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Rapid Aqueous-Phase Oxidation of An *α*-Pinene-Derived Organosulfate by Hydroxyl Radicals: A Potential Source of Some Unclassified Oxygenated and Small Organosulfates in the Atmosphere

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Abstract

Organosulfates (OSs) are ubiquitously present in atmospheric aerosols and cloud droplets, and affect aerosol-cloud-climate interactions via their distinct physicochemical properties. Although various formation pathways and transformation mechanisms have been proposed, the origins of many atmospheric OSs remain unclear or unexplained. In this study, we investigated the aqueous-phase oxidation of an α-pinene-derived organosulfate ($C_{10}H_{17}O_5SNa$, αpOS-249) by $^{\bullet}OH$ radicals as a potential source of some uncharacterized atmospheric OSs by quantifying the kinetics and characterizing the reaction products. An aqueous-phase photoreactor was used to conduct the aqueous-phase $^{\bullet}OH$ oxidation of αpOS-249, revealing a rate constant of $(2.2 \pm 0.2) \times 10^9$ L mol^{-1} s^{-1} and atmospheric lifetimes ranged from minutes to about 2 days under atmospherically relevant cloud conditions. The product analysis revealed that a variety of more oxygenated C_{10} OS products, smaller OS ($<C_{10}$) products, and inorganic sulfates (e.g., bisulfate and sulfate) can be produced via functionalization and fragmentation processes upon oxidation. Most of the OS products have been detected in the atmosphere, with some of them whose sources and formation mechanisms are unknown thus far. Our study provides a new perspective that the chemical transformation of larger OSs via aqueous-phase oxidation can proceed efficiently to yield a variety of new OSs, serving as a source for atmospheric OSs, particularly smaller OSs. These findings would be useful in field data interpretation and model simulations regarding the abundance, formation, transformation, and atmospheric fates of OSs.

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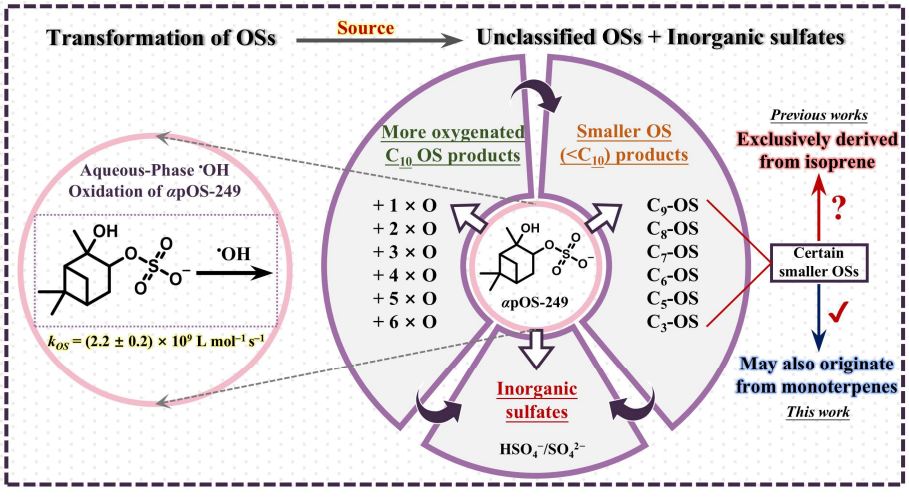

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1 Introduction

Organosulfates (OSs) have been identified as ubiquitous components in secondary organic aerosol (SOA) originated from volatile organic compounds (VOCs) in the presence of sulfur species, as evidenced by laboratory studies and atmospheric observations (Surratt et al., 2007; Surratt et al., 2008; Bruggemann et al., 2020; Fan et al., 2022). OSs have also been proven to constitute a significant fraction of the organic matter of atmospheric fine particulate matter ($PM_{2.5}$), contributing approximately 5–30 % (Hettiyadura et al., 2019; Chen et al., 2021; Hughes et al., 2021; Wang et al., 2022; Yang et al., 2024). In addition, atmospheric OSs exhibit various physiochemical properties including viscosity, acidity, morphology, hygroscopicity, and toxicity in relation to their molecular structures (Hansen et al., 2015; Riva et al., 2019), leading to their different environmental behaviors compared to inorganic sulfates (e.g., bisulfate (HSO_4^-) and sulfate (SO_4^{2-}) ions). Despite the potentially significant influence of aerosol physicochemical properties, the sources, formation and transformation mechanisms of OSs are still not well understood and are poorly constrained in current atmospheric model simulations (Shrivastava et al., 2017; Bruggemann et al., 2020).

Various mechanisms have been proposed for OS formation (Surratt et al., 2007; Iinuma et al., 2007; Surratt et al., 2010; Perri et al., 2010; Nozière et al., 2010; Darer et al., 2011; Zhang et al., 2012; Shang et al., 2016; Passananti et al., 2016; Barbosa et al., 2017; Jiang et al., 2022). However, the proposed reaction mechanisms cannot fully explain the sources, formation and composition of OSs detected in atmosphere. For instance, a review paper summarized the global overview of OS concentrations and identified various sources, including isoprene, monoterpenes, anthropogenic and unassigned sources (Bruggemann et al., 2020). The field observations revealed that OSs with unknown sources constituted 4.7 % to 99.8 % by mass in different regions (Bruggemann et al., 2020). Furthermore, a field study indicated that a significant fraction of organosulfur compounds, in particular OSs, remained unknown at the molecular level, accounting for 67 % to 79 % by mass in the eastern and western U.S. (Chen et al., 2021). These findings suggest that while hundreds of OSs have previously been identified, a significant portion of atmospheric OSs remains uncharacterized, with unknown precursors and formation mechanisms.

