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Molecular Characterization of Secondary Aerosol from Oxidation of Cyclic Methylsiloxanes

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Abstract

Cyclic volatile methylsiloxanes (cVMS) have been identified as important gas-phase atmospheric contaminants, but knowledge of the molecular composition of secondary aerosol derived from cVMS oxidation is incomplete. Here, the chemical composition of secondary aerosol produced from the OH-initiated oxidation of decamethylcyclopentasiloxane (D₅, C₁₀H₃₀O₅Si₅) is characterized by high performance mass spectrometry. ESI-MS reveals a large number of monomeric (300 < m/z < 470) and dimeric (700 < m/z < 870) oxidation products. With the aid of high resolution and MS/MS, it is shown that oxidation leads mainly to the substitution of a CH₃ group by OH or CH₂OH, and that a single molecule can undergo many CH₃ group substitutions. Dimers also exhibit OH and CH₂OH substitutions and can be linked by O, CH₂ and CH₂CH₂ groups. GC-MS confirms the ESI-MS results. Oxidation of D₄ (C₈H₂₄O₄Si₄) exhibits similar substitutions and oligomerizations to D₅, though the degree of oxidation is greater under the same conditions and there is direct evidence for the formation of peroxy groups (CH₂OOH) in addition to OH and CH₂OH.

Keywords

secondary organic aerosol; particle phase; oxygen-containing functional groups; organo silicon aerosol; particle formation

Introduction

Ambient nanoparticles (smaller than 100 nm in diameter) can disproportionately affect climate and human health relative to their mass loading in the atmosphere. These particles influence climate by scattering the incoming solar radiation [1-3] and/or serving as cloud condensation nuclei (CCN) [4]. They influence human health by penetrating deep into the respiratory system [5-7]. To better understand these effects, knowledge of the chemical composition is needed [8]. Organic aerosol constitutes a large portion of this matter and most of this contribution is secondary, meaning that it is formed through reaction of gas phase volatile organic compounds (VOC) with oxidants (OH, O₃, NO₃) to give semi- or non-volatile products [8, 9].

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Recently, silicon was reported as a frequent component of ambient nanoparticles [10-12]. Measurements with Nano Aerosol Mass Spectrometer (NAMS), which provides quantitative elemental composition of particles in the 10-30 nm diameter range [13-15], showed that Si was often observed in urban and suburban environments but rarely detected in a remote environment [16]. The location dependence suggests that Si in these particles is associated with human activity. One possible source is atmospheric oxidation of cyclic volatile methylsiloxanes (cVMS), which are commonly used in personal care products [17-19]. cVMS are considered to be environmentally acceptable cleaning agents [20] due to their inertness to ozone [21]. Owing to high vapor pressure, they are easily released into atmosphere where they may react with OH [21] to form semi- or non-volatile products. An atmospheric transport model for three most common cVMS in personal care products: (octamethylcyclotetrasiloxane, D₄; decamethylcyclopentasiloxane D₅; and dodecamethylcyclohexasiloxane, D₆) is consistent with cVMS as a possible source of nanoparticulate Si [16].

In this work, the molecular composition of secondary aerosol obtained from cVMS oxidation is studied in detail. D₅ was chosen as the precursor and D₅-derived secondary aerosol was produced through a Photo-oxidation Chamber (PC) to simulate photo-oxidation in the atmosphere by reaction with hydroxyl radical. Several measurements were performed including high-resolution ESI-MS, ESI-MSMS and EI-MS. Previous work used only low-resolution GC-MS analysis, which could only provide partial characterization of the oxidation products [22].

Experimental Section

Aerosol Formation and Particle Collection

Aerosol was generated in a Photo-oxidation chamber (PC) consisting of a 50L box shaped chamber made of a perfluoroalkoxy copolymer [23]. Before each experiment, the chamber was flushed continuously with clean, dry, air for 2-3 days. After flushing, background particle concentrations in the PC were below 100/cm³ and 0.5 µg/m³. The air was cleaned by passing compressed air through charcoal and high efficiency particulate matter air (HEPA) filters to remove organic vapors and particulates, and through silica gel to remove moisture. A Scanning Mobility Particle Sizer (SMPS; Model 3080/3078, TSI, St. Paul, Minnesota) was used to measure particle size distributions before and during experiments.

