

Comparison of the Yield and Chemical Composition of Secondary Organic Aerosol Generated from the OH and Cl Oxidation of Decamethylcyclopentasiloxane

Anita M. Avery,* Mitchell W. Alton, Manjula R. Canagaratna, Jordan E. Krechmer, Donna T. Sueper, Nirvan Bhattacharyya, Lea Hildebrandt Ruiz, William H. Brune, and Andrew T. Lambe*



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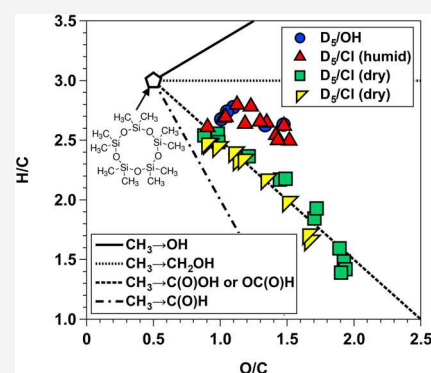
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ABSTRACT: Cyclic volatile methyl siloxanes (cVMS) that are emitted from industrial processes and consumer products often dominate the burden of volatile organic compounds (VOCs) in occupied spaces. cVMS may contribute to oxygenated VOC and secondary organic aerosol (SOA) formation following oxidation by gas-phase radicals in both indoor and outdoor source regions. Several recent studies examined the SOA formation potential of decamethylcyclopentasiloxane (D_5) following exposure to hydroxyl radicals (OH) and found that this reaction generates SOA in high yield following multiple days of oxidative aging. Chlorine atoms (Cl) may compete with OH for the oxidative loss of D_5 in indoor and outdoor source regions with active chlorine chemistry, but the SOA formation potential of D_5 + Cl reactions has not been studied. Here, we characterized the yield and chemical composition of SOA generated from Cl oxidation of D_5 in an oxidation flow reactor (OFR) under dry [relative humidity (RH) < 5%] and humid (RH = 40%) conditions and compared results to the yield and composition of SOA generated from OH oxidation of D_5 . D_5 was oxidized using integrated OH and Cl exposures (OH_{exp} and Cl_{exp}) ranging from 1.1×10^{12} to 8.2×10^{12} cm^{-3} s and from 1.6×10^{10} to 1.6×10^{12} cm^{-3} s, respectively. Like OH, Cl facilitated multistep SOA oxidative aging over the range of OFR conditions that were studied, with maximum SOA mass yields of 1.5 and 1.3 obtained following OH and Cl oxidation of D_5 under humid conditions. These results suggest that indoor and outdoor source regions that are significantly influenced by chlorine chemistry may enhance the atmospheric SOA formation potential of D_5 .

KEYWORDS: volatile methyl siloxanes, secondary organic aerosol, hydroxyl radicals, chlorine atoms, oxidation flow reactor, aerosol mass spectrometry, proton transfer reaction mass spectrometry



1. INTRODUCTION

Cyclic volatile methyl siloxanes (cVMS), such as hexamethylcyclotrisiloxane ($C_6H_{18}Si_3O_3$, D_3), octamethylcyclotetrasiloxane ($C_8H_{24}Si_4O_4$, D_4), and decamethylcyclopentasiloxane ($C_{10}H_{30}Si_5O_5$, D_5), are anthropogenic organosilicon compounds with Si–O–Si backbones that exist in the gas phase under typical atmospheric conditions. cVMS are emitted in large quantities from numerous industrial processes and consumer products and are often the most abundant class of volatile organic compounds (VOCs) in indoor densely occupied spaces.¹ Additionally, cVMS, along with other chemical products, were only recently identified as important precursors to ozone and secondary organic aerosol (SOA) formation in polluted urban areas.² As such, recent studies have focused on the atmospheric chemistry of cVMS. D_5 is usually emitted in higher concentrations than other cVMS, with typical indoor and outdoor D_5 mixing ratios ranging from approximately 4 to 20 ppbv and from 0.4 to 20 pptv, respectively.^{1,3–5}

The atmospheric lifetime of D_5 as a result of the reaction with the hydroxyl (OH) radical is approximately 3–5 days^{6,7} at a typical average ambient OH concentration of 1.5×10^6 cm^{-3} .⁸ Important early-generation gas-phase D_5 + OH oxidation products include siloxanol/silanol compounds.⁷ Compounds with similar functional groups have been detected in laboratory D_5 SOA particles.^{9,10} Given the lower volatility and higher emission factors of D_5 relative to other VMS, D_5 is a presumptive precursor to particulate Si in ambient aerosols.^{11–13} Recent studies investigating the OH oxidation of D_5 and its early-generation oxidation products have shown that the yield of SOA increases significantly beyond ≈ 10 days of

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atmospheric OH exposure.^{14–16} In addition to OH, chlorine atoms (Cl) may influence the atmospheric lifetime of D₅ in certain source regions, including the marine boundary layer,¹⁷ polluted coastal cities,¹⁸ and indoors following bleach washing.^{19–21} D₅ reacts almost 2 orders of magnitude faster with Cl than with OH and generates similar early-generation gas-phase oxidation products.⁷ However, SOA generation following Cl oxidation of D₅ has not been studied.

To investigate these knowledge gaps, we characterized the yield and chemical composition of laboratory SOA generated in an oxidation flow reactor (OFR) from the Cl oxidation of D₅. First, we characterized the yield and chemical composition of SOA obtained from OH oxidation of D₅ and compared our results to previous studies.^{14,16,22} OFRs use residence times that are on the order of minutes and oxidant concentrations that are typically 100–1000 times higher than ambient levels. Their ability to access photochemical aging time scales of up to several days was critical in previous studies examining D₅ + OH SOA formation as a result of the relatively long OH lifetime of D₅. While these factors may make the chemistry and microphysics in the OFR somewhat different from the chemistry and microphysics in the atmosphere,^{23,24} here, investigating D₅ Cl-SOA formation in an OFR enables a more direct comparison of the relative SOA yields obtained via OH and Cl oxidation (hereafter referred to as “OH-SOA” and “Cl-SOA”, respectively). To first order, the yield and composition of Cl-SOA generated from other precursors appears to be similar whether it is generated at lower oxidant concentrations over longer exposure times in environmental chambers or higher oxidant concentrations over shorter exposure times in OFRs.²⁵

2. EXPERIMENTAL SECTION

Experiments were conducted inside a Potential Aerosol Mass (PAM) OFR (Aerodyne Research, Inc.), which is a horizontal 13 L aluminum cylindrical chamber (46 cm long × 22 cm inner diameter) operated in continuous flow mode, with 6 L min^{−1} flow through the reactor.^{25,26} The corresponding calculated mean residence time in the OFR, τ_{OFR} , was approximately 130 s. An electroconductive Teflon coating was applied to the OFR to improve chemical compatibility with halogen precursors while maintaining high transmission of gases and particles.^{25,27} Two low-pressure mercury (Hg) lamps that were isolated from the sample flow using type 214 quartz sleeves were used to photolyze oxidant precursors. A fluorescent dimming ballast (IZT-2S28-D, Advance Transformer Co.) was used to regulate the current applied to the lamps. The ultraviolet (UV) irradiance was measured using a photodetector (TOCON-GaP6, sglux GmbH) and was varied across different experiments by changing the control voltage applied to the ballast between 1.5 and 10 volts of direct current (VDC). The corresponding actinic flux ranged from approximately 1×10^{14} to 3×10^{15} photons cm^{−2} s^{−1}.^{26,28}

2.1. Oxidant Generation. **2.1.1. OH Production and Quantification.** OH was generated from the combined photolysis of O₂ and H₂O at $\lambda = 185$ nm plus photolysis of O₃ at $\lambda = 254$ nm using two low-pressure ozone-producing UVC germicidal Hg lamps (GPH436TSVH/4P, Light Sources, Inc.); this method is hereafter referred to as “OFR185”. Across all experiments, a mean relative humidity (RH) of $40 \pm 1\%$ was established using a Nafion membrane humidifier (Perma Pure). The mean OFR temperature was 28 ± 2 °C. The integrated OH exposure (OH_{exp}) in the OFR, defined as the

product of the mean OH concentration and τ_{OFR} , was calculated using an estimation equation²⁶

$$\begin{aligned} \log[\text{OH}_{\text{exp}}] = & (10.098 + (0.15062 - 0.44244 \text{OHR}_{\text{ext}}^{0.18041} \\ & + 0.031146 \log[\text{O}_3 \times \text{OHR}_{\text{ext}}^{0.16721}]) \log[\text{O}_3] \\ & + \log[\text{H}_2\text{O}]) + \log\left(\frac{\tau_{\text{OFR}}}{124}\right) \end{aligned} \quad (1)$$

where OHR_{ext} (external OH reactivity, s^{−1}) is the product of the SOA precursor mixing ratio and its bimolecular OH rate coefficient (cm³ molecules^{−1} s^{−1}, hereafter “cm³ s^{−1}”) and [O₃] is the ozone concentration (molecules cm^{−3}, hereafter “cm^{−3}”) measured at the exit of the OFR. Over the range of conditions that were used, calculated OH_{exp} values ranged from 1.1×10^{12} to 8.2×10^{12} cm^{−3} s or from approximately 8 to 63 days of atmospheric oxidation at [OH] = 1.5×10^6 cm^{−3}.⁸ The estimated uncertainty in calculated OH_{exp} values was $\pm 50\%$.

