Organic Sulfur Products and Peroxy Radical Isomerization in the OH Oxidation of Dimethyl Sulfide

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ABSTRACT: The atmospheric oxidation of dimethyl sulfide (DMS) represents a large natural source of sulfate particles and thus is a major contributor to the global radiative effect of aerosols; however, its underlying chemical mechanism remains poorly constrained. In particular, DMS oxidation generates a variety of intermediate organic sulfur species, whose fate and kinetics govern the ultimate amount and distribution of sulfate aerosol. There is thus a need to understand the production and chemistry of such intermediates, including the recently discovered hydroperoxymethyl thioformate, formed from the isomerization of the methylthiomethylperoxy radical (CH₃SCH₂OO). Here, chamber experiments were performed to measure product formation from the OH-initiated oxidation of DMS. Three real-time mass spectrometers were used to measure the formation and evolution of a broad suite of gas- and aerosol-phase sulfur-containing compounds, including nearly all the closed-shell organic sulfur species included in current mechanisms; some additional species not predicted by such mechanisms are detected as well. The rapid decay of many of the more oxidized organic sulfur species suggests that aerosol uptake and loss to surfaces can be important processes under the conditions of this study. In addition, the isomerization rate constant of the CH₃SCH₂OO radical was experimentally determined to be 0.09 s⁻¹ (0.03–0.3 s⁻¹, 1σ), in broad agreement with results from other studies.

KEYWORDS: dimethyl sulfide, hydroxyl radical, peroxy radical, isomerization, chamber experiments, mass spectrometers

1. INTRODUCTION

Dimethyl sulfide (DMS, CH₃SCH₃) represents the largest natural source of sulfur emitted into the atmosphere.¹ Phytoplankton emit DMS into the marine boundary layer (MBL), where it can undergo atmospheric oxidation to form sulfuric acid, thereby contributing to new particle formation and growth.³ Key intermediate oxidation products, such as dimethyl sulfoxide (DMSO, CH₃S(O)CH₃), methanesulfonic acid (MSA, CH₃S(O)OH) and methanesulfonic acid (MSIA, CH₃S(O)OH), can also contribute to aerosol growth by partitioning to the aqueous phase or undergoing multi-phase reactions to produce sulfate.⁴ Because of its large contribution to sulfate aerosol, DMS oxidation represents an important contributor to the global radiative effects of aerosols.⁵

The atmospheric oxidation of DMS is a complex, incompletely understood process. Much of the complexity stems from the branching of key radicals (e.g., peroxy radicals, RO₂) and the multi-generational oxidation processes that directly determine the overall production distribution (and hence sulfate yield). Adding to the complexity is the dependence of this chemistry on key environmental variables such as the temperature and NOx level, which vary spatially and temporally. Therefore, despite decades of study, there remain large uncertainties in our understanding of the amount and distribution of sulfate aerosols from DMS oxidation in the MBL.⁶

Figure 1 summarizes our current understanding of the major pathways and products of atmospheric DMS + OH reactions, based on a review by Barnes et al.⁷ and the chemistry within the Master Chemical Mechanism, MCM V3.3.1⁸⁻⁹ (http://mcm.leeds.ac.uk/MCM). The initial OH oxidation proceeds via two channels, addition and abstraction, both of which generate SO₂ along with a variety of intermediate products. Major intermediate products in the addition channel include short-lived species, such as DMSO and MSIA, and longer-lived species, such as dimethyl sulfone (DMSO₂, CH₃S(O)₂CH₃).
In the abstraction channel, the methylthiomethylperoxy radical (CH$_3$SCH$_2$OO) is formed in the initial step. The conventional understanding is that CH$_3$SCH$_2$OO reacts with HO$_2$ to form methylthiomethyl hydroperoxide (CH$_3$SCH$_2$OOH) and then methylthioformate (CH$_3$SCHO) or reacts with NO to produce the alkoxy radical and eventually products such as MSA and methanesulfonyl peroxy nitrate (CH$_3$S(O)$_2$ONOO$_2$). The oxidation of CH$_3$SCHO can also form CH$_3$S(O)$_2$OONO$_2$ and MSA. These intermediate organic sulfur species can affect the loadings and distribution of sulfate aerosol, both by delaying the formation of SO$_2$ and sulfate and by the potential loss of intermediate species via deposition. Accurate modeling of sulfate formation from DMS oxidation thus relies critically on a detailed understanding of the formation and loss of these intermediate species. However, the detailed chemistry (formation yields, loss processes, etc.) of these intermediates is not always well-constrained, and it is possible that the mechanism shown in Figure 1 may be incomplete, with additional, as-yet undetected, intermediates playing a role in the oxidation process.

