[M + H]^+$ and $[M + H + H_2O]^+$ ions of a MW 120 product). Additionally, the API-MS spectrum after 1.0 min of irradiation shows the presence of ion peaks at 95 and 113 u which are attributed to the $[M + H]^+$ and $[M + H + H_2O]^+$ ions of a MW 94 product. After 2.0 min of irradiation (Figure 8D), the ion peaks associated with (CH₃)₃SiOH have disappeared, and the ion peaks present are those at 93, 111, and 129 u (from the MW 92 product); 121 and 139 u (from the MW 120 product); 95, 113, and 131 u (the $[M + H]^+$, $[M + H + H_2O]^+$ and $[M + H + 2H_2O]^+$ ions of the MW 94 product); and 123 and 141 u (not shown) (attributed to the $[M + H]^+$ and $[M + H + H_2O]^+$ ions of a MW 122 product). [The 135 and 137 u ion peaks observed in Figure 8 (parts B-D, respectively) could be the $[M + H]^+$ of $M = (CH_3)_2Si(OH)OCHO$ and the $[M + H + H_2O]^+$ of $(CH_3)_3SiOCHO$, respectively, formed from the (CH₃)₃SiOCH₃ impurity.]

We interpret these observations as involving the initial formation of $(CH_3)_2Si(OH)OCHO$ (MW 120) and $(CH_3)_2Si-(OH)_2$ (MW 92) from the reaction of $(CH_3)_3SiOH$, followed by reaction of the first-generation product $(CH_3)_2Si(OH)_2$ to form $CH_3Si(OH)_2OCHO$ (MW 122) and $CH_3Si(OH)_3$ (MW 94).

Discussion

The value of (8.5 \pm 0.9) \times 10 $^{-13}~cm^3$ molecule $^{-1}~s^{-1}$ for the OH radical rate constant measured in this work for tetramethylsilane is in good agreement with the value reported by Atkinson (6) and, to a lesser degree, with the measurement by Sommerlade et al. (7), with overall agreement within the reported error limits (see Table 1). However, our present OH radical rate constant of $(7.2 \pm 0.8) \times 10^{-13}$ cm³ molecule⁻¹ s^{-1} for trimethylsilanol is a factor of ${\sim}5$ lower than that of (3.95 ± 0.65) \times 10⁻¹² cm³ molecule⁻¹ s⁻¹ reported by Sommerlade et al. (7). The source of this discrepancy is not clear, but Sommerlade et al. (7) employed a much smaller reaction chamber than used in this work, and it is possible that their study (7) was complicated by wall losses of (CH₃)₃-SiOH but not of Si(CH₃)₄ and (CH₃)₃SiOSi(CH₃)₃. Trimethylsilanol, like tetramethylsilane, did not decay in our 5870 L chamber within the time frames of the kinetic experiments, and both trimethylsilanol and tetramethylsilane possess wellisolated absorption features that enabled their timeconcentration profiles to be measured with very good precision by FT-IR spectroscopy. As noted in Table 1, our previous data for the analogous case of (CH₃)₃SiOSi(CH₃)₃ (6) and (CH₃)₃SiOSi(CH₃)₂OH (9) also show that their OH radical rate constants do not differ to a significant degree, and this is also true for C(CH₃)₄ versus (CH₃)₃COH. No data for dimethylsilanediol have been reported in the literature, but the OH radical rate constant of $(8.1 \pm 1.0) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ measured in this work (Table 1) is very similar to those obtained for tetramethylsilane and trimethylsilanol.

From the above-measured OH radical rate constants and using a 24-h average OH radical concentrations of 1.0×10^6 molecules cm⁻³ (*21, 22*), tropospheric lifetimes of 14 days, 17 days, and 15 days are calculated for tetramethylsilane, trimethylsilanol, and dimethylsilanediol, respectively.