Additionally, the transformation of OSs after formation has also been noted in recent studies (Darer et al., 2011; Hu et al., 2011; Kwong et al., 2018; Xu et al., 2022; Ng et al., 2022; Lai et al., 2023; Xu et al., 2024; Lai et al., 2024; Lai et al., 2025). The importance of the transformation of OSs is largely contingent upon the fate of either retain or release inorganic sulfates through subsequent reactions. In the previous works on OSs (e.g., methyl sulfate,

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hydroxyacetone sulfate, and phenyl sulfate), aqueous-phase •OH oxidation has been shown to be an efficient removal pathway of OSs with rate constant between 10^8 to 10^9 L mol^{-1} s^{-1} (Lai et al., 2024; Gweme and Styler, 2024; Lai et al., 2025). Therefore, in this study, aqueous-phase •OH oxidation was applied to *α*-pinene-derived organosulfate ($C_{10}H_{17}O_5SNa$, *α*pOS-249, sodium 2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl sulfate), a model compound of monoterpene-derived OSs. *α*pOS-249 is the first generation product of the •OH initiated photooxidation of *α*-pinene in the presence of acidic sulfate aerosols and was selected due to its global atmospheric presence (Surratt et al., 2008), with its mass ratio to total OSs ranging from 0.1 % to 17.7 % (**Table S1**) (Kristensen and Glasius, 2011; Yttri et al., 2011; Ma et al., 2014; Wang et al., 2017; Wang et al., 2018; Wang et al., 2019). Particularly, the objectives of this work are (1) to examine the kinetics of the aqueous-phase •OH oxidation of *α*pOS-249, (2) to identify reaction products and propose reaction mechanisms, and (3) to examine whether larger OSs can serve as precursors for smaller OSs through fragmentation processes upon oxidation.

2 Experimental methods

2.1 Aqueous-phase oxidation

The synthesis of *α*pOS-249 was through the monosulfation of *α*-pinene diol with sulfur trioxide-pyridine complex directly (Wang et al., 2017). The purity of *α*pOS-249 was higher than 99 % based on nuclear magnetic resonance (NMR) spectra. Pure standard was stored in a freezer at −20 °C prior to the experiments. The experimental overview and conditions of aqueous-phase •OH oxidation of *α*pOS-249 were summarized in **Scheme S1** and **Table S2**, respectively. The experiments included kinetic experiments (*α*pOS-249 + reference compound (i.e., benzonic acid (BA) + •OH), product-capture experiments (*α*pOS-249 + •OH), and control experiments (*α*pOS-249 + UV light only and *α*pOS-249 + H_2O_2 only). All experiments were performed in a photoreactor with a volume of 150 mL (Witkowski and Gierczak, 2017; Witkowski et al., 2018; Witkowski et al., 2023; Witkowski et al., 2024). A quartz plate covered the top of the reactor and was sealed with flange clamps. The inner layer of the reactor held the reaction mixture, and circulating cooling water flowed through the outer layer to maintain a temperature of 298 ± 1 K, regulated by a refrigerated bath circulator (SD15R-30-A12E, PolyScience). The reaction mixture was continuously stirred with a magnetic stirrer to ensure homogeneity during the oxidation. A 300 W Xenon lamp (HSX-UV300, Beijing NBeT) equipped with a quartz UV filter maintained peak emission at 313 nm, which was used to

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generate •OH radicals through the photolysis of H_2O_2. The photoreactor was housed in a dark box to prevent interference from external light sources.

A typical kinetic experiment commenced (time zero) by activating the Xenon lamp to irradiate the reaction solution containing *α*pOS-249, BA, and H_2O_2. BA was added as a reference compound to track •OH. Under irradiation, a steady-state concentration of •OH ($[^{\bullet}OH]_{ss}$) of around $(6 - 9) \times 10^{-14}$ mol L^{-1} was generated, as calculated from the simulations using a box model (**Section S3**) (Witkowski and Gierczak, 2017; Otto et al., 2019). This concentration is in good agreement with previously reported $[^{\bullet}OH]_{ss}$ levels in cloud and fog water (Choudhary et al., 2023). The reaction progress was monitored by sampling 1.5 mL aliquots from the reactor at regular time intervals over a total duration of 3 hours (every 15 mins in the initial hour and every 30 mins in the subsequent two hours). Each sample was instantly mixed with 0.3 mL catalase solution (2 mg mL^{-1}) to decompose the residual H_2O_2 and stop further reactions (Witkowski and Gierczak, 2017; Witkowski et al., 2018). These samples were incubated at 298 K for 20 mins and then filtered through a PTFE syringe filter (45 mm, 0.2 µm pore size, Pall Corporation) before subsequent chemical analysis. The pH values of the reaction mixtures were monitored using an electrochemical meter (Orion Versastar Pro, Thermo Scientific) pre-calibrated with pH buffer solutions. The procedure for product-capture experiments was the same as the kinetic experiments, except that BA was not added. Two sets of control experiments were conducted. One involved irradiating a solution of *α*pOS-249 alone to examine the effects of light only. The other set combined *α*pOS-249 and H_2O_2 in the dark to isolate the effects of H_2O_2.

2.2 Chemical characterization with LC-ESI-Orbitrap MS

The decay of *α*pOS-249 and BA upon oxidation was quantified by a UHPLC system (Dionex Ultimate 3000, Thermo Fisher Scientific) coupled with an Orbitrap mass spectrometer (IQ-X Tribrid, Thermo Fisher Scientific) employing calibration curves. The calibration curves were established using the synthesized *α*pOS-249 and commercially available BA as standards. The uncertainties in the measurements of *α*pOS-249 and BA were determined by the reproducibility of integrated peak areas across multiple measurements at the same concentration. In addition, reaction products (e.g., OS products) formed upon oxidation were detected by the same system. Experimental details can be found in previous publications (Brüggemann et al., 2019; Wang et al., 2022). Briefly, chromatographic separation was performed by an Acquity UPLC HSS T3 column (2.1 mm × 100 mm, 1.8 µm; Waters) with a gradient elution program as follow: mobile phase consisting of eluent A (H_2O with 0.1 %