2.1.2. Cl Generation and Quantification. Cl was generated via photolysis of chlorine (Cl₂) at $\lambda = 369$ nm (Cl₂ + $h\nu \rightarrow 2\text{Cl}$) using two low-pressure UVA Hg lamps (F436T5/BLC/4P-369, LCD Lighting, Inc.) or photolysis of oxalyl chloride (C₂Cl₂O₂) at $\lambda = 254$ or 313 nm (C₂Cl₂O₂ + $h\nu \rightarrow 2\text{Cl} + 2\text{CO}$) using two low-pressure UVC or UVB Hg lamps (GPH436TL/4P, Light Sources, Inc.; F436T5/BLC/4P-313, LCD Lighting, Inc.). Here, C₂Cl₂O₂ usage enabled the investigation of Cl-SOA oxidative aging in the absence of potential heterogeneous Cl₂ uptake to the particles that could initiate secondary radical chain chemistry.²⁹ Photolysis of Cl-SOA at $\lambda = 254$ nm was expected to be minor under the conditions that were used here.²⁵ These methods are hereafter referred to as “OFR369-iCl₂” and “OFR254/313-iC₂Cl₂O₂” where applicable (“i” = inject; thus, “iCl₂” means that Cl₂ was the radical precursor injected into the OFR). The mean relative humidity (RH) was $4.9 \pm 0.2\%$ at $T = 29 \pm 2$ °C during “dry” and $41 \pm 1\%$ at $T = 27 \pm 2$ °C during “humid” OFR369-iCl₂ experiments. Similarly, the mean RH was $1.0 \pm 0.1\%$ at $T = 25 \pm 2$ °C during OFR254/313-iC₂Cl₂O₂ experiments.

A compressed gas cylinder containing 0.1% Cl₂ in N₂ (Praxair) was used to supply Cl₂ to the OFR. The Cl₂ mixing ratio entering the OFR (set to 1.9 or 24.4 ppmv) was calculated from the Cl₂ mixing ratio in the compressed gas mixture and the dilution ratio of 15–200 cm³ min^{−1} into 8000 cm³ min^{−1} carrier gas. C₂Cl₂O₂ vapor was supplied to the OFR using a sealed permeation tube (EMPTY-HE, VICI) filled with liquid C₂Cl₂O₂ and placed in a permeation tube oven that was heated to 80 °C. A carrier gas flow of 100 cm³ min^{−1} zero air was used to transfer C₂Cl₂O₂ vapor from the oven into the OFR. The calculated C₂Cl₂O₂ mixing ratio (C) was 4.2 ppmv.²⁵

Integrated Cl exposures (Cl_{exp}) were characterized in offline calibration experiments by measuring the decay of O₃ injected into the OFR following the reaction Cl + O₃ → ClO + O₂ and measured using an O₃ analyzer (2B Technologies) as a function of lamp voltage; we assumed $\pm 70\%$ uncertainty in Cl_{exp} values.²⁵ O₃ concentrations were allowed to stabilize before initiating Cl_{exp} measurements, during which steady-state levels of O₃ were obtained with the lamps turned off (O_{3,i}). Then, the lamps were turned on, and O₃ concentrations were allowed to stabilize before being measured at illuminated steady-state conditions (O_{3,f}) following reaction with Cl. Cl_{exp} at each condition was calculated using eq 2

$$\text{Cl}_{\text{exp}} = \frac{1}{k_{\text{O}_3}^{\text{Cl}}} - \ln \left(\frac{[\text{O}_{3,\text{f}}]}{[\text{O}_{3,\text{i}}]} \right) \quad (2)$$

where $k_{\text{O}_3}^{\text{Cl}} = 1.21 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ is the bimolecular Cl + O₃ reaction rate coefficient.³⁰ Calculated Cl_{exp} values in SOA experiments ranged from 1.6×10^{10} to $1.6 \times 10^{12} \text{ cm}^{-3} \text{ s}$ or from approximately 3 days to 10 months of atmospheric oxidation at [Cl] = $6 \times 10^4 \text{ cm}^{-3}$.³¹ These simple calculations should be interpreted as a rough estimate of the photochemical age in a representative source region with active Cl photochemistry and may vary by orders of magnitude elsewhere.³²

2.2. Oxygenated Volatile Organic Compound (OVOC)/SOA Generation and Measurement. SOA particles were generated via the reaction of OH or Cl with D₅ in the OFR. Liquid solutions containing D₅ diluted to 10% (v/v) in carbon tetrachloride (CCl₄) were injected into the OFR carrier gas flow at a liquid flow rate of $0.94 \mu\text{L h}^{-1}$ using a syringe pump. The D₅ mixing ratio with the corresponding D₅ mass concentration entering the OFR that was calculated from the liquid D₅ injection and dilution ratio into the carrier gas flow was 12 ppbv ($182 \mu\text{g m}^{-3}$). This value agrees with a mean D₅ mixing ratio of 14.1 ± 4.4 ppbv that was measured in a subset of experiments with a Vocus proton transfer reaction time-of-flight mass spectrometer³³ (hereafter referred to as “Vocus PTR”) at the exit of the OFR. Similarly, the calculated CCl₄ mixing ratio in the OFR was 440 ppbv. At these conditions, the corresponding OHR_{ext} and external Cl reactivity (ClR_{ext}) values contributed by CCl₄ were $<1 \times 10^{-7}$ and $5 \times 10^{-12} \text{ s}^{-1}$.^{34,35} These OHR_{ext} and ClR_{ext} values were negligible compared to those contributed by D₅ (0.6 and 55 s^{-1}).

The Vocus PTR was operated using proton transfer (H₃O⁺) reagent ion chemistry, which is selective toward compounds with proton affinities greater than that of H₂O, and its response to D₅ was quantified by comparing to known injected quantities from a prepared dilute calibration gas cylinder (Apel-Riemer Environmental). The Vocus PTR was operated with an E/N value of 127, corresponding to an axial gradient of 607 V, a focusing ion molecule reaction region (fIMR) pressure of 2.2 mbar, and a fIMR temperature of 60 °C. The nominal resolving power of the instrument was 9770 at *m/z* 500 amu.

Particle number concentrations and mobility size distributions were measured with a TSI scanning mobility particle sizer (SMPS). Ensemble aerosol mass spectra were measured with an Aerodyne long high-resolution time-of-flight aerosol mass spectrometer (L-ToF-AMS). In one subset of experiments, gas-phase OVOCs generated from OH/Cl oxidation of D₅ were characterized with the Vocus PTR. In another subset of experiments, SOA chemical composition was characterized using a Vocus Inlet for Aerosols (hereafter VIA).³⁶ The VIA operates by passing the sample air through a honeycomb activated carbon denuder to remove all gas-phase constituents. The surviving aerosol is then evaporated in a Sulfinert-coated stainless-steel thermal desorption oven that was heated to 220 °C at a flow of 1.5 standard liters per minute to vaporize the particles prior to ionization and detection in the Vocus 2R PTR. The Vocus PTR was operated using the same source, voltage, and pressure conditions when in the gas phase or VIA mode.