D₅ vapor was generating by passing clean, dry air with a flow rate of ~700 cpm (cm³/min) over the surface of D₅ fluid (CAS No.541-02-6, Gelest, Morrisville, Pennsylvania) in a gently heated gas flask bubbler. Ozone was generated by passing clean air around a mercury lamp (Model No.81-1025-01, BHK Inc., Ontario, California) and the ozone concentration was monitored with a Model 49i O₃ Analyzer (Thermo Fisher Scientific Inc., Waltham, MA). The gas flow of D₅ was sent into the PC along with additional 1 cpm flow of 15-20 ppmv ozone and 240cpm flow of water vapor, which was created by bubbling air through deionized water. These flows yielded a nominal residence time of 40 min in the PC. Once the gas flows, ozone concentration and relative humidity were stabilized, reaction was initiated by irradiating the chamber with UV lamps to generate OH from ozone and water. Using the method described by Hall and Johnston [23], the OH mixing ratio for these

experiments was estimated to be $\sim 1.5 \times 10^8 \text{ cm}^{-3}$. Particulate matter in the air flow exiting the PC was collected at a flow rate of $\sim 2 \text{ lpm}$ for 20-24 hrs onto a Teflon coated, glass fiber filter (GF/D, CAT No.1823-025, Whatman, GE Healthcare, Piscataway, NJ) for chemical analysis. Under the conditions used in this study, the secondary aerosol mass concentration was $\sim 60 \mu\text{g}/\text{m}^3$, more than one hundred times larger than the background concentration. Generally, 0.3 to 0.5 mg of aerosol was collected in each experiment for analysis. In all experiments, background aerosol samples were collected prior to the injections of reactants to identify and eliminate any artifacts.

After particle collection, the filter was sonicated for one hour with $\sim 8 \text{ ml}$ acetonitrile (ACN) (CAS No. 75-05-8, Fisher Scientific, Pittsburgh, Pennsylvania) and the resulting solution was filtered through a polyvinylidenedifluoride (PVDF) filter (CAT No. 6747-2504, GE Healthcare, Piscataway, NJ). The filtered solution was then concentrated nearly to dryness ($<0.5 \text{ ml}$) with a Speed Vac Concentrator (Model SC110A, Thermo Scientific, Waltham, Massachusetts). Finally, the sample was reconstituted to $1 \text{ mg}/\text{ml}$ with ACN. Reconstitution with methanol or ACN/ H_2O 50/50 by volume gave similar mass spectrometry results.

A few experiments were performed by bubbling air through a solution of D_4 rather than D_5 . All other conditions for the experiment remained the same. The D_4 concentration in the chamber for these experiments was not estimated, though the aerosol mass loading was similar to the D_5 oxidation experiments.

Mass spectrometry

High resolution electrospray mass spectra (ESI-MS) in both positive and negative ion modes were obtained with Q-Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Scientific, Waltham, Massachusetts) equipped with a heated electrospray ionization source (HESI). Samples were injected at a flow rate of $0.5 \mu\text{L}/\text{min}$ with a spray voltage of 3.5 kV and a temperature of 250°C . Mass spectra were obtained over the range $50\text{--}950 \text{ m/z}$ with a nominal mass resolving power of 70000. Typically, data were acquired for 1 min with ~ 60 spectra averaged. For ESI-MS/MS experiments, a quadrupole mass filter isolated each chosen precursor, with subsequent analysis using collision induced dissociation (CID) with the collision energy adjusted between 10 and 30 eV depending on the precursor ion.

Samples were also analyzed by GC-MS with a Waters GCT Premier high-resolution time-of-flight mass spectrometer with a scan range of $50\text{--}950 \text{ m/z}$ coupled to an Agilent 7890A gas chromatograph. Ionization was performed by 70 eV EI with a source temperature of 180°C . Chromatographic separation was performed with an Agilent HP-5 column using a $3 \mu\text{L}$ injection volume and an injection port temperature of 280°C .

Four separate experiments of D_5 oxidation were performed under the conditions given above, and only those ions which were detected by ESI-MS in all four experiments are discussed below. These ions represented $\sim 85\%$ of the total number of ions detected. Ions that were detected in fewer than four experiments generally had very low signal intensities, which may have inhibited detection in some experiments and/or may have compromised accurate m/z measurement.