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formic acid) and eluent B (acetonitrile with 0.1 % formic acid), at a flow rate of 0.3 mL min^{-1}. Eluent B was initially set at 5 % for 1.0 min, gradually increased to 99 % in 8.0 min, held at 99 % for 2.0 min, and then rapidly decreased back to 5 % within 0.1 min, and maintained at 5 % for the final 2.9 min, resulting in a total run time of 13.0 min. The injection volume was 3 µL. The Orbitrap MS detection was performed in negative electrospray ionization mode, under the following settings: spray voltage at 2300 V, sheath gas at 40 Arb, auxiliary gas at 10 Arb, sweep gas at 2 Arb, RF Lens of 30 %, ion transfer tube temperature of 300 °C, and the vaporizer temperature of 320 °C. The analysis began with a full MS scan. For MS/MS data acquisition, the MS was operated in data-dependent acquisition mode with stepped HCD collision energy of 15 %, 25 %, and 40 %. The intensity threshold for triggering MS/MS data acquisition was set at 1×10^5. The MS resolution was configured to 120,000 and 30,000 for full MS scan and MS/MS scan, respectively. The *m*/*z* range for the full MS scan was 50−1200 and 50−500 for the MS/MS scan. The data were analyzed using Xcalibur (version 4.1) as well as the open-source software package MZmine 2.38, following the workflows and methods previously described (Brüggemann et al., 2019; Wang et al., 2022).

2.3 Quantification of inorganic sulfates with Ion Chromatography

The formation of inorganic sulfates (HSO_4^-/SO_4^{2-}) during the aqueous $^{\bullet}OH$ oxidation of *α*pOS-249 was determined using ion chromatography (IC). The details have been given in previous studies (Xu et al., 2022; Lai et al., 2023). Briefly, the samples were analyzed with a Dionex ICS-1100 IC system (Thermo Fisher Scientific). Inorganic sulfate anions were separated using an IonPac AS11-HC analytical column (4 mm × 250 mm) and an IonPac AG11-HC guard column (4 mm × 50 mm). The IC system operated in negative mode with 15 mmol L^{-1} NaOH as the eluent at a flow rate of 0.8 mL min^{-1}. Moreover, the concentration of SO_4^{2-} anions quantified by IC represents the total amount of HSO_4^- and SO_4^{2-} (Xu et al., 2022; Lai et al., 2023). In this work, the quantity of inorganic sulfates was measured based on its peak area in the chromatogram and quantified using a Na_2SO_4 standard calibration curve. The uncertainty of inorganic sulfate measurements was found to be 2.5 % from repeated measurements.

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3 Results and discussion

3.1 Oxidation kinetics

Control experiments were conducted to account for any non •OH losses, including αpOS-249 photolysis due to UV radiation alone and the reaction of αpOS-249 with H_2O_2 in the absence of light (**Section S4**). **Figure S1** reveals that αpOS-249 neither photolyzes nor reacts with H_2O_2 unless light is present to generate •OH. Relative method was adopted to determine the second-order rate constants for •OH oxidation of αpOS-249 (k_{OS}) by comparing the measured rate constants to that of a reference compound (BA) with a well-known •OH reaction rate of $k_{Ref} = (5.5 \pm 0.3) \times 10^9$ L mol^{-1} s^{-1} at a solution pH of 4.5 (Hems and Abbatt, 2018), a condition that is the same as our experiments (**Section S5**). In the reaction mixture, •OH reacts with both αpOS-249 (**R1**) and BA (**R2**) as described in the reactions shown below (Hems and Abbatt, 2018). The second-order rate constants for the •OH oxidation of αpOS-249 (k_{OS}) were calculated using **Eqn. 1**, where [αpOS-249] and [BA] are the concentrations of αpOS-249 and BA, respectively, at the initial (time = *0*) and intermediate (time = *t*) time:

$$\text{•OH} + \alpha\text{pOS-249} \xrightarrow{k_{OS}} \text{products} \quad \text{(R1)}$$

$$\text{•OH} + \text{BA} \xrightarrow{k_{Ref}} \text{products} \quad \text{(R2)}$$

$$\ln\left(\frac{[\alpha\text{pOS-249}]_0}{[\alpha\text{pOS-249}]_t}\right) = \frac{k_{OS}}{k_{Ref}} \ln\left(\frac{[\text{BA}]_0}{[\text{BA}]_t}\right) \quad \text{(Eqn. 1)}$$

Figure 1 (a) illustrates the relative kinetic plot, yielding a k_{OS} value of $(2.2 \pm 0.2) \times 10^9$ L mol^{-1} s^{-1} at 298 K. The uncertainty of k_{OS} was calculated by propagating the two standard deviations (2σ) from multiple experiments, the reported uncertainty of the rate constant for the reference compound, and the uncertainties from measurements of αpOS-249 and BA (Witkowski and Gierczak, 2017). The rate constant is compared with that predicted by the structure-activity relationship (SAR) model which has been widely used to estimate the reactivity of various organic compounds towards •OH radicals in aqueous phase (Monod and Doussin, 2008; Doussin and Monod, 2013). Our recent laboratory work revealed the strong deactivating effect of the sulfate group ($-OSO_3^-$) on aqueous-phase •OH radicals oxidation kinetics, and extended the SAR model to include OSs (Lai et al., 2024), by introducing new interaction parameters for the $-OSO_3^-$ group (F (α-position) = 0.22 and G (β-position) = 0.44). Here, we predicted the second-order rate constant for the aqueous-phase •OH oxidation of αpOS-249 to be 3.1×10^9 L mol^{-1} s^{-1} (**Section S6** and **Figure S2**), which is higher than our

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measured value of (2.2 ± 0.2) × 10^9 L mol^{-1} s^{-1}. This difference is within an acceptable range when considering the performance of the SAR model (58 % of simulated rates within ± 20 % and 76 % within ± 40 % of experimental data) (Monod and Doussin, 2008; Doussin and Monod, 2013). This suggests that the SAR model is a valuable tool for predicting the aqueous-phase •OH oxidation rate constants of a variety of atmospheric OSs.