2.3. Analysis. **2.3.1. L-ToF-AMS and Vocus PTR/VIA.** L-ToF-AMS spectra were analyzed using ToF-AMS analysis software,³⁷ which yielded non-refractory organic and inorganic aerosol mass concentrations, high-resolution mass spectra, and, for the organic aerosol, hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios and abundances of the default C_xH_y⁺, C_xH_yO⁺, C_xH_yO_{>1}⁺, C_xH_ySi_zO_n⁺, and Cl⁺ + HCl⁺ ion groups. Elemental analysis was performed using the methods of Canagaratna et al.³⁸ The AMS analysis software was modified to additionally calculate the oxygen-to-silicon (O/Si) and carbon-to-silicon (C/Si) ratios of the organic aerosol (Squirrel version 1.65D and Pika version 1.25D). These O/Si and C/Si values implicitly assume equal AMS sensitivity to C and Si, which has not been evaluated. Similarly, Vocus PTR and VIA spectra were analyzed using Tofware analysis software, which yielded high-resolution mass spectra and formulas of ions that were detected following proton transfer reactions between H₃O⁺ and sample analytes. The number of double bond equivalents (DBEs) was calculated for certain VIA analytes using eq 3

$$\text{DBE} = \text{C} + \text{Si} + 1 - \text{H}/2 \quad (3)$$

where C, Si, and H were the numbers of carbon, silicon, and hydrogen atoms in the compound formula. Using this definition, D₅ has DBE = 1.

2.3.2. SOA Yields. SOA mass yields were calculated from the ratio of SOA mass formed to precursor gas reacted. The SOA mass was calculated from the integrated SMPS particle volume and the material density, which was calculated from H/C and O/C values extracted from the AMS spectra.³⁹ Because this calculation implicitly assumes that the particles were spherical, which was not independently verified, calculated SOA yield values reported in this paper represent upper limits. We estimated the fraction of precursor gas reacted from the product of OH_{exp} or Cl_{exp} and the bimolecular rate coefficients of D₅ + OH/Cl. Our calculations suggested that >90% of D₅ reacted across the OFR conditions summarized in section 2.1. SOA yields were corrected for size-dependent particle wall losses in the OFR.⁴⁰ Here, the particle wall loss correction factors ranged from 1.10 to 1.29 for mean volume-weighted particle mobility diameters ranging from approximately 125 to 45 nm. We assumed that low-volatility organic compound (LVOC) vapor wall losses were negligible compared to gas-phase oxidative loss and condensation onto aerosols^{25,41,42} and did not modify SOA yield values to account for them.

3. RESULTS

3.1. Overview of D₅ SOA Generation. As mentioned in section 2.1, D₅ was introduced to the OFR at OH_{exp} ranging from 1.1×10^{12} to $8.2 \times 10^{12} \text{ cm}^{-3} \text{ s}$ and Cl_{exp} ranging from 1.6×10^{10} to $1.6 \times 10^{12} \text{ cm}^{-3} \text{ s}$. At the lowest OH_{exp} and Cl_{exp}, approximately 90 or 94% of D₅ precursor was consumed by reaction with OH or Cl⁷ (panels a and e of Figure 1), yet SOA concentrations were negligible. However, a series of C₅–C₁₀ OVOCs were detected at these OH and Cl exposures, including $\sum_{n=0}^4 \text{C}_{5+n}\text{H}_{18+2n}\text{O}_{9-n}\text{Si}_5$ and $\sum_{n=0}^3 \text{C}_{6+n}\text{H}_{22+2n}\text{O}_{9-n}\text{Si}_5$ compounds as well as C₈H₂₂O₈Si₅, C₉H₂₄O₇Si₅, C₁₀H₂₈O₇Si₅, and C₁₀H₃₀O₆Si₅. Several of these compounds were also detected in D₅ SOA using the VIA (section 3.3.1) and, as such, were likely semivolatile under our experimental conditions.²² We hypothesize that multigenerational OH/Cl oxidation of these early-generation D₅ + OH/Cl OVOCs was necessary to generate SOA.

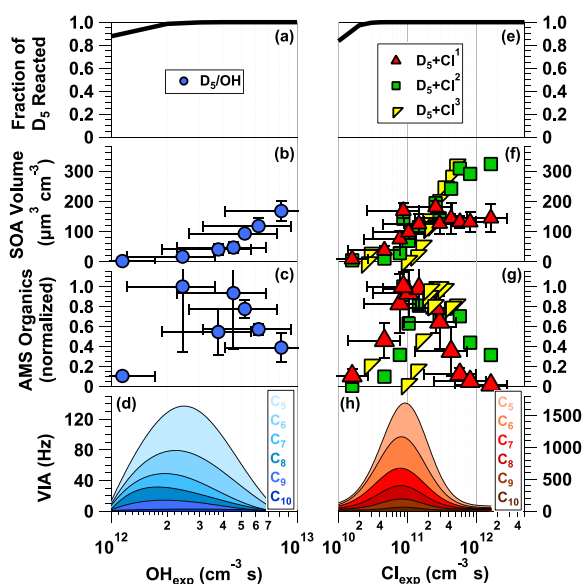


Figure 1. (a) Fraction of D_5 reacted, (b) SOA volume concentration, (c) normalized AMS OA concentration, and (d) VIA $C_5H_7O_2Si_3H^+$ signals as a function of OH_{exp} and (e) fraction of D_5 reacted, (f) SOA volume concentration, (g) normalized AMS OA concentration, and (h) VIA $C_5H_7O_2Si_3H^+$ signals as a function of Cl_{exp} (humid Cl-SOA only). In panels c and g, OA concentrations were normalized to the maximum OA concentration measured for each SOA type. In panels d and h, to reduce the density of data symbols and make the figures easier to read, separate Gaussian or log-normal curves were fit to the summed $C_5H_7O_2Si_3H^+$, $C_6H_7O_2Si_3H^+$, $C_7H_7O_2Si_3H^+$, $C_8H_7O_2Si_3H^+$, $C_9H_7O_2Si_3H^+$, and $C_{10}H_7O_2Si_3H^+$ signals. Representative error bars indicate $\pm 1\sigma$ uncertainty in binned values, $\pm 50\%$ uncertainty in OH_{exp} values, and $\pm 70\%$ uncertainty in Cl_{exp} values. Additional figure notes: 1Cl generated using OFR369- iCl_2 under humid conditions, 2Cl generated using OFR369- iCl_2 under dry conditions, and 3Cl generated using OFR254/313- $iC_2Cl_2O_2$ under dry conditions.

Figure 1b shows that the D_5 OH-SOA volume concentration increased monotonically from 2.2 to $168 \mu m^3 cm^{-3}$ as a function of OH_{exp} . For humid D_5 Cl-SOA, the SOA volume concentration increased from 8.6 to $144 \mu m^3 cm^{-3}$ as Cl_{exp} increased from 1.6×10^{10} to $4.3 \times 10^{11} cm^{-3} s$ then was approximately constant up to $Cl_{exp} = 1.6 \times 10^{12} cm^{-3} s$ (Figure 1f). The volume concentration of dry D_5 Cl-SOA generated using OFR369- iCl_2 or OFR254/313- $iC_2Cl_2O_2$ increased monotonically from 4.7 to $323 \mu m^3 cm^{-3}$ over a similar range of Cl_{exp} . This apparent humidity dependence upon the Cl-SOA yield is discussed further in sections 3.3.1 and 3.3.3. Notably, unlike OH/Cl-SOA generated from other precursors,^{25,43} the D_5 SOA volume concentration did not decrease at higher OH_{exp} and Cl_{exp} as a result of fragmentation reactions that generated higher volatility oxidation products.

In contrast to the continuous increase in OH-SOA and Cl-SOA volume concentrations calculated from the SMPS data, as shown in panels b and f of Figure 1, the organic aerosol (OA) mass concentrations measured by the AMS increased and then decreased as a function of OH_{exp} and Cl_{exp} (panels c and g of Figure 1). AMS chloride concentrations followed the same trend as AMS OA concentrations (not shown), as did concentrations of $C_{5-10}H_7O_2Si_3$ signals detected in OH-SOA and Cl-SOA with the VIA (panels d and h of Figure 1 and Figure S4 of the Supporting Information). Because both AMS and VIA heat the SOA particles to detect them in the gas phase

(whereas the SMPS does not), this suggests that the SOA became refractory as a function of oxidative aging. Additional observations supporting this hypothesis are presented in sections 3.3.1 and 3.3.3.