Results and Discussion

Figure 1 shows mass spectra of D₅-derived secondary aerosol from one of the four replicate experiments. Both monomer and dimer products are observed. As described in supplementary information, a few additional experiments were performed with a lower mass loading of aerosol in the PC. The monomer signal intensity appeared to increase relative to the dimer signal intensity when the mass loading was decreased (Figure S1), though more work is needed to explore this dependence thoroughly.

Ions observed in all four experiments were further characterized in the following way. First, background peaks from the PC and filter were removed from consideration, as were peaks with <0.5% (positive spectrum) and 0.1% (negative spectrum) relative intensity. This left a total of 190 (positive spectrum) and 233 (negative spectrum) peaks between 50 and 950 m/z. Chemical formulas with theoretical m/z values within ± 5 ppm of the measured m/z values were determined with the mass spectrometer software (X calibur). Reasonable formulas were selected based on the following general criteria: a) C₀₋₁₀H₁₋₃₀O₁₋₂₀Si₁₋₅ for monomers and C₁₀₋₂₀H₃₀₋₆₀O₁₀₋₃₀Si₅₋₁₀ for dimers, b) up to 1 Na atom for peaks in the positive ion spectrum, and c) H/C atomic ratio between 2.7 and 3.8.

Of the original 190 peaks in the positive spectrum, 154 peaks (81%) were assigned a reasonable single formula based on the above criteria. Of the original 233 peaks in the negative spectrum, 203 peaks (87%) were assigned a single, reasonable formula. The average mass difference between measured and theoretical m/z for peak assignments was 1.28 ppm. The majority of the assigned peaks in the positive ion spectrum (72%) contained one Na atom. Additionally, there was no evidence for multiply charged peaks. Only 30 peaks from the positive spectra and 26 peaks from the negative spectra could not be assigned a reasonable formula, and their relative intensities were generally < 1%. Assigned peaks are given in Table S1 of the supplementary information. The mass weighted signal intensity fractions (MIF) [24] of these ions showed that the average O/Si atomic ratio increased from 1 in D₅ to ~1.3 in the oxidized aerosol while the C/Si atomic ratio decreased from 2 to ~1.7 under the experimental conditions used in this study.

Peak assignments from the positive and negative ion spectra were combined, and redundancies due to charge (assuming MH⁺, MNa⁺, M-H⁻) and isotopic substitution were removed, giving 135 unique molecular formulas for the (neutral) products. The products were divided into three types: fragmented products, unsaturated products and saturated substituted products. Fragmented products were defined as those where the siloxane ring had to be broken, i.e. silicon numbers of 1-4 (monomers) or 6-9 (dimers); representative examples are C₈H₂₄O₄Si₄ and C₁₀H₃₂O₈Si₆. Unsaturated products were defined as those having silicon numbers of 5 (monomers) or 10 (dimers) but with an H/C atomic ratio less than 3, indicating the presence of unsaturated functional group(s); representative examples are C₉H₂₆O₈Si₅ and C₁₈H₅₂O₁₂Si₁₀. Saturated, substituted products were defined as those having silicon numbers of 5 (monomers) or 10 (dimers), but H/C ≥ 3 and O/Si > 1; representative examples are C₉H₂₈O₇Si₅ and C₁₈H₅₄O₁₁Si₁₀. Under the conditions of these experiments, more than 95% of the total mass weighted signal intensity was encompassed by

fragmented and saturated products (Table S2). Therefore, only these two product types are discussed below.

Fragmented Oxidation Products of D₅

A total of 58 neutral fragmented products were assigned. The molecular formulas suggest the presence of both cyclic and linear siloxane structures with different numbers of subunits, e.g. D₂, D₃, D₄, L₂, L₃, L₄ (D=cyclic; L=linear) with various fragmentations and substitutions e.g. loss of a CH₃ group, substitution of an OH group for a CH₃ group, etc. (See Table S3.) Figure S2 gives the positive ESI mass spectrum of pure D₅ as a control. Several fragmentation peaks are observed, some examples being 355.069 m/z assigned as (CH₃)₉(OSi)₅⁺ and 297.082 m/z assigned as (CH₃)₈(OSi)₄H⁺. It is likely that oxidation products of D₅ will also fragment during ESI analysis, making it difficult to distinguish whether or not the fragmentation products observed in this work are the result of photooxidation or an ESI artifact.