We also assessed the significance of aqueous-phase •OH oxidation in its atmospheric fate by estimating the atmospheric lifetimes (**Figure 1 (b)**), $\tau = 1/(k_{OS} \times [^{\bullet}OH])$ (Wen et al., 2021). The estimated lifetimes based on the newly obtained experimental data varied from approximately 3 mins in remote aerosol conditions ([•OH] = 3 × 10^{-12} mol L^{-1}) to about 2 days in urban cloud conditions ([•OH] = 3.5 × 10^{-15} mol L^{-1}) (Herrmann et al., 2010). In addition, using SAR predictions with higher rate constant yield shorter lifetimes, ranging from about 2 mins in remote aerosol conditions to about 1 day in urban cloud conditions. Given these relatively short atmospheric lifetimes, the aqueous-phase •OH oxidation could likely serve as a significant transformation pathway for *α*pOS-249.

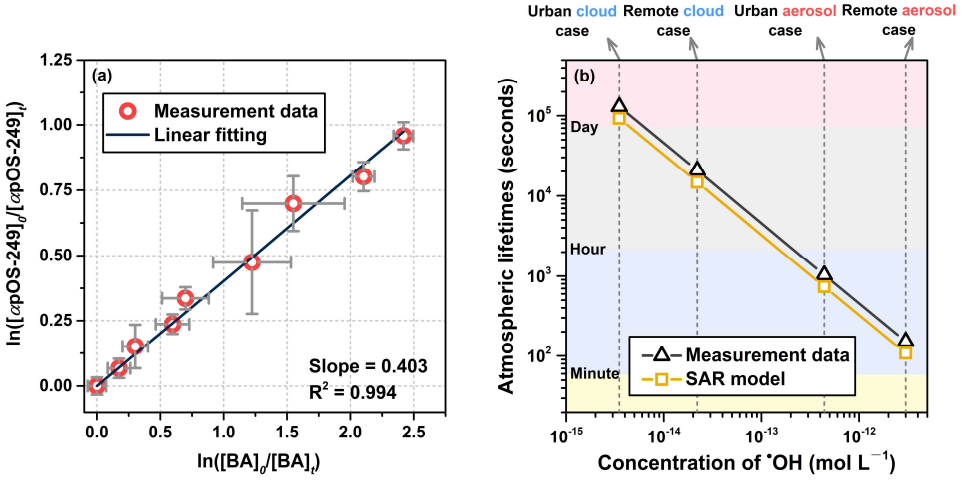

Figure 1. (a) Relative kinetic plot of aqueous-phase •OH oxidation of *α*pOS-249 in accordance with **Eqn. 1** using benzoic acid as the reference compound. (b) Atmospheric lifetimes of *α*pOS-249 against the aqueous-phase •OH oxidation was calculated under various scenarios using rate constant obtained from this study (measurement data) and the SAR model. The concentrations of •OH in the aqueous phase under four different scenarios were obtained from the modeling study (Herrmann et al., 2010).

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3.2. Oxidation products formed upon oxidation

Figure S3 shows the total ion chromatograms (TICs) obtained from the product-capture experiments. Before oxidation (**Figure S3 (a)**, t_0), a dominant peak corresponding to the [M–H]$^-$ ion of αpOS-249 (m/z = 249.08, $C_{10}H_{17}O_5S^-$) is observed at a retention time (RT) of 4.7 min. After 45 mins of $^{\bullet}$OH oxidation (**Figure S3 (b)**, t_{45}), the intensity of αpOS-249 significantly decreases, accompanied by the emergence of new product peaks with low intensities. After 3 hours of oxidation (**Figure S3 (c)**, t_{180}), αpOS-249 is almost completely consumed. Notably, some new product peaks observed at t_{45} exhibit a declining trend, suggesting their susceptibility to $^{\bullet}$OH oxidation. A number of new OS products were detected based on two primary criteria: i) their absence prior to oxidation (t_0), and ii) the presence of fragmentation patterns in their MS^2 spectra, primarily showing the bisulfate anion (HSO_4^-, m/z = 96.96), and often accompanied by other sulfur-containing ions such as the sulfite ion radical ($SO_3^{\bullet-}$, m/z = 79.96), and bisulfite anion (HSO_3^-, m/z = 80.97) (Surratt et al., 2008; Huang et al., 2018; Xu et al., 2022). These identified OS products were summarized in **Table S5** and were grouped into two categories: more oxygenated C_{10} OS products, formed through functionalization processes via the addition of oxygenated functional groups, and smaller OS ($<C_{10}$) products, which result from fragmentation processes.

Figure 2 (a) shows the time-dependent evolution of intensities for more oxygenated C_{10} OS products from different generations. These products were grouped according to the number of added oxygen atoms (e.g., + 1 × O, + 2 × O, etc). The highest intensity of first-generation products (+ 1 × O) peaked at 45 mins into the reaction, followed by a noticeable decrease, while the second-generation products (+ 2 × O) showed a gradual increase, lagged their peak at 90 mins before gradually declining. Third (+ 3 × O) and fourth-generation (+ 4 × O) products followed a similar pattern, with a relatively lower intensity compared to the first and second-generation products. They showed a slow increase, peaking at 120 mins with a minimal decrease. Additionally, fifth-generation (+ 5 × O) products had even lower intensity, peaking at 150 mins, while sixth-generation (+ 6 × O) products showed the lowest intensity and a continued slow increasing trend. This evolution pattern can be well described as multi-generation sequential oxygenation processes (Kroll et al., 2015).

The intensities of smaller OS ($< C_{10}$) products are categorized by their carbon atoms (e.g., C_9, C_8, C_7 etc), and their time-dependent evolutions are shown in **Figure 2 (b)**. C_9 OS products show the highest intensity, peaking at 120 mins before a slight decrease. Meanwhile, C_7 OS products show the second highest intensity, but significantly lower than C_9 OS products, displaying a consistent upward trend. The other OS groups all demonstrate a continued

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increasing trend with low intensities. Unlike more oxygenated C_{10} OS products, the evolution of smaller OS products always keep increasing with reaction time, suggesting that fragmentation likely begins to gain increased significance as oxidation proceeds.