3.2. Yields of D_5 OH-SOA and Cl-SOA. Panels a and b of Figure 2 show mass yields of D_5 OH-SOA and Cl-SOA as a

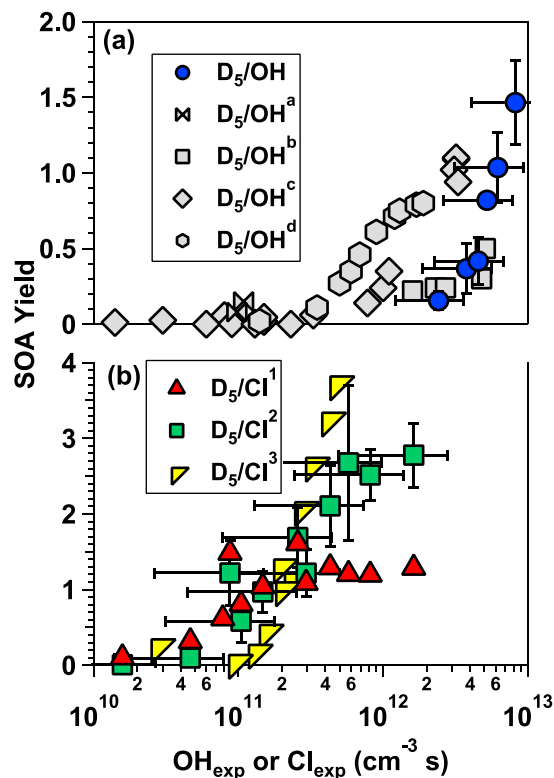


Figure 2. SOA mass yields obtained from (a) OH and (b) Cl oxidation of D_5 as a function of OH_{exp} and Cl_{exp} . Different y-axis scales are used in each subpanel. Representative error bars indicate $\pm 1\sigma$ uncertainty in binned SOA yield values, $\pm 50\%$ uncertainty in OH_{exp} exposure values, and $\pm 70\%$ uncertainty in Cl_{exp} exposure values. Additional figure notes: a Wu and Johnston,^{22b}Janecek et al.,^{14c}Charan et al.,^{16d}Han et al.,⁴⁴ 1Cl generated using OFR369- iCl_2 under humid conditions, 2Cl generated using OFR369- iCl_2 under dry conditions, and 3Cl generated using OFR254/313- $iC_2Cl_2O_2$ under dry conditions.

function of OH_{exp} and Cl_{exp} . Results obtained from OH oxidation of D_5 in previous studies are shown for reference in Figure 2a. Here, the D_5 OH-SOA yield increased monotonically from 0.02 to 1.5 as a function of OH_{exp} (Figure 2a). These values agree within $\pm 35\%$ of those obtained by Janecek et al.¹⁴ and Charan et al.¹⁶ between $OH_{exp} = 2.3 \times 10^{12}$ and $5.2 \times 10^{12} cm^{-3} s$ and encompass the range of yields (0.02 – 0.80) obtained by Han et al.⁴⁴ between $OH_{exp} = 1.4 \times 10^{11}$ and $1.9 \times 10^{12} cm^{-3} s$. The OH-SOA yield nearly doubled from 0.82 to 1.5 between $OH_{exp} = 5.2 \times 10^{12}$ and $8.2 \times 10^{12} cm^{-3} s$. OH-SOA yields between 0.08 and 0.15 were measured by Wu and Johnston²² at lower OH_{exp} values ($\approx 10^{11} cm^{-3} s$) than were used in this study.

Figure 2b shows that yields of D_5 Cl-SOA increased from <0.10 at $Cl_{exp} = 1.6 \times 10^{10} cm^{-3} s$ to 1.3 at $Cl_{exp} = 2 \times 10^{11}$ to $3 \times 10^{11} cm^{-3} s$ in both dry and humid conditions. At higher Cl_{exp} , yields of Cl-SOA remained approximately constant at 1.3 under humid conditions, whereas yields of Cl-SOA generated in dry conditions increased to 2.7 (OFR369- iCl_2) and 3.8

(OFR254- $i\text{-C}_2\text{Cl}_2\text{O}_2$) at the highest Cl_{exp} . Assuming an upper-limit D_5 SOA yield value of approximately 1.8 via generation of hypothetical oxidation product $\text{C}_{10}\text{H}_{10}\text{O}_{25}\text{Si}_5$ (MW = 670 g mol^{-1}) via $\text{CH}_3 \rightarrow \text{C}(\text{O})\text{OH}$ functionalization reactions, Cl-SOA yield values ranging from 2.7 to 3.8 are chemically implausible. Because similar maximum yields were obtained with OFR369- $i\text{Cl}_2$ and OFR254/313- $i\text{-C}_2\text{Cl}_2\text{O}_2$ methods, this suggests that organic chlorides, which could, in principle, be generated as artifacts following reactive uptake of Cl_2 to the SOA, did not contribute a significant additional SOA yield. Järvinen et al.⁴⁵ generated non-spherical α -pinene SOA particle aggregates following coagulation of highly viscous nucleated (spherical) particles at low RH.⁴⁵ We hypothesize that a similar phenomenon may have occurred for dry D_5 Cl-SOA particles generated at the highest Cl_{exp} used here. If so, this process would reduce the density of aggregates relative to the calculated material density (which implicitly assumes spherical particle morphology as applied here), thereby biasing the calculated dry Cl-SOA yield values high. Figure S1 of the Supporting Information shows that the mean particle mobility diameter (D_m) of humid Cl-SOA decreased while D_m of dry Cl-SOA generated via OFR369- $i\text{Cl}_2$ and OFR254/313- $i\text{-C}_2\text{Cl}_2\text{O}_2$ increased as a function of Cl_{exp} . Because particle density is proportional to the ratio of the particle aerodynamic diameter (D_a) and mobility diameter,⁴⁶ hypothetically, constant D_a coupled with decreasing D_m (humid Cl-SOA) or increasing D_m (dry Cl-SOA) would support our hypothesis. However, in the absence of available D_a measurements in these studies, definitive conclusions about changes in humidity-dependent particle density are not possible.

3.3. Chemical Composition of D_5 OH-SOA and Cl-SOA. 3.3.1. AMS Spectra of D_5 OH-SOA and Cl-SOA. Figure 3

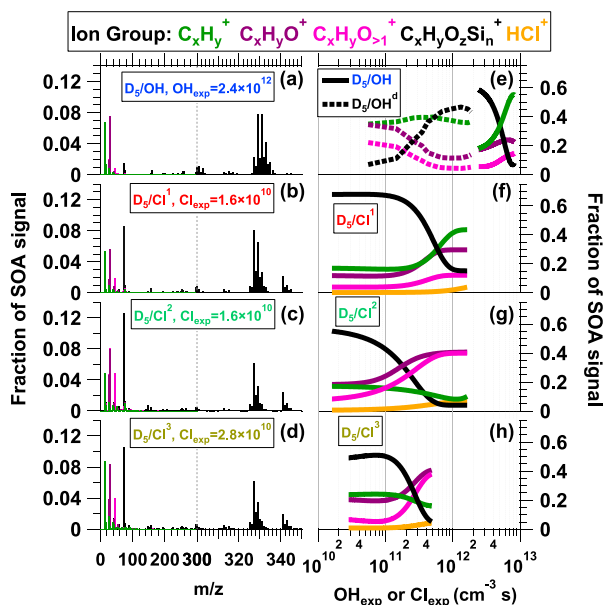


Figure 3. AMS spectra of SOA generated from (a and e) OH oxidation of D_5 , (b and f) Cl oxidation of D_5 under humid conditions, and (c, d, g, and h) Cl oxidation of D_5 under dry conditions. OH_{exp} and Cl_{exp} values listed in panels a–d are in units of $\text{cm}^{-3} \text{ s}$. Additional figure notes: ¹Cl generated using OFR369- $i\text{Cl}_2$ under humid conditions, ²Cl generated using OFR369- $i\text{Cl}_2$ under dry conditions, ³Cl generated using OFR254/313- $i\text{-C}_2\text{Cl}_2\text{O}_2$ under dry conditions, and ^dHan et al.⁴⁴

shows AMS spectra of SOA generated from the OH and Cl oxidation of D_5 at $\text{OH}_{\text{exp}} = 2.4 \times 10^{12} \text{ cm}^{-3} \text{ s}$ and $\text{Cl}_{\text{exp}} = 1.6 \times 10^{10} \text{ cm}^{-3} \text{ s}$, respectively. At these exposures, as a result of the relative reaction rates of $\text{D}_5 + \text{OH}$ and $\text{D}_5 + \text{Cl}$,⁷ we anticipate that the extent of OH and Cl oxidation of D_5 and/or its oxidation products is the same within $\approx 30\%$ uncertainty. Both D_5 OH-SOA and Cl-SOA spectra were dominated by $\text{C}_x\text{H}_y\text{O}_2\text{Si}_n^+$ ion groups, which contributed 61 and 69% of the total OH-SOA and Cl-SOA signal, respectively (panels e and f of Figure 3). Within this ion group, m/z 329 ($\text{C}_4\text{H}_{13}\text{O}_8\text{Si}_5^+$) and m/z 331 ($\text{C}_4\text{H}_{11}\text{O}_{10}\text{Si}_4^+$) were the largest signals in the OH-SOA spectrum, whereas m/z 73 ($\text{C}_3\text{H}_9\text{Si}^+$), m/z 327 ($\text{C}_5\text{H}_{15}\text{O}_7\text{Si}_5^+$), and $\text{C}_4\text{H}_{13}\text{O}_8\text{Si}_5^+$ were the largest signals in the Cl-SOA spectra and an AMS spectra of D_5 OH-SOA measured elsewhere.⁴⁷ Han et al.⁴⁴ assigned $\text{C}_{12}\text{H}_{11}\text{O}_2\text{Si}_5^+$, $\text{C}_9\text{H}_9\text{O}_8\text{Si}_5^+$, and $\text{C}_5\text{H}_{15}\text{O}_9\text{Si}_4^+$ to signals at m/z 327, 329, and 331 in their AMS spectrum of D_5 OH-SOA. These formulas can also explain our signals at those nominal m/z values but require significantly more complex fragmentation in the AMS than our proposed assignments. Other signals that were present at large abundances in both OH-SOA and Cl-SOA spectra include m/z 15 (CH_3^+), which corresponds to methyl groups that were bonded to Si atoms, m/z 29 (CHO^+), a marker for alcohols,³⁸ and m/z 44 (CO_2^+), a marker for organic acids⁴⁸ and potentially also formate esters.^{49,50}