Saturated Oxidation Products of D₅

Under the experimental conditions of this study, saturated products represent the majority of the mass-weighted signal intensity (~70%). Relative to D₅ and its dimer, these products contain higher amounts of oxygen and lower amounts of carbon and hydrogen. Figure 2 provides a graphical summary of these formulas as a function of carbon to silicon (C/Si) and oxygen to silicon (O/Si) atomic ratios. The change in O/Si and C/Si ratios between the D₅ reactant and its oxidation products indicate the types of reactions that take place [11]. For example, substituting a CH₂OH group for a CH₃ group increases the O/Si ratio while the C/Si ratio remains constant, i.e. oxidizing (CH₃)₁₀(SiO)₅ to produce (CH₃)_{10-x}(CH₂OH)_x(SiO)₅. Substituting an OH group for a CH₃ group decreases C/Si ratio and increases O/Si ratio, i.e. oxidizing (CH₃)₁₀(SiO)₅ to produce (CH₃)_{10-y}(OH)_y(SiO)₅. For monomers, the assigned product formulas indicate various combinations of OH and CH₂OH substitution with up to 6 CH₃ groups replaced (Fig. 2a). The same types of substitutions are observed for dimers (Fig. 2b), but with the additional complication that the two monomers in a dimer can be linked with several species i.e. O, CH₂ and CH₂CH₂.

OH substitution for a CH₃ group

Figure 3a and 3b show ESI-MSMS spectra of the C₉H₂₈O₆Si₅ product in positive and negative ion modes, which is considered to have one OH substitution for a CH₃ group. The positive spectrum in Figure 3a shows the dissociation of the precursor at 373.080 m/z(+) which is assigned as C₉H₂₉O₆Si₅⁺, with -2.43 ppm mass accuracy, while the negative spectrum in Figure 3b shows the dissociation of the precursor at 371.066 m/z(-) which is assigned as C₉H₂₇O₆Si₅⁻ with mass accuracy -1.06 ppm. The first neutral loss in positive spectrum is H₂O (C₉H₂₉O₆Si₅⁺ to C₉H₂₇O₅Si₅⁺), while the corresponding loss in the negative spectrum is CH₄ (C₉H₂₇O₆Si₅⁻ to C₈H₂₃O₆Si₅⁻). These products are consistent with protonation of the OH group in the positive spectrum and deprotonation of the OH group in the negative spectrum. Other diagnostic ions are protonated and deprotonated trimethyl silanol, [Si(CH₃)₃OH+H⁺] and [Si(CH₃)₃O⁻] respectively, neutral loss of Si(CH₃)₄, and a series of protonated/deprotonated products corresponding to successive loss of siloxane subunits e.g. loss of C₄H₁₂O₂Si₂ or C₆H₁₈O₃Si₃.

It should be noted that a nearby precursor ion is observed in the positive mass spectrum at 373.043 m/z(+), which is assigned as the unsaturated product $C_8H_{25}O_7Si_5^+$ (−2.17 ppm). While this ion could lead to some of the products in Figure 3a, several product ions including the first neutral loss cannot be explained by its molecular formula (precursor has fewer carbon atoms than product). Furthermore, when the collision energy is increased from 10eV to 30eV, the product ion signal intensities increase substantially. At the same time, the normalized intensity of the precursor of interest 373.080 m/z(+) decreases by almost a factor of 6 (1.8E6 to 3.4E5), while the normalized intensity for the “impurity” precursor at 373.043 m/z(+) hardly changes at all (8.0E5 to 6.5E5). Taken together, the inconsistency of several product ions with the “impurity” precursor and the disparities in signal intensity suggest that the OH substituted product at 373.080 m/z(+) is the main contributor to the spectrum in Figure 3a and 3b.

CH₂OH substitution for a CH₃ group

Figure 3c shows the product ion mass spectrum for the 387.098 m/z(+) precursor $C_{10}H_{31}O_6Si_5^+$ (+0.22 ppm) which corresponds to one CH₂OH substitution for a CH₃ group. The first neutral loss is H₂O, consistent with protonation of the OH functionality. The second and more intense neutral loss is 355.069 m/z(+) ($C_9H_{27}O_5Si_5^+$, 2.92 ppm), which corresponds to the loss of CH₃OH from the precursor. Another diagnostic ion is $C_4H_{13}OSi^+$, which corresponds to protonated trimethylsilyl-methanol.