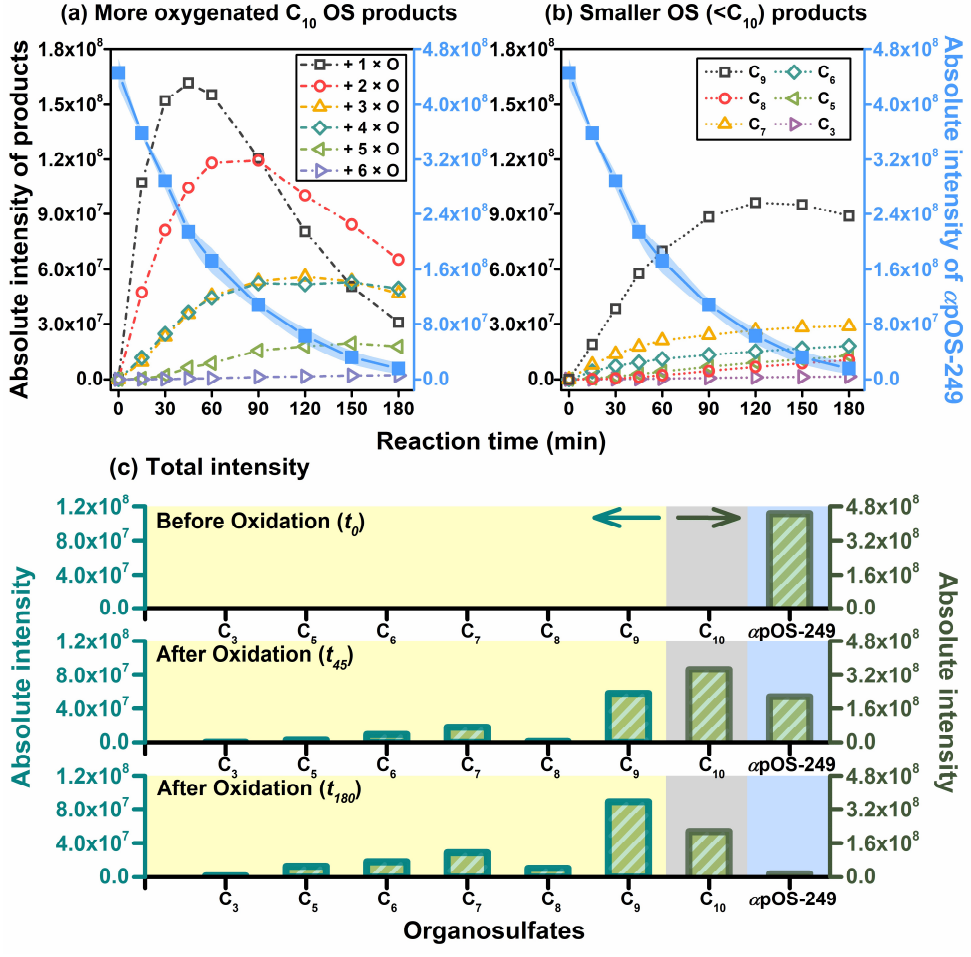

Figure 2. Time-dependent evolution of absolute intensities for αpOS-249 decay and reaction products formed during the aqueous-phase •OH oxidation of αpOS-249, (a) more oxygenated C_{10} OS products, (b) smaller OS (<C_{10}) products, and (c) total intensity.

Figure 2 (c) shows the variation in absolute intensity of αpOS-249 and its oxidation products with different carbon atoms before (t_0) and after (t_{45} and t_{180}) oxidation. The total intensity of C_{10} OS products initially exhibits a significant increase followed by a decline.

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Meanwhile, the intensity of smaller OS ($<C_{10}$) products steadily increases throughout the reaction. This implies that functionalization processes likely dominate over the fragmentation processes in the early oxidation stages (e.g., within the initial hour). However, as oxidation proceeds, fragmentation processes begin to gain comparable significance (**Figure S4**). It is important to note that this simple comparison relies on the assumption that OS products have the same ionization efficiency as that of αpOS-249. This assumption may be reasonable because previous studies show that the ionization efficiency of αpOS-249 reflects the averaged level observed among the investigated OSs (e.g., 2-hydroxy-carene OS, limonaketone OS, 2-hydroxy-β-caryophyllene OS, methylsulfonic acid, and octyl sulfate) (Brüggemann et al., 2019; Zhao et al., 2020; Wang et al., 2022). Furthermore, this observed trend agrees with the hypothesis that as oxidation continues, the addition of functional groups to the parent compound increases, leading to a higher probability of alkoxy radicals' formation with functional groups on the β-carbon (Kroll et al., 2011; Kessler et al., 2012; Lambe et al., 2012; Wiegel et al., 2015; Hems and Abbatt, 2018; Jiang et al., 2023). This, in turn, enhances the fragmentation processes, as the addition of oxygenated functional groups on the β-carbon plays an activating role and reduces the energy barrier for decomposition (Wiegel et al., 2015). Furthermore, other factors such as higher O/C ratios and increased polarity can enhance the alkoxy decomposition, thereby favoring the fragmentation process at later stages of oxidation (Wiegel et al., 2015).

3.3 Reaction mechanisms

Upon oxidation, the $^{\bullet}$OH radical can initially attack different reaction sites. **Table S4** and **Figure S2** show the partial rate constants for hydrogen abstraction at various reaction sites, as derived from the SAR model. The model predicts that the relative reactivity ranges from 2.3 % at 5-C to 21.2 % at 3-C. $^{\bullet}$OH radicals do not exhibit an overall strong preference for specific carbon types (primary carbons: 34.8 %, secondary carbons: 29.7 %, and tertiary carbons: 32.6 %) (**Table S4**). For simplicity and clarity, we proposed the mechanisms involving the three types of carbon atoms with the highest predicted partial rate constants in **Scheme 1**. A generic reaction scheme outlining the formation of the identified OS products was shown in **Scheme S2**, based on well-established reaction pathways reported in the literatures (Russell, 1957; Bennett and Summers, 1974; Hearn et al., 2007; Smith et al., 2009; George and Abbatt, 2010; Kroll et al., 2015).