Figure S2 of the Supporting Information shows AMS $\text{C}_x\text{H}_y\text{O}_2\text{Si}_n^+$ signals that were detected in D_5 OH-SOA and Cl-SOA spectra above m/z 350. In general, AMS signals in this range of higher m/z are less common as a result of high-energy electron impact ionization of 70 eV and flash vaporization at $T = 600^\circ\text{C}$ that result in thermal decomposition and fragmentation of the analyte molecules; their presence here underscores the stability of siloxanes that undergo both processes. The most prominent feature of the OH-SOA spectrum (Figure S2a of the Supporting Information) was a cluster of ion signals observed at m/z 639–671, whereas several distinct ion clusters were detected in the Cl-SOA spectrum between m/z 579–587, 595–602, 637–647, 653–661, and 669–675 (Figure S2b of the Supporting Information). Additional ion clusters were detected in both spectra at m/z 895–902, 909–916, 923–930, 955–962, 969–976, and 983–990. Unambiguous assignment of chemical formulas to the ion signals shown in Figure S2 of the Supporting Information is difficult as a result of the limited range of the AMS m/z calibration ($m/z \leq 355$, $\text{C}_9\text{H}_{27}\text{O}_5\text{Si}_5^+$); however, the relative abundances of ²⁹Si and ³⁰Si isotopes suggest that they contain 10 Si atoms. Thus, at these OH_{exp} and Cl_{exp} values, dimers were present in D_5 SOA, as observed in earlier studies.^{10,22} The different fragmentation patterns shown in panels a and b of Figure S2 of the Supporting Information reflect differences in the chemical composition of dimers that were present in D_5 OH-SOA and Cl-SOA.

Panels e–h of Figure 3 plot fractional contributions of the C_xH_y^+ , $\text{C}_x\text{H}_y\text{O}^+$, $\text{C}_x\text{H}_y\text{O}_2^+$, $\text{C}_x\text{H}_y\text{O}_2\text{Si}_n^+$, and $\text{Cl}^+ + \text{HCl}^+$ ion groups ($f_{\text{C}_x\text{H}_y^+}$, $f_{\text{C}_x\text{H}_y\text{O}^+}$, $f_{\text{C}_x\text{H}_y\text{O}_2^+}$, $f_{\text{C}_x\text{H}_y\text{O}_2\text{Si}_n^+}$, and f_{HCl^+}) present in D_5 OH/Cl-SOA as a function of oxidant exposure. Here, f_{HCl^+} was used as a marker for condensed-phase organic chlorides (ROCl),^{25,51,52} assuming that uptake of gas-phase HCl to the SOA was negligible. Minimal signals were observed at other $\text{C}_x\text{H}_y\text{O}_2\text{Cl}^+$ -containing ions. In all cases, $f_{\text{C}_x\text{H}_y\text{O}_2\text{Si}_n^+}$ decreased monotonically over the range of OH_{exp} and Cl_{exp} used here. In a different study,⁴⁴ $f_{\text{C}_x\text{H}_y\text{O}_2\text{Si}_n^+}$ of D_5 OH-SOA increased from

0.07 to 0.47 as OH_{exp} was increased from 1.5×10^{11} to $1.3 \times 10^{12} \text{ cm}^{-3} \text{ s}$ before it began to decrease. Taken together with our results, this suggests that the AMS $\text{C}_x\text{H}_y\text{O}_z\text{Si}_n^+$ ion group represents a class of intermediate oxidation products whose consumption following reaction with OH/Cl generates extremely low-volatility oxidation products that contribute to higher SOA yields observed at higher OH_{exp} or Cl_{exp} .

For OH-SOA and humid Cl-SOA, $f_{\text{C}_x\text{H}_y^+}$, $f_{\text{C}_x\text{H}_y\text{O}_1^+}$, and $f_{\text{C}_x\text{H}_y\text{O}_{21}^+}$ increased, whereas for dry Cl-SOA, $f_{\text{C}_x\text{H}_y^+}$ decreased while $f_{\text{C}_x\text{H}_y\text{O}_1^+}$ and $f_{\text{C}_x\text{H}_y\text{O}_{21}^+}$ increased. The maximum $f_{\text{C}_x\text{H}_y\text{O}_1^+}$ and $f_{\text{C}_x\text{H}_y\text{O}_{21}^+}$ values were lower in humid Cl-SOA (0.12) than in dry Cl-SOA (0.38–0.40). Despite the lack of double bonds in D_5 for direct Cl or Cl_2 addition, evidence of ROCl formation was observed in Cl-SOA: f_{HCl^+} followed the same trend as $f_{\text{C}_x\text{H}_y\text{O}_{21}^+}$ with increasing Cl_{exp} as observed in other Cl-SOA types.²⁵ One possible source of ROCl may have been the reaction $\text{RO}_2 + \text{Cl} \rightarrow \text{RO} + \text{ClO}$ followed by the reaction $\text{RO}_2 + \text{ClO} \rightarrow \text{ROCl} + \text{O}_2$,^{53,54} where RO_2 represents organic peroxy radicals derived from Cl oxidation of D_5 and/or its oxidation products and RO represents alkoxy radicals.

3.3.2. VIA Spectra of D_5 OH-SOA and Cl-SOA. Figure 4a shows a VIA spectrum of SOA generated from the OH

Si(O)O₂]. Similarly, carbonyl siloxanols detected at m/z 361 ($\text{C}_6\text{H}_{20}\text{O}_8\text{Si}_5\text{H}^+$) and m/z 367 ($\text{C}_3\text{H}_{14}\text{O}_{11}\text{Si}_5\text{H}^+$) were likely generated by two and five $\text{CH}_3 \rightarrow \text{OH}$ fragmentation reactions plus one $\text{SiO}_2(\text{CH}_3)_2 \rightarrow \text{Si(O)O}_2$ fragmentation reaction. Other significant product ions with 2 or fewer DBEs were detected at m/z 377, 379, 381, and 383. These signals represent siloxanols that were generated by three to six $\text{CH}_3 \rightarrow \text{OH}$ fragmentation reactions.

Panels b and c of Figure 4 show VIA spectra of SOA generated from the Cl oxidation of D_5 at $\text{Cl}_{\text{exp}} = 4.6 \times 10^{10} \text{ cm}^{-3} \text{ s}$ under dry and humid conditions (comparison spectra were not available at both conditions at $\text{Cl}_{\text{exp}} = 1.6 \times 10^{10} \text{ cm}^{-3} \text{ s}$). Many of the same ions detected in Cl-SOA spectra were also detected in the OH-SOA spectrum. However, signals at m/z 357 ($\text{C}_8\text{H}_{24}\text{O}_6\text{Si}_5\text{H}^+$), 359 ($\text{C}_7\text{H}_{22}\text{O}_7\text{Si}_5\text{H}^+$), and 361 ($\text{C}_6\text{H}_{20}\text{O}_8\text{Si}_5\text{H}^+$), which were generated by zero to two $\text{CH}_3 \rightarrow \text{OH}$ fragmentation reactions plus one $\text{SiO}_2(\text{CH}_3)_2 \rightarrow \text{Si(O)O}_2$ fragmentation reaction, were enhanced in Cl-SOA relative to OH-SOA, as were signals at m/z 373 ($\text{C}_9\text{H}_{28}\text{O}_6\text{Si}_5\text{H}^+$), 375 ($\text{C}_8\text{H}_{26}\text{O}_7\text{Si}_5\text{H}^+$), 377 ($\text{C}_7\text{H}_{24}\text{O}_8\text{Si}_5\text{H}^+$), and 379 ($\text{C}_6\text{H}_{22}\text{O}_9\text{Si}_5\text{H}^+$). Further, $\text{C}_8\text{H}_{24}\text{O}_6\text{Si}_5\text{H}^+$ and $\text{C}_7\text{H}_{22}\text{O}_7\text{Si}_5\text{H}^+$ as well as ions at m/z 385 and 387 that contained ≥ 3 DBEs were enhanced in the dry Cl-SOA spectrum relative to the humid Cl-SOA spectrum.