Product studies for both dimethylsilanediol and trimethylsilanol could not be carried out on pure samples due to their inherent tendencies to form condensation products in the bulk sample or in the gaseous reaction mixtures. Thus, the investigation of the fates of their respective alkoxy radicals, formed after the initial OH radical and/or Cl atom abstraction of an H atom from a methyl group, was complicated by formation and subsequent reaction of these impurities. In the case of dimethylsilanediol, the possible interferences from a number of these products limited the analysis by FT-IR spectroscopy, although the product spectra provided evidence for the formation of formate ester intermediates from both dimethylsilanediol and trimethylsilanol. The most significant results were provided by API-MS analysis which indicated formation of methylsilanetriol from dimethylsilanediol and of both dimethylsilanediol and methylsilanetriol from trimethylsilanol. Our present findings combined with previous observations that (CH₃)₃SiOSi(CH₃)₂OH is formed from (CH₃)₃SiOSi(CH₃)₃ via the hydrolysis of the formate ester (CH₃)₃SiOSi(CH₃)₂OCHO (8) provide further support to the following tropospheric degradation scheme for tetramethylsilane and product silanols via OH radical initiation:

$$Si(CH_3)_4 + OH \rightarrow (CH_3)_3 Si\dot{C}H_2 + H_2O$$
(3)

 $(CH_3)_3Si\dot{C}H_2 + O_2 \rightarrow [(CH_3)_3SiCH_2O\dot{O}] \rightarrow$ (CH₃)₃SiOCH₂O (4)

$$(CH_3)_3SiOCH_2\dot{O} + O_2 \rightarrow (CH_3)_3SiOCHO + HO_2$$
 (5)

 $(CH_3)_3SiOCHO + H_2O \rightarrow (CH_3)_3SiOH + HC(O)OH$ (6)

and similarly for (CH₃)₃SiOH:

$$\begin{array}{c} (\mathrm{CH}_{3})_{3}\mathrm{SiOH} \xrightarrow{\mathrm{OH}} (\mathrm{CH}_{3})_{2}\mathrm{Si}(\mathrm{OH})\mathrm{\dot{CH}}_{2} \xrightarrow{\mathrm{O}_{2}} \rightarrow \\ (\mathrm{CH}_{3})_{2}\mathrm{Si}(\mathrm{OH})\mathrm{OCH}_{2}\mathrm{\dot{O}} \xrightarrow{\mathrm{O}_{2}} (\mathrm{CH}_{3})_{2}\mathrm{Si}(\mathrm{OH})\mathrm{OCHO} \xrightarrow{\mathrm{H}_{2}\mathrm{O}} \\ (\mathrm{CH}_{3})_{2}\mathrm{Si}(\mathrm{OH})_{2} \end{array}$$

and similarly for (CH₃)₂Si(OH)₂:

$$(CH_{3})_{2}Si(OH)_{2} \xrightarrow{OH} CH_{3}Si(OH)_{2}\dot{C}H_{2} \xrightarrow{O_{2}} \rightarrow CH_{3}Si(OH)_{2}OCH_{2}O \xrightarrow{O_{2}} CH_{3}Si(OH)_{2}OCHO \xrightarrow{H_{2}O} CH_{3}Si(OH)_{3}Si(OH)_{3}$$

The above reaction schemes can probably be extended to include the transformation of CH₃Si(OH)₃ to Si(OH)₄ [SiO₂· *x*H₂O], even though the latter was not detected in extended irradiations of dimethylsilanediol-Cl2-air and trimethylsilanol-Cl₂-air mixtures described above. The presence of two hydroxyl groups in dimethylsilanediol and its observed decay behavior in the chamber suggest that surfaces will play a significant role in its atmospheric removal, and this is also expected to be the case for methylsilanetriol. Since dimethylsilanediol will be released into the atmosphere at concentrations where autocondensation will be negligible, incorporation into aerosols (and subsequent washout) could be significant removal pathways for dimethylsilanediol in the atmosphere in addition to reaction with OH radicals and wet deposition from the gas phase.