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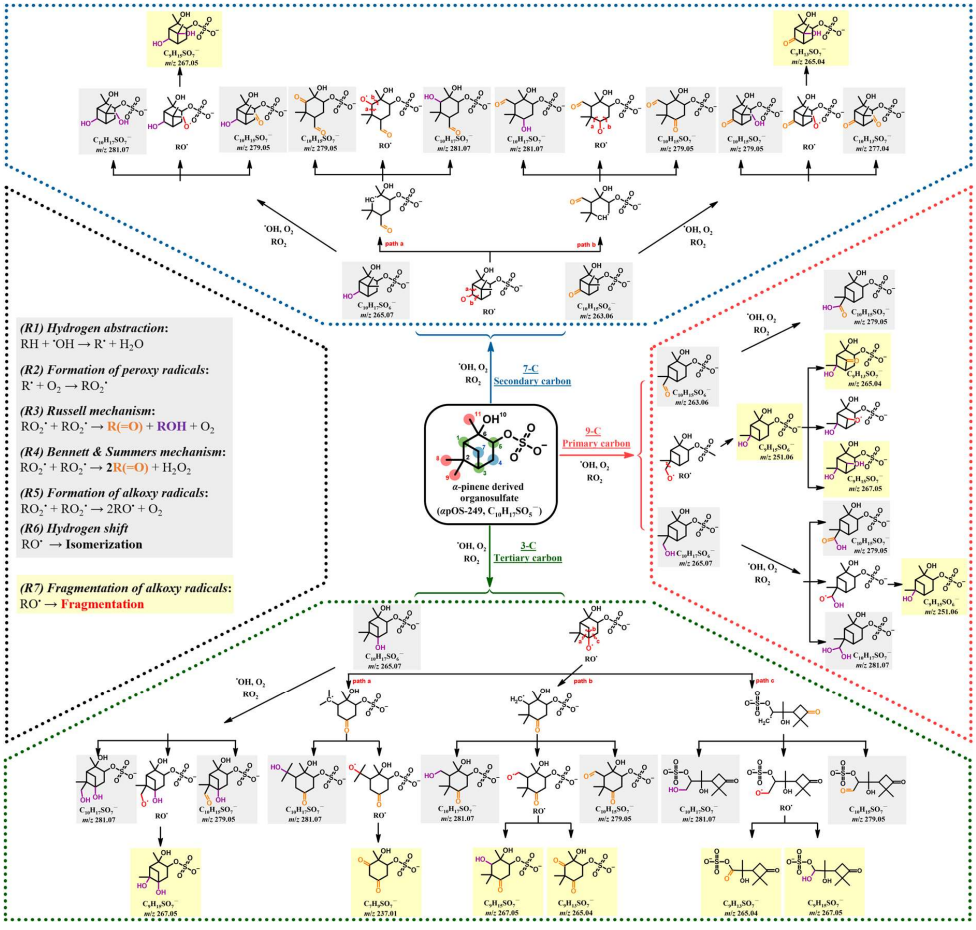

Scheme 1. Proposed mechanisms for the formation of C_{10} OS products and smaller OS ($<C_{10}$) products through functionalization and fragmentation processes during the aqueous-phase ·OH oxidation of *α*pOS-249, using 3-C, 7-C, and 9-C as representative examples with the highest predicted partial rate constants (For simplicity and clarity, we only proposed the mechanisms up to the second-generation products). Grey and yellow base colours distinguish the C_{10} OS products and smaller OS products, respectively.

3.3.1 C_{10} OS products

As shown in **Scheme 1** and **Table S5**, a number of more-oxygenated C_{10} OS products were detected during oxidation, likely formed through functionalization processes. These processes initiate with hydrogen abstraction by ·OH radicals from *α*pOS-249, leading to the formation of an alkyl radical (R·). The alkyl radicals then rapidly combine with O_2 to yield peroxyl radical (RO_2·). The subsequent self-reactions of RO_2· could lead to the formation of

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diverse products, incorporating oxygenated functional groups (e.g., hydroxyl (−OH), and carbonyl (=O) groups) into the parent molecule (i.e., αpOS-249) without breaking the C-C bonds (Kroll et al., 2009; Lambe et al., 2012). Generally, the addition of n number of oxygenated functional groups to αpOS-249 represents the n^{th} generation of oxygenation (Wilson et al., 2012; Ng et al., 2022). For example, as shown in **Scheme 1**, first-generation products are formed by adding either one hydroxyl group or one carbonyl to αpOS-249, yielding compounds such as $C_{10}H_{17}SO_6^-$ (m/z = 265.07) and $C_{10}H_{15}SO_6^-$ (m/z = 263.06). These OS products show an increase of one oxygen atom (+ 1 × O) compared to the parent compound. Different structural isomers of $C_{10}H_{17}SO_6^-$ and $C_{10}H_{15}SO_6^-$ can be formed depending on different initial reaction sites. The presence of multiple peaks with different retention times during LC-MS analysis for a given OS ion supports the presence of the isomeric products **(Table S5)**.

Upon oxidation, first-generation products can transform into second-generation products. These second-generation products arise from the addition of an extra oxygen atom, continually incorporating carbonyl or hydroxyl groups into the first-generation products, thereby adding two oxygen atoms to the parent compound (+ 2 × O). Three combinations of this transformation are possible: the addition of two hydroxyl groups, one carbonyl and one hydroxyl group, or two carbonyl groups. For example, as shown in **Scheme 1**, $C_{10}H_{17}SO_7^-$ (m/z = 281.07) represents the first case through the addition of two hydroxyl groups. $C_{10}H_{15}SO_7^-$ (m/z = 279.05) represents the second case, formed by incorporating both carbonyl and hydroxyl groups into parent compound. This compound can result from carbonyl addition to first-generation hydroxyl products, or hydroxyl addition to first-generation carbonyl products. Lastly, $C_{10}H_{13}SO_7^-$ (m/z = 277.04) represents the third case, involving the addition of two carbonyl groups. Furthermore, the progression towards more oxygenated C_{10} OS products can be sustained, enabling the continual incorporation of new functional groups into parent compound. Among the identified OS products (**Table S5**), the most oxygenated C_{10} OS products were found to be $C_{10}H_{15}SO_{11}^-$ (m/z = 343.03), inferring the addition of six oxygenated functional groups.