Dimer Linkages by O and CH₂

Figure 4a shows the product ion spectrum of the 727.140 m/z(+) precursor assigned as $C_{18}H_{55}O_{11}Si_{10}^+$ (−3.47 ppm), while Figure 4b shows an expansion of the product ion spectrum between 350 and 380 m/z(+). Two dimer linkages are possible for the precursor molecular formula. One is linkage by an O atom with all side groups as CH₃ (Scheme 1a) and the other by a CH₂ group with one side group as OH and the remaining as CH₃ (Scheme 1b). The two C₉ product ions labeled in black in Figure 4a cannot distinguish between the two linkages since they are expected products of both structures as shown in Scheme 1a and b. However, insight can be gained from other product ions in the spectrum. The first fragmentation from this precursor ($C_{17}H_{51}O_{11}Si_{10}^+$, −1.90 ppm) corresponds to a neutral loss of CH₄ while no H₂O loss is detected (Figure 4a). When compared with the neutral losses in Figures 3a and 3c, this observation suggests that very few precursors have an OH group and, therefore, the two siloxane rings are linked by an O atom in most dimers. However, the expansion in Figure 4b shows the presence of very low intensity fragment ions that are consistent with a CH₂ linkage. In particular, the $C_{10}H_{29}O_5Si_5^+$ product ion cannot be obtained from a dimer linked by an O atom (see structures in Scheme 1a and 1b). Taken together, there is strong evidence that both O and CH₂ linkages exist, though products unique to the O linkage have much greater intensity than those unique to the CH₂ linkage.

Dimer linkage by CH₂CH₂ (m/z 795.128)

A CH₂CH₂ linked dimer has been discussed previously as a product of D₄ oxidation [22]. Here, there are many precursors having formulas consistent with a CH₂CH₂ linkage, but it is very difficult in to distinguish by MSMS a structure having a CH₂ linkage with a CH₂OH substitution from one having a CH₂CH₂ linkage with an OH substitution. Nonetheless, one

precursor at 795.128 m/z(+) assigned as $C_{19}H_{56}O_{13}Si_{10}Na^+$ with (-3.18 ppm) provides clear evidence for a CH_2CH_2 linkage. This precursor must have either a CH_2 linkage with 3 CH_2OH substitutions or a CH_2CH_2 linkage with 2 CH_2OH substitutions and 1 OH substitution. The key product ion shown in Figure 4c is $C_{11}H_{30}O_7Si_5Na^+$ (-1.12 ppm), which can only be formed from a precursor having a CH_2CH_2 linkage as illustrated by the structure in Scheme 1c.

Comparison to previous work

GC-MS data are included as supplementary information. These data provide the opportunity to check consistency with ESI MSMS analysis and compare with previous work. Similar to the study of Sommerlade [22], GC-MS confirms that major components of D_5 -derived secondary aerosol are D_5 (presumably partitioned to the particle phase and/or bound within dimers), and an oxidation product corresponding to one OH substitution for CH_3 (see Figure S3). Our GC-MS results and those of Sommerlade provide evidence for a CH_2OH substitution product and the presence of dimers (O and CH_2 linked dimers), which is consistent with ESI-MS results, though the full range of products observed with ESI cannot be characterized by GC-MS.

The major products characterized in this work can be explained by OH abstraction of a hydrogen atom from D_5 as the initial step. Scheme 2 shows possible formation pathways for several of these products. Formation of the OH substitution product is similar to the reaction sequence proposed by Atkinson [25]. Note that formation of a multiply substituted product does not necessarily require multiple OH abstractions, since an auto-oxidation process based on internal hydrogen rearrangements [26] could lead to several substitutions.

D_4 -derived secondary aerosol

Secondary aerosol derived from OH oxidation of D_4 ($C_8H_{24}O_4Si_4$) was briefly studied for comparison to D_5 -derived aerosol. The ESI-MS spectra for D_4 -derived aerosol showed many more peaks than D_5 -derived aerosol, especially in the dimer and trimer regions. By applying the analysis procedure as discussed previously for D_5 , of the original 736 peaks in the positive spectrum, 671 peaks (91%) were assigned a reasonable, single formula. Of the original 455 peaks in the negative spectrum, 409 peaks (90%) were assigned a single, reasonable formula. The average mass difference between measured and theoretical m/z for peak assignments was 2.56 ppm. After removing redundancies due to charge (assuming MH^+ , MNa^+ , $M-H^-$) and isotopic substitution, 529 unique molecular formulas for the (neutral) products were obtained, which could be subdivided into fragmented, unsaturated and saturated products. About 96 % of the total products were fragmented or saturated, but more fragmented products were observed for D_4 -derived aerosol than D_5 -derived aerosol. MIF analysis showed the O/Si ratio increased from 1 in D_4 to ~1.48 in the oxidized aerosol while the C/Si ratio decreased from 2 to ~1.56 for the conditions used in this study.