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Literature Cited

- (1) Allen, R. B.; Kochs, P.; Chandra, G. Industrial Organosilicon Materials, their Environmental Entry and Predicted Fate. In Organosilicon Materials, The Handbook of Environmental Chemistry; Chandra, G., Ed.; Springer-Verlag: Berlin, 1997; Vol. 3, Part H, p 1.
- (2) Chandra, G.; Maxim, L. D.; Sawano, T. The Silicone Industry and its Environmental Impact. In Organosilicon Materials, The Handbook of Environmental Chemistry; Chandra, G., Ed.; Springer-Verlag: Berlin, 1997; Vol. 3, Part H, p 295.
- (3) Fendinger, N. J.; Lehmann, R. G.; Mihaich, E. M. Polydimethylsiloxane. In Organosilicon Materials, The Handbook of Environmental Chemistry; Chandra, G., Ed.; Springer-Verlag: Berlin, 1997; Vol. 3, Part H, p 181.
- (4) Lehmann, R. G.; Miller, J. R. Environ. Toxicol. Chem. 1996, 15, 1455.
- Hobson, J.; Atkinson, R.; Carter, W. P. L. Volatile Methylsiloxanes. (5)In Organosilicon Materials, The Handbook of Environmental Chemistry; Chandra, G., Ed.; Springer-Verlag: Berlin, 1997; Vol. 3, Part H, p 137.
- (6) Atkinson, R. Environ. Sci. Technol. 1991, 25, 863.
- Sommerlade, R.; Parlar, H.; Wrobel, D.; Kochs, P. Environ. Sci. Technol. 1993, 27, 2435.
- Atkinson, R.; Tuazon, E. C.; Kwok, E. S. C.; Arey, J.; Aschmann, (8)S. M.; Bridier, I. J. Chem. Soc., Faraday Trans. 1995, 91, 3033.
- (9) Atkinson, R.; Aschmann, S. M.; Arey, J. 1993, Unpublished data cited in refs 5 and 16.
- (10) Tuazon, E. C.; Carter, W. P. L.; Atkinson, R.; Pitts, J. N., Jr. Int. J. Chem. Kinet. 1983, 15, 619.
- (11) Tuazon, E. C.; Carter, W. P. L.; Atkinson, R.; Winer, A. M.; Pitts, J. N., Jr. Environ. Sci. Technol. 1984, 18, 49.
- (12) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. J. Phys. Chem. A 1997, 101, 8042.
- (13) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. Int. J. Chem. Kinet. 1980, 12, 231. (14) Kantor, S. W. J. Am. Chem. Soc. 1953, 75, 2712.
- (15) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. J. Phys. Chem. Ref. Data, 1999, 28, 191. (16) Atkinson, R. J. Phys. Chem. Ref. Data 1994, Monograph 2, p
- 1 216.(17) Teton, S.; Mellouki, A.; Le Bras, G.; Sidebottom, H. Int. J. Chem. Kinet. 1996, 28, 291.
- (18) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. Introduction to Infrared and Raman Spectroscopy; Academic Press: New York, 1964; p 248
- (19) Pouchert, C. J. The Aldrich Library of FTIR Spectra, 1st ed.; Aldrich Chemical Co., Inc.: 1989; Vol. 3, pp 605-633.
- (20) Spivack, J. L.; Pohl, E. R.; Kochs, P. Organoalkoxysilanes, Organosilanols and Organosiloxanols. In Organosilicon Materials, The Handbook of Environmental Chemistry, Chandra, G., Ed.; Springer-Verlag: Berlin, 1997; Vol. 3, Part H, p 105. (21) Prinn, R.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.;
- Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. Science 1995, 269, 187.
- (22) Hein, R.; Crutzen, P. J.; Heimann, M. Global Biogeochem. Cycles **1997**, 11, 43.

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