For example, it has only recently been shown that CH$_3$SCH$_2$OO can undergo a two-step isomerization process to form hydroperoxymethyl thioformate (HPMTF, CH$_3$(OOH)SCHO)$_{10-12}$ highlighted in red in Figure 1. The formation of HPMTF was first suggested by Wu et al.$^{10}$ and was later measured in laboratory flow-tube experiments by Berndt et al.$^{11}$ Recent in situ observations by Veres et al.$^{12}$ and Vermeuel et al.$^{13}$ confirmed the atmospheric prevalence of HPMTF as a major DMS oxidation product and an important form of atmospheric sulfur in addition to DMS and SO$_2$ in the remote MBL. However, the isomerization rate constant ($k_{\text{isom}}$) of CH$_3$SCH$_2$OO is highly uncertain: the three determinations of $k_{\text{isom}}$ (two from quantum chemical techniques$^{10,12}$ and one from a direct measurement$^{11}$) span a range of nearly 2 orders of magnitude (from 0.041 to 2.1 s$^{-1}$ at 293–295 K). The large discrepancy in $k_{\text{isom}}$ represents a major uncertainty in our understanding of the mechanism of, and sulfate formation from, DMS oxidation.

In order to address the above unknowns in DMS chemistry, here we describe the laboratory chamber studies of DMS oxidation, with a focus on organic sulfur product species in the gas and particle phases, as well as the inorganic aerosol sulfate produced. From these measurements, we are able to (1) characterize the formation and loss of a broad suite of products in DMS oxidation and map them to the known gas-phase oxidation mechanism (Figure 1) and (2) constrain the $k_{\text{isom}}$ of CH$_3$SCH$_2$OO based on the observed rate of formation of HPMTF.

2. METHODS

2.1. Reaction Conditions and Instruments. Experiments were carried out in a 7.5 m$^3$ Teflon environmental chamber at 20 °C and RH < 3%. Dry conditions were used for simplicity and to focus on gas-phase chemistry only; the role of humidity, which is likely to affect multi-phase chemistry, is beyond the scope of this study but is an important topic for future research. The chamber was purged with zero air from a clean air generator (Aadco 737 Series) before the experiments, ensuring a clean gas and particle background. A constant tracer in the beginning of the experiments, enabling determination of the dilution rate; this dilution rate is applied to all reported concentrations. About 175 ppb of DMS was injected in the beginning of the experiment. The chamber was filled with ammonium sulfate seed particles before DMS injection, providing dry, inert surfaces for the condensation of low-volatility species; these were generated by atomizing dilute ammonium sulfate solution and then drying in a diffusion dryer. Two experiments were carried out, using HONO or
H2O2 as the OH source in the chamber. H2O2 was introduced into the chamber by bubbling an H2O2 solution. Here, we focus on the results from the HONO experiment; the H2O2 experiment suffered from a methanol contamination, so it was not used for investigating the products and kinetics in DMS oxidation. However, the H2O2 experiment provided a unique data set to identify and quantify HPMTF using iodide chemical ionization mass spectrometry, as discussed in detail in Section 2.3.