3.3.2 Smaller OS (<C_{10}) products

Smaller OS (<C_{10}) products were also detected, ranging from C_3 to C_9 OS products. Detailed molecular information about these OS products is summarized in **Table S5**. Unlike more oxygenated C_{10} OS products, the formation of fragmentation products is likely occurred through multiple pathways across various oxidation generations. For simplicity, we proposed

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in **Scheme 1** several possible mechanisms, involving three specific carbon atom types and focusing on RO• decomposition through C-C bond scission (George and Abbatt, 2010).

Upon oxidation, the fragmentation processes initiate with the same mechanisms as the functionalization processes until the alkoxy radicals (RO•) form following the self-reactions of RO_2•. For example, for tertiary carbon 3-C, with the highest partial rate constant, three scission pathways (path a, b, and c, **Scheme 1**) from RO• radicals generate smaller OS products such as $C_7H_9SO_7^-$ (m/z = 237.01), $C_9H_{15}SO_7^-$ (m/z = 267.05), and $C_9H_{13}SO_7^-$ (m/z = 265.04). These C_9 OS products can also be formed during initial hydrogen abstraction from primary (9-C) and secondary carbon sites (7-C) with different structures. We acknowledge that various reaction pathways can potentially lead to the same smaller OS products, with **Scheme 1** outlining certain possible pathways. For example, $C_9H_{15}SO_6^-$ (m/z = 251.06) could originate from the decomposition of RO• following initial hydrogen abstraction from the primary (9-C) carbon site or from the subsequent oxidation of $C_{10}H_{17}SO_6^-$ (m/z = 265.07).

3.3.3 Inorganic sulfates

Previous studies on the heterogeneous •OH oxidation of various OSs, involving aliphatic, isoprene-derived, and pinene-derived OSs, have reported the formation of inorganic sulfates (e.g., HSO_4^- and SO_4^{2-}) (Kwong et al., 2018; Chen et al., 2020; Xu et al., 2022). We also investigated the significance of this conversion from organosulfur in *α*pOS-249 to inorganic sulfur upon aqueous-phase •OH oxidation (**Section S10**). **Figure S5** shows the ion chromatograms before (t_0) and after (t_{45} and t_{180}) aqueous-phase •OH oxidation of *α*pOS-249. Before oxidation, a minor presence of inorganic sulfates (3.2 ± 0.1 % of total sulfur molar) was detected, likely due to *α*pOS-249 hydrolysis (**Figure S5**) (Xu et al., 2022). This amount has been corrected for the quantification of inorganic sulfate formed upon oxidation. After oxidation (**Figure S5**), a continued increase in the inorganic sulfate signal was observed. This inorganic sulfate formation was not detected in any control experiments and inferring that it is formed during aqueous-phase •OH oxidation of *α*pOS-249. **Figure 3** shows the temporal evolution of *α*pOS-249 and inorganic sulfate (HSO_4^- and SO_4^{2-}) concentrations during the aqueous-phase •OH oxidation of *α*pOS-249. Over the 3-hour oxidation period, *α*pOS-249 was nearly full consumed, while inorganic sulfate concentration steadily increased. The inorganic sulfate yield, calculated as the moles of inorganic sulfate formed per mole of *α*pOS-249 reacted over reaction time, reached of 46 ± 2 % at the end of experiment (**Figure S6**). These results suggest that within the timeframe of aqueous-phase •OH oxidation, about half of the sulfur in reacted *α*pOS-249 upon oxidation was converted to inorganic sulfate.

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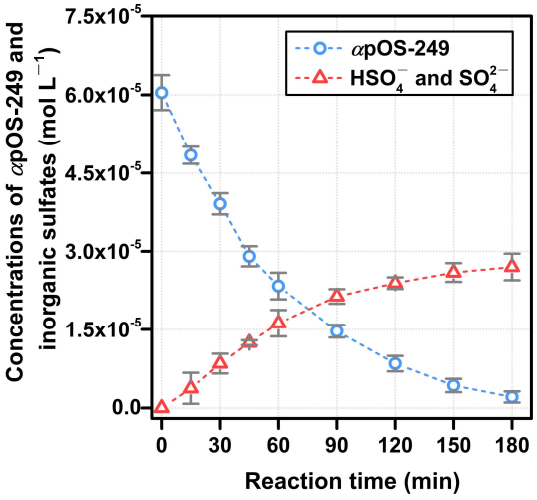

Figure 3. Concentrations of αpOS-249 and inorganic sulfates (HSO_4^- and SO_4^{2-}) as function of reaction time during the aqueous-phase $^{\bullet}OH$ oxidation of αpOS-249.

Upon oxidation, the generation of inorganic sulfates involves the formation and reactions of sulfate radical anion ($SO_4^{\bullet-}$) (Ng and Chan, 2023). This sulfur radical species is likely derived from the cleavage of C-O bond, occurring when a $RO^{\bullet}$ is created with the $-O^{\bullet}$ situated at the β position of the $-OSO_3^-$ group (Ng and Chan, 2023). In the presence of H_2O, $SO_4^{\bullet-}$ can subsequently converted into HSO_4^-, which can exist in equilibrium with SO_4^{2-}. Both HSO_4^- and SO_4^{2-} contribute the yield of inorganic sulfates (Lai et al., 2023). Based on SAR predictions (**Figure S2**), hydrogen abstraction at the α-position 5-C reaction site, leading to the direct formation of $SO_4^{\bullet-}$, shows the lowest relative reactivity (2.3 %) compared to other sites. This small reactivity can be explained by the electron-withdrawing nature of $-OSO_3^-$ groups, which lower the electron density of the α C−H bond and decrease the rate of hydrogen abstraction (Berruti et al., 2022; Lai et al., 2024). Considering this low reactivity, the generation of $SO_4^{\bullet-}$ through C-O bond cleavage in the 5-C alkoxy radical directly from αpOS-249, and its subsequent conversion to inorganic sulfates (**Scheme S3**), may not be a favorable reaction pathway.