As was the case with AMS spectra, another notable difference between VIA spectra of D_5 OH-SOA and Cl-SOA was the relative abundance and composition of signals between m/z 660 and 860 that represent $\text{C}_x\text{H}_y\text{O}_z\text{Si}_{10}$ dimer oxidation products. In OH-SOA, three clusters of signals between m/z 687–697, 703–715, and 721–733 were detected, whereas at least eight clusters were detected in Cl-SOA. While a detailed discussion of the $\text{C}_x\text{H}_y\text{O}_z\text{Si}_{10}$ composition of each SOA type is beyond the scope of this analysis, we briefly note that the 37 $\text{C}_x\text{H}_y\text{O}_z\text{Si}_{10}$ species identified in D_5 OH-SOA by Wu and Johnston¹⁰ were detected in our VIA OH/Cl-SOA spectra along with numerous additional compounds. Additionally, Figure 4 shows that the relative yield of dimers was lowest in D_5 OH-SOA and highest in dry Cl-SOA. Because reaction with OH and/or hydroperoxyl radicals (HO_2) was the dominant RO_2 loss pathway in OH-SOA experiments (section 4), formation of dimers via $\text{RO}_2 + \text{RO}_2$ reactions was suppressed in OH-SOA relative to Cl-SOA. As will be discussed in section 4, H_2O also appears to suppress dimer formation to some extent in humid Cl-SOA relative to dry Cl-SOA.

A comparison of the AMS and VIA spectra shown in Figures 3 and 4 suggests that there was significant overlap between the major $\text{C}_x\text{H}_y\text{O}_z\text{Si}_5^+$ signals detected by both techniques at the lowest oxidant exposures that were used ($\text{OH}_{\text{exp}} = 2.4 \times 10^{12}$ and $\text{Cl}_{\text{exp}} = 1.6 \times 10^{10}$ to $4.6 \times 10^{10} \text{ cm}^{-3} \text{ s}$). For example, $\text{C}_5\text{H}_{18}\text{O}_9\text{Si}_5$ was detected at $\text{C}_5\text{H}_{18}\text{O}_9\text{Si}_5\text{H}^+$ in the VIA, and we hypothesize that the same compound fragmented into $\text{C}_4\text{H}_{13}\text{Si}_5\text{O}_8^+ + \text{CH}_3^+$ ions in the AMS along with H_2O elimination. Similarly, we hypothesize that $\text{C}_6\text{H}_{20}\text{O}_8\text{Si}_5$ was detected at $\text{C}_6\text{H}_{20}\text{O}_8\text{Si}_5\text{H}^+$ in the VIA and $\text{C}_5\text{H}_{15}\text{O}_7\text{Si}_5^+ + \text{CH}_3^+$ in the AMS, again accompanied by H_2O elimination. While a more extensive series of dimers was observed in both AMS and VIA spectra of Cl-SOA compared to OH-SOA (Figure S2 of the Supporting Information and Figure 4), a direct comparison between $\text{C}_x\text{H}_y\text{O}_z\text{Si}_{10}^+$ signals detected in the AMS and VIA spectra was not possible. This is presumably because dimer oxidation products experienced more complex fragmentation/decomposition in the AMS than monomers. Additionally, there was less overlap between AMS and VIA

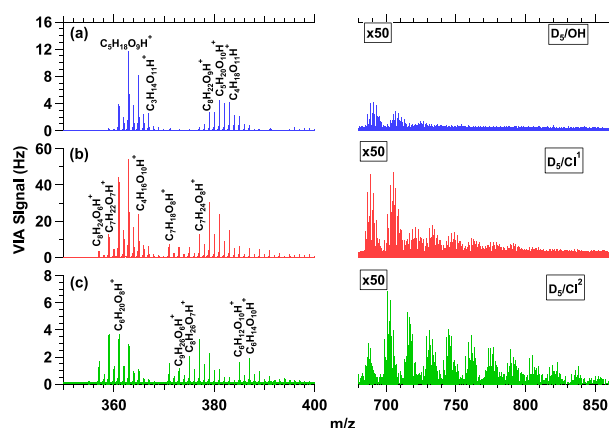


Figure 4. VIA spectra of SOA generated from (a) OH oxidation of D_5 ($\text{OH}_{\text{exp}} = 2.4 \times 10^{12} \text{ cm}^{-3} \text{ s}^{-1}$), (b) Cl oxidation of D_5 under humid conditions ($\text{Cl}_{\text{exp}} = 4.6 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$), and (c) Cl oxidation of D_5 under dry conditions ($\text{Cl}_{\text{exp}} = 4.6 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$). Signals shown are unmodified ($\text{M} + \text{H}$)⁺ formulas. Additional figure notes: ¹Cl generated using OFR369- iCl_2 under humid conditions and ²Cl generated using OFR369- iCl_2 under dry conditions.

oxidation of D_5 at the same OH_{exp} as the AMS spectrum shown in Figure 3a. Here, signals between m/z 350–400 and 660–860 are shown; full product spectra are shown on a logarithmic scale in Figure S3a of the Supporting Information. A list of molecular formulas of major $\text{C}_x\text{H}_y\text{O}_z\text{Si}_5$ compounds detected with the VIA is shown in Table S1 of the Supporting Information. The OH-SOA spectrum shown in Figure 4a was dominated by two clusters of signals between m/z 361–369 and 377–387. The ions at m/z 363 ($\text{C}_5\text{H}_{18}\text{O}_9\text{Si}_5\text{H}^+$, detected previously in D_5 SOA²²) and m/z 365 ($\text{C}_4\text{H}_{16}\text{O}_{10}\text{Si}_5\text{H}^+$) were the largest signals in the OH-SOA spectrum. We hypothesize that $\text{C}_5\text{H}_{18}\text{O}_9\text{Si}_5$ and $\text{C}_4\text{H}_{16}\text{O}_{10}\text{Si}_5$ are carbonyl siloxanols generated following three and four $\text{CH}_3 \rightarrow \text{OH}$ fragmentation reactions, respectively,^{22,50} plus the replacement of two adjacent methyl groups with a carbonyl [$\text{SiO}_2(\text{CH}_3)_2 \rightarrow$

spectra obtained at higher OH_{exp} and Cl_{exp} than in those shown in Figures 3 and 4. Specifically, later-generation carboxylic acids/formate ester oxidation products were more efficiently detected by the AMS than by the VIA as a result of the lower selectivity of H_3O^+ reagent toward highly oxidized compounds.⁵⁵ Implications of the different instrument responses to early- versus later-generation D_5 oxidation products are discussed in the following section, where we examine changes in the elemental composition of D_5 SOA to provide information about the nature of associated oxidative aging pathways.⁵⁶