To generate HONO, a continuous 1 lpm flow was sent over ∼50 mL of 1 M NaNO2, to which a 15 μL aliquot of 1 M H2SO4 was added; this air was then sent into the chamber. This provided an initial concentration of 96 ppb HONO; this flow continued throughout the experiment, with an additional 0.1 μL min⁻¹ drip of 1 M H2SO4 providing a continuous source of HONO to the chamber. The chamber was surrounded by 48 ultraviolet lamps (maximum irradiance at 350 nm, Sylvania) with a total photon flux that yielded a photolysis rate constant³ of NO2 (j(No2) of 0.06–0.08 min⁻¹. Photo-oxidation was initiated by turning on the UV lamps to photolyze HONO. NO concentrations are estimated using a box model constrained by the experimental data (Section 2.3).

While NO2 measurements were unavailable for these experiments, modeled NO levels were ∼1 ppb, roughly the limit of quantification of our NO monitor. The exact NO concentrations are thus not well-constrained; as described in the Supporting Information (Section 7), [NO] is assigned a large (factor of 1.5) uncertainty.

The real-time gas- and particle-phase composition of the reaction mixture was measured by three time-of-flight mass spectrometry techniques: proton-transfer-reaction mass spectrometry (PTR-MS, Ionicon Analytik, PTR-TOF 8000, m/Δm ~ 5000), iodide-chemical ionization mass spectrometry (I-CIMS, Aerodyne Research Inc., m/Δm ~ 5000), and aerosol mass spectrometry (AMS, Aerodyne Research Inc., m/Δm ~ 2000). Details of the instruments and their calibration are provided in the Supporting Information (Figures S1 and S2). PTR-MS calibration was done either by comparing with the known initial amount in the chamber (for DMS) or by assuming an average sensitivity based on the use of calibration standards (for DMS oxidation products). The maximum sensitivity of an I-CIMS was determined by the sensitivity of N2O5, and the relative sensitivity was estimated using voltage scanning (also discussed below). The chamber and instrument backgrounds for all measured species were determined before the initiation of the photochemistry and subtracted prior to the calculation of product concentrations. The ionization efficiency of the AMS was calibrated using ammonium nitrate particles. In addition, a scanning particle mobility sizer was used to monitor the aerosol size distribution. Measurements of inorganic sulfur species in the gas phase (SO2 and OCS) were not available for these experiments, so we focus our analysis on organic sulfur species and inorganic sulfate aerosol only.

### 2.2. Identification of C2H2SO3 by I-CIMS

The identification of HPMTF is challenging due to the similarity in masses between the C2H2SO3-iodide cluster (C2H2SO3I⁻, m/z 234.8931) and the N2O5-iodide cluster (m/z 234.8857) and the moderate mass resolving power (m/Δm ~ 5000) of the I-CIMS. Here, we separate the two ions by adduct declustering using the voltage-scanning technique. Figure 2a shows the time series of m/z 235 signal (integrated ion counts of the peak in the m/z ~ 234.83–234.94 region) during the experiment. The double-peaked shape of the time series suggests that both the C2H2SO3I⁻ and the N2O5I⁻ adduct contributed to m/z 235, each dominating at different times. Figure 2b shows the dV50 (the voltage at which 50% of the analyte–iodide adduct has dissociated) of ions in this mass range, from voltage scans occurring every 10 min. The declustering profiles of N2O5I⁻ from an experiment with N2O3 but not C2H2SO3 (in which the precursor was xylene) is shown as the inset figure, together with the declustering profile of C2H2SO3I⁻ from an experiment with C2H2SO3 but not N2O5I⁻ (in which DMS was oxidized by OH generated by H2O2, with no NO present). The change of dV50 at m/z 235 in Figure 2b indicates a shift from C2H2SO3I⁻ (dV50 ~ 5 V) to N2O5I⁻ (dV50 ~ 8 V). With the two temporal peaks identified in Figure 2a, the time series of m/z 235 was then deconvolved into C2H2SO3I⁻ and N2O5I⁻ by fitting the data to the sum of two curves described by the gamma kinetic parameterization (Figure S5) and using these fits to apportion the signal between the two compounds, as shown in Figure 2c.