Saturated products are shown graphically in Figure 5 where C/Si vs. O/Si is plotted for each observed molecular formula. Both OH and CH_2OH substitutions for CH_3 were identified, and relative to D_5 , a greater fraction of the CH_3 groups were found to be oxidized in D_4 .

Furthermore, monomer products having more than 8 oxygen atoms added to the D₄ molecule were detected, indicating that peroxy groups (CH₂OOH) must also be formed.

Conclusions

The molecular composition of cVMS-derived secondary aerosol was characterized by high performance mass spectrometry. The products can be divided into three types: fragmented products, unsaturated substituted products and saturated substituted products. Fragmented products arise at least in part as artifacts of electrospray ionization. Saturated substituted products exhibit the highest signal intensities. Based on a mass-weighted intensity fraction analysis, gas phase D₅ (O/Si=1, C/Si=2) was oxidized to produce aerosol whose detected products have an average O/Si $\approx$ 1.3 and an average C/Si $\approx$ 1.7 under the conditions studied. Gas phase D₄ was oxidized to produce trimers in addition to monomers and dimers, with the detected products having average O/Si $\approx$ 1.5 and C/Si $\approx$ 1.6 under the conditions studied. ESI-MS/MS analysis of the D₅-derived aerosol provided evidence for major substitution types along the siloxane ring and the linkages of two siloxane rings to produce dimers. The results showed that OH and CH₂OH substitutions are prevalent, and dimers can be linked by O, CH₂ and CH₂CH₂ groups. D₄-derived aerosol gave evidence for the presence of peroxy groups (CH₂OOH). GC-MS with EI generally confirmed the ESI analysis, though products were incompletely characterized owing to the greater extent of ion fragmentation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure. 1.
Representative ESI mass spectra of secondary aerosol from D₅ oxidation.

Figure. 2.

Plots of C/Si versus O/Si for saturated products of D₅ oxidation in the monomer (a) and dimer (b) regions. Each dot represents an assigned molecular formula of a saturated oxidation product. The arrows in the monomer plot extend from unoxidized D₅ and represent the two types of substitution that can occur. The arrows in the dimer plot take into account different possible linkages between monomers.

Figure 3.

Product ion spectra for isolation of a) 373 m/z (+), b) 371 m/z (-) and c) 387 m/z (+). These precursors correspond to the oxidation product of D_5 having one OH substitution for a CH_3 group (Fig. 3a and Fig. 3b), and D_5 having one CH_2OH substitution for a CH_3 group (Fig. 3c).

Figure 4.

Product ion spectrum of 727 m/z(+). a) Complete product ion spectrum. b) An expansion of 350 to 380 m/z(+). Peaks corresponding to an O linkage are marked with red. Peaks corresponding with a CH₂ linkage are marked with blue. Peaks consistent with both are marked in black. c) Expansion of the product ion spectrum of 795 m/z(+) between 380 and 470 m/z(+). Peaks corresponding with a CH₂CH₂ linkage are marked with blue.

Figure 5.

Plots of C/Si versus O/Si for saturated products of D₄ oxidation in the a) monomer and b) dimer regions. Each dot represents an assigned molecular formula of a saturated oxidation product. The arrows in the monomer plot extend from unoxidized D₄ and represent the two main types of substitution that occur. The arrows in the dimer plot take into account different possible linkages between monomers. Circles represent monomer products where all eight CH₃ groups have been substituted. Formulas to the right of the circles (same C/Si but higher O/Si) must contain peroxy groups.

Scheme 1.

Dimer structures with a) $-O-$, b) $-CH_2-$, and c) $-CH_2CH_2-$ linkages. The OH group in b) could be located anywhere around the siloxane ring. The locations of the two CH_2OH groups in c) can be anywhere on the left hand ring, while the location of the OH group can be anywhere on the right hand ring. The C_{11} product confirms the existence of a CH_2CH_2- linkage. Other labeled ions are consistent with, but not unique to, this linkage.

Scheme 2.

Possible pathways for product formation from OH oxidation of D₅.