3.3.3. Elemental Composition of OH-SOA and Cl-SOA.

Diagrams that show C/Si as a function of O/Si can be used to track $\text{CH}_3 \rightarrow \text{CH}_2\text{OH}$ ($\Delta\text{C}/\text{Si}/\Delta\text{O}/\text{Si} = 0$) and $\text{CH}_3 \rightarrow \text{OH}$ ($\Delta\text{C}/\text{Si}/\Delta\text{O}/\text{Si} = -1$) functionalization and fragmentation reactions in D_5 SOA,¹⁰ where O/Si may, in principle, increase from 0.5 to 4 with an accompanying decrease in C/Si from 2 to 0 following conversion of D_5 to orthosilicate (SiO_4^{4-}) as a hypothetical oxidation end product. Ensemble C/Si and O/Si values extracted from AMS spectra of D_5 OH-SOA and Cl-SOA are shown in Figure S5 of the Supporting Information. C/Si and O/Si of the least oxidized D_5 OH/Cl-SOA ranged from 2.5 to 3.5 and from 1.8 to 2.9, respectively. While these C/Si values are larger than C/Si of D_5 , they may be plausible within the uncertainty of unknown AMS sensitivity to Si. However, Figure S5 of the Supporting Information shows that C/Si and O/Si both increased to maximum values ranging from 22 to 60 and from 10 to 67, respectively, as a function of OH_{exp} or Cl_{exp} . While loss of particulate Si is possible,^{10,44} it seems unlikely that it can occur to the extent that would be necessary to explain these observations. There are two alternative explanations for these results. First, conversion of particulate Si to refractory aerosol with aging may have decreased its volatility relative to the carbon-containing functional groups attached to the siloxane backbone. An accompanying change in thermal decomposition/fragmentation mechanisms may have resulted in less volatile Si species producing lower Si/C ratios than higher volatility species. This bias would not be accounted for in the elemental analysis method used here. Second, early-generation oxidation products that generated $\text{C}_x\text{H}_y\text{O}_z\text{Si}_n^+$ signals in the AMS may have been converted to later-generation oxidation products in the OFR that preferentially generated Si^+ (m/z 27.97) and/or SiO^+ (m/z 43.97) signals, which were difficult to isolate from N_2^+ and CO_2^+ signals at the same nominal m/z 28 and 44 values. We estimated upper limit contributions of Si^+ and SiO^+ by adding them to the AMS peak list and then recalculating C/Si and O/Si for dry Cl-SOA, which had the highest O/Si of all D_5 SOA types examined here. While this analysis yielded maximum C/Si and O/Si values of 4.2 and 4.8 (down from C/Si = 60 and O/Si = 67 without fitting Si^+ and SiO^+), which may be plausible within uncertainties, it did not significantly change the overall trends of C/Si and O/Si as a function of oxidant exposure. Because the analysis of C/Si and O/Si values was inconclusive (perhaps as a result of inefficient detection of Si, SiO, or RSiO compounds), we instead constructed a Van Krevelen diagram that showed H/C as a function of O/C to examine oxidative aging pathways of the methyl groups present in D_5 SOA.

Ensemble H/C and O/C values extracted from AMS spectra of D_5 SOA are shown in Figure 5. The atomic O/C and H/C values of D_5 as well as trendlines for $\text{CH}_3 \rightarrow \text{CH}_2\text{OH}$, $\text{CH}_3 \rightarrow \text{OH}$, $\text{CH}_3 \rightarrow \text{CH}_2\text{OH}$, $\text{CH}_3 \rightarrow \text{C(O)OH}$ or OC(O)H , and

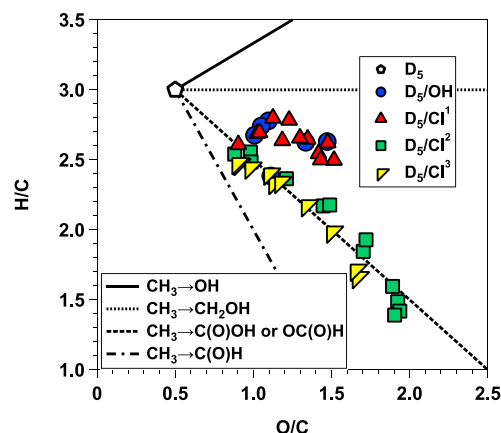


Figure 5. Van Krevelen diagrams showing the H/C ratio as a function of the O/C ratio for D_5 OH-SOA and Cl-SOA. Additional figure notes: ^1Cl generated using OFR369- iCl_2 under humid conditions, ^2Cl generated using OFR369- iCl_2 under dry conditions, and ^3Cl generated using OFR254/313- $\text{iC}_2\text{Cl}_2\text{O}_2$.

$\text{CH}_3 \rightarrow \text{C(O)H}$ functionalization/fragmentation reactions are shown for reference. These trendlines have Van Krevelen slopes ($\Delta\text{H}/\text{C}/\Delta\text{O}/\text{C}$) of 0.67, 0, -1 , and -2 , respectively. Functionalization reactions that convert methyl groups to peroxide groups may also have occurred, with a corresponding Van Krevelen slope of 0. Because peroxides are known to fragment in the Vocus PTR,⁵⁷ we could not unambiguously identify them in our measurements; thus, they are not discussed further here.

Figure 5 shows that D_5 OH-SOA had O/C and H/C ranging from 1.0 to 1.5 and from 2.6 to 2.8, respectively. Dry Cl-SOA had O/C = 0.88–1.9 and H/C = 1.4–2.5, whereas humid Cl-SOA had O/C = 0.90–1.5 and H/C = 2.5–2.8. In OH-SOA and humid Cl-SOA, H/C increased from 2.6 to 2.8 as O/C increased from 1.0 to 1.2 before H/C decreased to 2.5 at O/C = 1.5. Corresponding average Van Krevelen slopes were -0.27 (OH-SOA) and -0.11 (humid Cl-SOA). This overall trend was consistent with expected $\text{CH}_3 \rightarrow \text{OH}$ and/or $\text{CH}_3 \rightarrow \text{CH}_2\text{OH}$ reactions at lower OH_{exp} or Cl_{exp} ,^{10,50} followed by the formation of carbonyl, carboxylic acid, and/or formate ester functional groups at higher oxidant exposures. On the other hand, H/C of dry Cl-SOA decreased continuously from 2.5 to 1.4 with increasing O/C, with an average Van Krevelen slope ranging from -1.03 (OFR254/313- $\text{iC}_2\text{Cl}_2\text{O}_2$) to -1.07 (OFR369- iCl_2). This trend, along with the accompanying increase in AMS CO_2^+ signal, suggests that $\text{CH}_3 \rightarrow \text{C(O)OH}$ and/or $\text{CH}_3 \rightarrow \text{OC(O)H}$ reactions were significant in dry Cl-SOA.

Table S1 of the Supporting Information lists 24 major $\text{C}_x\text{H}_y\text{O}_z\text{Si}_5$ tracers that were detected with the VIA and presented in Figure 4. Compounds with ≤ 2 DBEs were generated via $\text{CH}_3 \rightarrow \text{OH}$ reactions, including the series of $\text{C}_9\text{H}_{28}\text{O}_6\text{Si}_5$ through $\text{C}_4\text{H}_{18}\text{O}_{11}\text{Si}_5$ siloxanols and $\text{C}_8\text{H}_{24}\text{O}_6\text{Si}_5$ through $\text{C}_3\text{H}_{14}\text{O}_{11}\text{Si}_5$ carbonyl siloxanols. These compounds have atomic O/C values ranging from 0.67 to 3.67, which more than span the range of ensemble O/C values extracted from AMS spectra. However, their corresponding H/C values (3.0–4.7) were higher than AMS-derived H/C values, and this divergence increased with increasing O/C. A series of $\text{C}_{6-8}\text{H}_{12-20}\text{O}_{7-10}\text{Si}_5$ compounds measured with VIA that contain ≥ 2 DBEs more closely tracked ensemble O/C and H/C values of D_5 OH/Cl-SOA. We hypothesize that these

compounds represent dehydration/decarboxylation products of thermally labile species in the VIA whose behavior in the instrument is not yet known. Thus, we cannot yet make definitive conclusions about their composition or contributions to D_5 SOA at higher OH_{exp} and Cl_{exp} .

4. DISCUSSION

Differences in D_5 OH-SOA and Cl-SOA composition that are summarized in Figures 3–5 are associated with differences in the fate of RO_2 derived from OH or Cl oxidation of D_5 and its early-generation oxidation products. To investigate the fate of RO_2 in these studies, we calculated the fractional oxidative loss of a generic siloxy RO_2 (F_{RO_2}) generated from the OH or Cl oxidation of 12 ppbv D_5 as a function of OH_{exp} or Cl_{exp} using the KinSim chemical kinetic solver.⁵⁸ Kinetic data used in these calculations^{7,30,59–64} are provided in Table S2 of the Supporting Information; the corresponding reactions were added to the KinSim mechanism published previously by our group.²⁵ Here, we assumed RO_2 reacted with OH, HO_2 , Cl, ClO, RO_2 , and/or underwent autoxidation via sequential isomerization and O_2 addition. Alton and Browne⁵⁰ proposed a humidity-dependent mechanism for the gas-phase OH/Cl oxidation of D_3 in which RO that was generated following RO_2 isomerization reacted with H_2O , generating a silanol and OH as co-products. To evaluate the potential effect of this reaction on the RO_2 fate, we set the $RO + H_2O$ rate coefficient to $4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ to make this reaction proceed at the same rate as RO_2 isomerization/autoxidation reactions and then calculated F_{RO_2} in D_5 /Cl experiments with and without this reaction enabled in the model.