In addition to using voltage scanning, the peaks of C2H2SO3I⁻ and N2O5I⁻ in Figure 2a can also be qualitatively separated by their isotopic signals, since sulfur has a relatively high isotope abundance at 34S (4.21%). Figure S6 shows the mass spectral signal at m/z 237 collected by the I-CIMS toward the end of the experiment. The signal at m/z 236.89 is significantly lower than what would be expected if the m/z 235 signal was predominantly C2H2SO3I⁻, indicating that the peak at m/z 234.89 is dominated by ions other than C2H2SO3I⁻ toward the end of the experiment. This is consistent with the conclusion derived using the voltage-scanning technique that the first peak in Figure 2a is contributed by the formation of...
C₂H₆SO₃ and the latter peak is from the formation of N₂O₅. A more detailed description of C₂H₆SO₃⁺ and N₂O₅⁻ separation is provided in the Supporting Information.

2.3. Box Modeling. A 0-D model (the framework for 0-D atmospheric modeling, F0AM\(^7\)) coupled with the MCM was used to constrain the concentration of OH, NO, and HO₂ (Figures S7–S10), which were not directly measured in the experiments. The DMS oxidation scheme used is outlined in Figure 1; this includes the standard MCM chemistry, modified to include the HPMTF chemistry shown in Figure 1 (RO₂ isomerization to form HPMTF and OH followed by the loss of HPMTF via the OH reaction). The rate constants were those in Wu \(\text{et al.}\)^\(\text{1}\) except for the isomerization rate constant, which was taken from Berndt \(\text{et al.}\)^\(\text{1}\) before it was replaced with our own derived value and the HPMTF + OH rate constant, which was assumed to be $1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (the value used by Vermeuel \(\text{et al.}\)^\(\text{1}\)). The model simulation used known experimental parameters, including the temperature (293 K), relative humidity (1%), precursor concentration, chamber dilution rate constant, and UV irradiance derived from $\text{NO}_2$. The estimated OH concentration, which is consistent with the observed DMS decay (see the Supporting Information), is on the order of $1 \times 10^7$ molecule cm$^{-3}$ over the 6 h duration of the experiment; assuming an average atmospheric OH concentration of $1.5 \times 10^9$ molecule cm$^{-3}$, this is equivalent to a total OH exposure time of $\sim 40$ h under ambient conditions. The estimated concentrations of NO and HO₂ are $\sim 5.1 \times 10^9$ molecule cm$^{-3}$ and $\sim 1.5 \times 10^8$ molecule cm$^{-3}$, respectively. Therefore, RO₂ + NO reactions are expected to dominate over RO₂ + HO₂ but as we show below, RO₂ isomerization can compete as well. RO₂ + RO₂ reactions are found to be negligible. Details regarding the derivation of the concentration of OH, NO, and HO₂ are given in the Supporting Information and summarized in Table S2.

Detailed, quantitative comparisons between the measured and modeled DMS oxidation products are beyond the scope of this paper, due to the uncertainties in the mechanisms and instrument calibration, as well as the relatively limited range of reaction conditions accessed. Instead, the F0AM model, in addition to providing the estimates of concentrations of key radical species, is used to help identify the observed products and match them to our current understanding of DMS chemistry (as given in Figure 1).

3. RESULTS AND DISCUSSION

Our measurements using multiple mass spectrometers capture a broad suite of sulfur-containing DMS oxidation products in both the gas and particle phases; these are summarized in Table S1 and discussed in detail below. In this section, we first match the formulas of the measured products with those predicted by the MCM\(^5,\text{9}\) and Barnes \(\text{et al.}\)^\(\text{7}\) (depicted in Figure 1). We then broadly classify the measured species as early-generation products or later-generation products based on their overall temporal behavior in the experiment and compare them to generation numbers in the mechanism. If the observed formation of a species temporally corresponds to the rapid consumption of DMS in the early stage (first 2 h) of the experiment, the species is considered an early-generation product. If there is a significant delay (an “induction period”) in its formation, and/or its concentration continues to increase after the majority of the DMS has been consumed, the species is considered a later-generation product. We are thus able to examine the ability of our instrument suite to detect the key intermediates in the oxidation mechanism, as well as identify the possible key processes and species that are not currently included in the mechanisms. We then use the measured rate of HPMTF formation to constrain the CH₃SCH₂OO isomerization rate constant ($k_{\text{isom}}$).

3.1. Product Identification and Evolution. Figure 3 shows the time series of the sulfur-containing species measured using the three mass spectrometers. These include the precursor and relatively reduced gaseous organic sulfur products measured by PTR-MS (panel a), more oxygenated gaseous organic sulfur products measured by the I-CIMS (panel b), and the particle-phase sulfur species monitored by the AMS (panel c). The full list of measured formulas and their assigned species are listed in Table S1. We detect most of the closed-shell organic sulfur products in the mechanism summarized in Figure 1, though as described below some ions in the mass spectra indicate additional species that have received little to no previous study.

Products observed by PTR-MS (Figure 3a) include C₂H₆SO, C₃H₆SO₂, C₄H₇SO, and CS. The formula of the species C₂H₆SO and its temporal behavior are consistent with DMSO (CH₃S(O)CH₃), a first-generation product from the addition channel that undergoes further oxidation by OH (Figure 1). C₂H₆SO₂ could be DMSO₂ (CH₃S(O)₂CH₃) from

Figure 3. Products of DMS oxidation from PTR-MS (a), I-CIMS (b), and AMS (c). Measurements have been corrected for chamber dilution. The decay of DMS concentration was monitored using the PTR-MS and is shown on the left y axis in all panels. Concentrations of products are shown on the right y axis of each panel. Note that the three panels have different y-axis scales.
the addition channel or methylthiomethyl peroxide (CH3CHSCH2OOH) from the abstraction channel (followed by the RO2 + HO2 reaction). Given the low HO2 concentration, CH3H2SO2 is likely to be dominated by DMSO2. A small amount of CH3H2SO2 was found to increase with DMS when DMS was injected into the chamber. This leads to the 1 ppbS intercept of C2H4S2 at t = 0 in Figure 3a and is likely due to the impurity in the precursor. The temporal behavior of C2H4SO2 is consistent with an early-generation product, in agreement with the mechanism of DMSO2 formation shown in Figure 1 (though Barnes et al. suggest that DMSO2 can also be formed from DMSO oxidation). The formula of C2H4SO2 is consistent with methylthioformate (MTF, CH3SCHO), which was previously detected in chamber studies run under low-NOx conditions. The peak concentration of C2H4SO2 appears later than that of C2H4SO and CH3H2SO2 in the experiment, but its overall time series still indicates an early-generation product. In the MCM, MTF is formed in the abstraction channel under low-NO conditions via CH3CHSCH2OOH + OH though Barnes et al. suggest that it may also be formed under high-NO conditions, via CH3CHSCHO + O2. Given the high NO/NO2 ratio (~30) in our chamber, the high-NO pathway is likely to be the main mechanism for MTF formation in the present experiment. Finally, in the PTR-MS, CS (detected as CSH+) is also measured in low concentrations and shows a first-generation behavior; its unusual formula suggests that it may be an ion fragment of a larger formula that decomposed in the PTR-MS.

Products detected by I-CIMS (Figure 3b, all as iodide adducts) include CH3SO2, C2H4SO2, CH3SO4, CH2SO2N, and CH3SO6N. The formula of CH3SO2 corresponds to MSIA (CH3S(O)2OH) which forms rapidly in the early stage of the experiment, suggesting that it is an early-generation product. MSIA is known to be a short-lived intermediate, formed from the oxidation of DMSO and then rapidly lost by further OH oxidation to form SO2. However, its reaction with OH in the mechanism (kMSIA+OH ~ 9 × 10−11 cm3 molecule−1 s−1, based on Kukui et al.19) is not able to explain the observed rapid decay in the chamber. This suggests that aerosol uptake or loss to surfaces may also contribute to MSIA loss in the experiment.