In D_5 /OH studies, the main RO_2 loss pathways were $RO_2 + HO_2$ and $RO_2 + OH$ reactions: $F_{RO_2+HO_2}$ decreased from 0.36 to 0.17 and F_{RO_2+OH} decreased from 0.63 to 0.83 as a function of OH_{exp} (Figure 6a). RO_2 consumption as a result of isomerization/autoxidation and reaction with other RO_2 were minor (<1% of total RO_2 loss). In D_5 /Cl studies, the RO_2 fate was more complex. With the $RO + H_2O$ reaction enabled (e.g., in humid conditions), as a function of Cl_{exp} , $F_{RO_2+RO_2}$ decreased from 0.11 to 0.003, F_{RO_2} as a result of isomerization/autoxidation decreased from 0.15 to 0.002, F_{RO_2+Cl} increased from 0.24 to 0.33, and F_{RO_2+ClO} increased from 0.21 to 0.32 (Figure 6b). As a result of OH formation via the $RO + H_2O$ reaction, F_{RO_2+OH} was likewise significant and increased from 0.29 to 0.35 as a function of Cl_{exp} . Under dry conditions, at low Cl_{exp} , $F_{RO_2+RO_2} = 0.24$, $F_{RO_2+Cl} = 0.30$, $F_{RO_2+ClO} = 0.27$, and $F_{RO_2} = 0.19$ as a result of isomerization/autoxidation were all higher than under humid conditions (Figure 6c). As expected, these trends are qualitatively consistent with the higher yields of dimers and ROCl that were observed in dry Cl-SOA relative to humid Cl-SOA and OH-SOA (Figures 3 and 4). Likewise, the higher SOA oxidation state of dry Cl-SOA was associated with higher yields of carboxylic acids/formate esters formed via isomerization/autoxidation and/or $RO_2 + Cl/ClO$ reactions (Figures 3 and 5). As was observed for RO_2 generated in humid D_5 /Cl studies, $F_{RO_2+RO_2}$ and F_{RO_2} as a result of isomerization/autoxidation approached zero at high Cl_{exp} , where F_{RO_2+Cl} and F_{RO_2+ClO} were the only important RO_2 loss pathways.

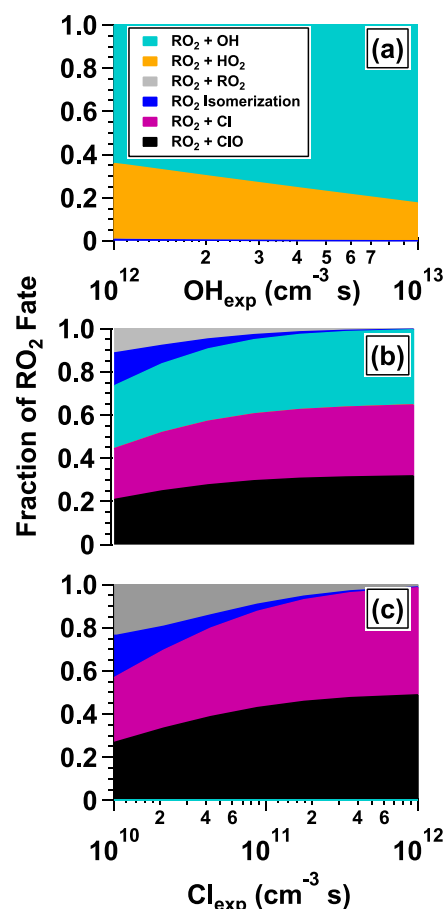


Figure 6. Fate of organic peroxy radicals (RO_2) generated from (a) OH, (b) Cl (humid), and (c) Cl (dry) oxidation of D_5 as a function of OH_{exp} or Cl_{exp} . Reactions and kinetic rate coefficients used in these calculations are provided in Table S2 of the Supporting Information.

5. CONCLUSION

In this study, we characterized the yields, mass spectra, and elemental composition of SOA generated from the OH and Cl oxidation of D_5 . D_5 OH-SOA and humid Cl-SOA had the highest degree of similarity, and dry Cl-SOA was the most unique; these similarities and differences are most closely associated with the overall RO_2 fate in each SOA type. Results presented in section 3.2 indicate the high SOA formation potential of D_5 : SOA yields of OH-SOA and humid Cl-SOA approached 1.5 and 1.3 at the highest OH_{exp} and Cl_{exp} values that were used. These SOA yields are comparable to or greater than yields of SOA obtained from OH/Cl oxidation of alkanes studied previously.^{25,52,65–69} While $CH_3 \rightarrow OH$ fragmentation reactions resulting in carbon loss occurred, the fact that the majority of oxidation products detected by the AMS and the VIA contained 5 or 10 Si atoms suggests that the cyclic Si–O backbone of D_5 was mostly retained. Therefore, the average volatility of the oxidation products continued to decrease as remaining C atoms experienced fragmentation reactions, to the point that the SOA became more refractory at the highest oxidant exposures.

Multiple days of equivalent atmospheric OH exposure were required to achieve significant OH-SOA formation. However, most of the exposure time that was required was associated with the long OH lifetime of D_5 . As noted throughout this paper, lower Cl concentrations were required to generate SOA

because the $D_5 + Cl$ reaction rate is nearly 2 orders of magnitude faster than that of $D_5 + OH$.⁷ Because estimated atmospheric Cl concentrations vary between 10^3 and 10^5 cm^{-3} , the corresponding atmospheric Cl-SOA formation potential of D_5 ranges from insignificant to potentially important on time scales of a day or so in source regions influenced by active chlorine chemistry.³² Indoor Cl concentrations that reach 10^5 to 10^8 cm^{-3} following bleach cleaning or disinfection activities^{19,70} may also be sufficient to achieve D_5 Cl-SOA formation in occupied spaces with low air exchange rates.

Our results indicate that SOA generated from the OH/Cl oxidation of D_5 and potentially other cVMS pose several unique challenges for the AMS that warrant further investigation in future studies. First, the refractory nature of D_5 SOA suggests that only a fraction of it is detected at typical AMS operating conditions. To improve AMS detection of cVMS SOA, future studies should investigate the effect of increasing the vaporizer temperature from the nominal 600 °C set point that is commonly used to ~800 °C.^{71,72} Second, the AMS ionization efficiency of Si has not been measured directly because inorganic Si standards, such as silicon dioxide and silicic acid, are refractory. Measurements of cVMS SOA (section 3.3.3 and Figure S5 of the Supporting Information) and D_{15} – D_{18} siloxanes⁷³ suggest that the AMS sensitivities to organosilicon and non-Si-containing organic compounds are within a factor of 2 of each other. In principle, to provide better constraints, non-refractory inorganic Si aerosol standards would be required. Third, the relatively high thermal stability of D_5 SOA results in significant formation of product ions at $m/z > 350$, yet there are few, if any, instrument background signals in this m/z range that can be used to constrain ion formula assignments. Simultaneous measurement of high-molecular-weight aerosol standards, such as Fomblin pump oils,⁷⁴ may be required for this purpose.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00304>.

AMS spectra of D_5 SOA between m/z 350 and 1000, additional VIA spectra of D_5 SOA, volume-weighted diameter of D_5 SOA size distributions, C/Si and O/Si ratios of D_5 SOA extracted from AMS spectra, list of molecular formulas of major $D_5 + OH/Cl$ oxidation products detected with VIA, and kinetic data used in our KinSim model to estimate the RO_2 fate (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Anita M. Avery – Aerodyne Research, Incorporated, Billerica, Massachusetts 01821, United States; orcid.org/0000-0002-6130-9664; Email: aavery@aerodyne.com

Andrew T. Lambe – Aerodyne Research, Incorporated, Billerica, Massachusetts 01821, United States; orcid.org/0000-0003-3031-701X; Email: lambe@aerodyne.com

Authors

Mitchell W. Alton – University of Eastern Finland, 70210 Kuopio, Finland; orcid.org/0000-0002-7119-3706

Manjula R. Canagaratna – Aerodyne Research, Incorporated, Billerica, Massachusetts 01821, United States

Jordan E. Krechmer – Aerodyne Research, Incorporated, Billerica, Massachusetts 01821, United States; Present Address: Jordan E. Krechmer: Bruker Scientific, Billerica, Massachusetts 01821, United States

Donna T. Sueper – Aerodyne Research, Incorporated, Billerica, Massachusetts 01821, United States

Nirvan Bhattacharyya – Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78758, United States; orcid.org/0000-0003-3911-6492

Lea Hildebrandt Ruiz – Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78758, United States; orcid.org/0000-0001-8378-1882

William H. Brune – Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0002-1609-4051

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00304>

Notes

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