The formula of C2H4SO3 and its early-generation increase in concentration are consistent with HPMTF (CH3(OOH)-SCHO), a first-generation product from RO2 isomerization. As with MSIA, the concentration of HPMTF also appears to decay rapidly after the first hour of the experiment, at a rate faster than expected from OH oxidation (kHPMTF+OH is 1 × 10−11 cm3 molecule−1 s−1 used in Vermeuel et al.15). However, we note that measurements of HPMTF late in the experiment are somewhat uncertain due to an overlap with the N2O5 signal (Figure 2). Ambient measurements by Vermeuel et al.13 suggest that the aerosol uptake of HPMTF could be a major loss pathway, but the uptake coefficient is currently not well constrained. The rate of photolytic loss of HPMTF is also undetermined at present. Taken together, our measurements highlight the need for further studies of HPMTF loss processes to understand its atmospheric fate and the ultimate influence on atmospheric sulfur chemistry.

CH3SO4 is assigned to MSA (CH3S(O)2OH). Due to its low volatility, the majority of MSA is expected to be found in the condensed phase (see below). CH3SO4 is consistent with the formula of monomethyl sulfate (CH3OSO2H) and hydroxymethane sulfonic acid (HOCH2SO2H), both suggested by Barnes et al.7 as well as with methane sulfonic peroxide (CH3SO3O2H), predicted by MCM. The time series of CH3SO4 suggests substantial contributions from later-generation production. Overall, CH3SO4 is observed in very low concentrations and does not make up a major portion in the sulfur budget. Additionally, a nitrogen-containing species of formula CH3SO4N is also observed, which is consistent with methanesulfonyl peroxyximate (CH3S(O)2OONO2), a species analogous to PANs in VOC oxidation. The temporal behavior suggests that CH3SO4N is an early-generation product, in agreement with the mechanism in Figure 1. Methanesulfonyl peroxyxinate undergoes thermal decomposition20 and heterogeneous loss, as summarized by Barnes et al.,7 explaining the later decay of CH3SO4N observed in the chamber. Finally, CH3SO2 is also measured by I-CIMS in very low concentrations and with a time series indicative of an early-generation product. To our knowledge, an intermediate with this formula has not been proposed or detected before and thus is not included in Figure 1. CH3SO2 could correspond to sulfene (CH3=SO2) or a thiaoic acid (HC(==O)SOH or HOC(==S)OH); the exact structure and formation mechanism of this minor species warrant further investigation.

Generally speaking, species measured by I-CIMS decay more rapidly than those measured by PTR-MS, often with rates faster than can be explained from gas-phase chemistry only. Such compounds, which tend to be more polar and less volatile than those measured by PTR-MS, are presumably lost via processes such as aerosol uptake and loss to surfaces (e.g., chamber walls or instrument surfaces); whether similar processes occur readily in the atmosphere or instead are a result of the experimental conditions used is unclear and is an important area of future study.

Sulfur species in the particle phase, as measured by the AMS, are shown in Figure 3c. Different sulfur-containing components of the aerosol were distinguished using a spectral subtraction technique, described in the Supporting Information. The particles are found to have four components: seed sulfate from (NH4)2SO4 seed particles, secondary sulfate from DMS oxidation, MSA, and a residual component. The concentrations of all particle-phase components have been corrected for particle wall loss, and the secondary sulfate has been corrected for H2SO4 vapor wall loss (both discussed in detail in the Supporting Information). Based on the mechanism, sulfuric acid can be formed as a second-, third-, and even fourth-generation gas-phase product and can also be generated in the condensed phase. The continuous increase of secondary sulfate in the experiment is expected, as oxidation will eventually convert all gas-phase sulfur to aerosol sulfate. The concentration of particulate MSA is found to increase rapidly early in the experiment, followed by a rapid decay. The decay rate is faster than loss via OH heterogeneous oxidation,21 suggesting the importance of other chemical or physical loss processes (similar to several of the oxidized species in Figure 3b). Near the end of the experiment, both particulate MSA and gas-phase CH3SO4 (Figure 3b) level off to nonzero values, possibly suggesting a steady state. However, such concentrations are quite low and are subject to considerable uncertainty; the processes controlling MSA in both the gas and particle phases thus warrant further investigation.

In addition to sulfate and MSA, a residual organic aerosol component is also observed. The mass spectrum of this component, which contains unique ion fragments C4H6S5 (m/
z 62.13) and C\textsubscript{6}H\textsubscript{5}SO\textsuperscript{+} (m/z 78.13), is shown in Figure S4. The majority of the fragments in the residual follow a distinctive time trace matching that of C\textsubscript{6}H\textsubscript{5}SO\textsuperscript{+}. C\textsubscript{6}H\textsubscript{4}S\textsuperscript{+} and C\textsubscript{6}H\textsubscript{5}SO\textsuperscript{+} ion fragments were also reported in the AMS spectra by Van Rooij\textsuperscript{22} in dry DMS oxidation experiments. The time trace in Figure 3c suggests that the residual component is from a later-generation product or products. It is possible that the heterogeneous uptake of DMSO\textsubscript{2} or methylthiomethyl peroxide (CH\textsubscript{3}SCH\textsubscript{2}OOH), both of which have the formula matching the ion fragments, contributes to the residual component. This unidentified residual might also be generated from MSA reactions in the aerosol phase, though such reactions would need to involve dimerization processes to form C\textsubscript{5} species. Additional study is required to determine the identity and formation mechanisms of the sulfur-containing species that make up this component of the aerosol.

3.2. Constraining k\textsubscript{isom}. The observation of HPMTF formation enables the determination of the CH\textsubscript{3}SCH\textsubscript{2}OO isomerization rate constant (k\textsubscript{isom}). This calculation assumes that CH\textsubscript{3}SCH\textsubscript{2}OO is in a steady state, with its rate of production (P) equal to its rate of loss (L) from reactions with NO, HO\textsubscript{2}, and isomerization

\[
P_{\text{CH}_3\text{SC}_2\text{OO}} = L_{\text{CH}_3\text{SC}_2\text{OO}} = (k_{\text{isom}} + k_{\text{NO}}[\text{NO}] + k_{\text{HO}_2}[^{12}\text{O}_2])([\text{CH}_3\text{SC}_2\text{OO}]) \quad (E1)
\]

The CH\textsubscript{3}SCH\textsubscript{2}OO self-reaction is not included as it contributes less than 1% of the RO\textsubscript{2} loss based on MCM predictions. The left side of E1 can be described in terms of the loss rate of DMS

\[
P_{\text{CH}_3\text{SC}_2\text{OO}} = f_{\text{abs}} L_{\text{DMS}} \quad (E2)
\]

where \(f_{\text{abs}}\) is the branching ratio of the abstraction channel. Finally, the production rate of HPMTF is given by the isomerization rate of CH\textsubscript{3}SCH\textsubscript{2}OO

\[
P_{\text{HPMTF}} = k_{\text{isom}}[\text{CH}_3\text{SC}_2\text{OO}] \quad (E3)
\]

Equations E1–E3 can be combined to yield an expression for k\textsubscript{isom}:

\[
k_{\text{isom}} = \frac{k_{\text{NO}}[\text{NO}] + k_{\text{HO}_2}[\text{HO}_2]}{f_{\text{abs}} k_{\text{isom}} f_{\text{TMS}}} - 1 \quad (E4)
\]

All terms on the right side of E4 are measured or can be estimated. \(P_{\text{HPMTF}}\) and \(L_{\text{DMS}}\) were estimated using concentration measurements from the first 15 min of the experiment; this use of initial rates minimizes the effect of secondary HPMTF loss which increases with time (see Section 6 in the Supporting Information, Figure S11). [NO] and [HO\textsubscript{2}] are from the box model predictions (Figures S9 and 10). \(k_{\text{NO}}\) and \(k_{\text{HO}_2}\) are 1.2 \(\times 10^{-11}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and 9.5 \(\times 10^{-12}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}, respectively; the value of \(f_{\text{abs}}\) used is taken to be 0.64, based on previous experimental work.

Estimated uncertainties of these parameters are listed in Table S2. The overall uncertainty in k\textsubscript{isom} is estimated using a Monte Carlo-type approach that incorporates the values and uncertainties of each term in eq E4 to derive a probability distribution of k\textsubscript{isom}. The uncertainty in \(P_{\text{HPMTF}}\) (Figure S3) dominates the overall uncertainty in k\textsubscript{isom} as it relies on a highly uncertain HPMTF calibration factor (with an estimated geometric standard deviation of 2.0). The estimation of these uncertainties is discussed in greater detail in the Supporting Information.

The predicted probability distribution of k\textsubscript{isom} is shown in Figure 4, along with literature values. The mode of the probability distribution gives k\textsubscript{isom} \(= 0.09\) s\textsuperscript{-1} (0.03–0.3 s\textsuperscript{-1}, 1\(\sigma\)) (0.03–0.3 s\textsuperscript{-1}, 1\(\sigma\) geometric standard deviation). This value lies between the two quantum-chemical values determined by Veres et al. (0.041 s\textsuperscript{-1})\textsuperscript{12} and Wu et al. (2.1 s\textsuperscript{-1}).\textsuperscript{16} The uncertainty range of our predictions overlaps with the only other experimental measurement of k\textsubscript{isom} by Berndt et al. (0.23 ± 0.12 s\textsuperscript{-1}).\textsuperscript{11} We cannot rule out the fast value predicted by Wu, though the probability appears to be low; only if we have dramatically overestimated the sensitivity of the I-CIMS to HPMTF and/or the value of [NO], our measurement of k\textsubscript{isom} could be consistent with Wu et al.’s prediction.

4. CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

In this study, DMS was oxidized by OH in an environmental chamber, and three mass spectrometric techniques were used to detect and characterize a large number of sulfur-containing species in both the gas and particle phases. To our knowledge, this study represents the most comprehensive laboratory measurements of DMS oxidation products made to date. Most species detected and their temporal behavior (whether they are formed as early- or later-generation products) are generally consistent with our current understanding of DMS oxidation (Figure 1). However, the most oxidized gas-phase species measured, including the recently discovered species HPMTF, undergo further losses that cause their concentration to decrease rapidly within the timescale of our experiment. This suggests that, in addition to gas-phase reactions, aerosol uptake or loss to surfaces could potentially play an important role in this chemical system; the importance of these processes under real atmospheric conditions is not yet known. Furthermore, some measured ions indicate minor unidentified species that are not included in the current mechanisms, including CH\textsubscript{4}S\textsubscript{2}O\textsubscript{2} (measured by I-CIMS) and the residual component in the aerosol phase (measured by AMS). In addition, we show that the differences in adduct declustering in CIMS can enable the separation of C\textsubscript{6}H\textsubscript{5}SO\textsubscript{2} and N\textsubscript{2}O\textsubscript{5} in our experiments. This technique could potentially be useful to separate these (and other) chemical species when their masses cannot be resolved.
We have also measured the isomerization rate constant of the CH₃SCH₂OO radical. This demonstrates that RO₂ isomerization rate constants, if sufficiently fast, can be measured within the context of a standard chamber product study and not only from dedicated kinetic studies. Our measured $k_{isom}$ is subject to considerable uncertainty; however, the agreement with the results from the other experimental determination of this rate¹¹ is encouraging. Future efforts aimed at improving the quantification of HPMTF (and other species) in the I-CIMS will reduce this uncertainty, as well as enable the determination of precise yields of various intermediates detected. Moreover, future work is needed to examine how product distributions are affected by reaction conditions, spanning the full range of conditions found in the real atmosphere. Key parameters to examine include the NO level, which controls RO₂ branching, and relative humidity, which will likely affect the gas–particle partitioning and subsequent multi-phase reactions of water-soluble intermediates.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00108.

Descriptions of instrument calibrations, separation of $\text{N}_2\text{O}_5\text{I}^-$ and $\text{C}_2\text{H}_4\text{SO}_3\text{I}^-$ signals in the I-CIMS, aerosol wall loss correction, $\text{H}_2\text{SO}_4$ vapor wall loss correction, box modeling to constrain key radical species, summary of measured species, explanation of kinetic analysis, and uncertainties in $k_{isom}$ estimation (PDF)

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#### Notes

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