Possible explanations the sulfur conversion from αpOS-249 to inorganic sulfate could be: 1) enhanced likelihood of α-position alkoxy radical decomposition to $SO_4^{\bullet-}$ as oxidation proceeds, altering site selectivity of $^{\bullet}OH$ hydrogen abstraction when more oxygenated and

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functional groups are added to the carbon backbone (e.g., different generations of oxygenated C_{10} OS products), 2) increased production of smaller OS products leading to easier C-O bond cleavage and inorganic sulfate formation due to fewer carbon atoms, 3) in addition to $SO_4^{\bullet-}$ pathway, the formation of inorganic sulfates may also occur through the non-$SO_4^{\bullet-}$ reaction pathway. For example, a recent laboratory study proposed an alternative mechanism for inorganic sulfate formation, suggesting the involvement of sulfite radical anion ($SO_3^{\bullet-}$) from the cleavage of (C)O−S bonds, triggering a series of chain reactions resulting in inorganic sulfate formation (Xu et al., 2024), and 4) when oxidation proceeds, more tertiary OS products are likely produced. This could increase the possibility of inorganic sulfates formed from the hydrolysis of these tertiary OS products. For instance, the efficient hydrolysis can occur for certain tertiary OSs, such as isoprene-derived OSs, under relevant ambient acidities (Hu et al., 2011).

It is important to note that the formation of $SO_4^{\bullet-}$ via C-O bond cleavage in $RO^{\bullet}$ can also lead to the formation of non-sulfated products (Xu et al., 2022). For example, C_{10} products such as $C_{10}H_{18}O_2$ (m/z = 170.13) and $C_{10}H_{16}O_2$ (m/z = 168.12) can be formed (**Scheme S3**). Their predicted Henry's law constants, calculated using HENRYWIN through the bond contribution method (Mackay and Shiu, 1981), are 4.08×10^3 M atm^{-1} and 9.17×10^1 M atm^{-1}, respectively. These predicted values are lower than that of αpOS-249 (1.35×10^9 M atm^{-1}). Given their low solubilities, these two non-sulfated products are likely partition to the gas phase and have not been detected in our product analysis. Additionally, some non-volatile products could be formed. For instance, $C_9H_{16}O_4$ (m/z = 188.10) and $C_9H_{14}O_4$ (m/z = 186.09) can be produced alongside $SO_4^{\bullet-}$ (**Scheme S3**), with predicted Henry's law constants are 1.71×10^8 M atm^{-1} and 9.52×10^6 M atm^{-1}, respectively, about one to two orders of magnitude lower than αpOS-249 (Mackay and Shiu, 1981). Among these two products, $C_9H_{14}O_4$ (m/z = 186.09) was detected in our product analysis, but $C_9H_{16}O_4$ (m/z = 188.10) was not identified.

4 Atmospheric implications

We would like to note that as shown in **Table 1** and **Table S5**, 34 out of 40 OS products formed upon aqueous-phase $^{\bullet}$OH oxidation of αpOS-249 have been detected in ambient samples with significant atmospheric abundance. Among the detected OS products, the most prevalent OS product, $C_5H_7SO_7^-$ (m/z = 210.99), has been observed at concentrations up to 131 ng m^{-3} and was previously thought to originate primarily from isoprene (**Table S5**) (Hettiyadura et al., 2019). Our findings also suggest that this OS product could also originated from the aqueous-phase $^{\bullet}$OH oxidation of αpOS-249. This can also apply to other smaller OSs

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(<C_{10}), including $C_3H_5SO_5^-$, $C_7H_9SO_7^-$, and $C_8H_{11}SO_7^-$ (**Table 1**), previously linked to isoprene as a precursor. This finding also addresses that some atmospheric smaller OSs can also originate from the transformation of larger OSs (e.g., *α*pOS-249), particularly in the regions where the monoterpene emissions are significant. More importantly, among the identified OS products, 13 out of 40 OS products have unknown sources and 20 out of 40 OS products have unknown formation pathways (**Table 1**), suggesting that the aqueous ·OH oxidation of *α*pOS-249 could be a previously unrecognized formation pathway of these ambient-detected OSs (**Figure S7**).

Table 1. Overview of detected OS products upon the aqueous ·OH oxidation of *α*pOS-249 (identified in previous studies along with suggested precursors and formation pathways).

	Previous studies			This work	
Formula	**Suggested precursor**	**Suggested formation pathway**	**Ref.**	**Additional formation pathway**	**Suggested new formation pathway**
Smaller OS (<C_{10}) products					
$C_3H_5SO_5^-$	Isoprene/glycolaldehyde/ hydroxyacetone	Isoprene + ·OH + (NO) + acidic/neutral sulfate seed	(Surratt et al., 2008)	✓	
$C_5H_7SO_7^-$	Isoprene	Isoprene + ·OH + acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_6H_9SO_6^-$	Anthropogenic	**Unknown**	(Hettiyadura et al., 2019)		✓
$C_6H_7SO_7^-$	**Unknown**	**Unknown**	–		✓
$C_6H_9SO_8^-$	**Unknown**	**Unknown**	–		✓
$C_7H_9SO_7^-$	Isoprene	Methyl vinyl ketone + $SO_4^{\cdot-}$	(Nozière et al., 2010)	✓	
$C_7H_9SO_8^-$	**Unknown**	**Unknown**	–		✓
$C_7H_{11}SO_8^-$	**Unknown**	**Unknown**	–		✓
$C_7H_{11}SO_9^-$	**Unknown**	**Unknown**	–		✓
$C_7H_{11}SO_{10}^-$	**Unknown**	**Unknown**	–		✓
$C_8H_9SO_6^-$	**Unknown**	**Unknown**	–		✓
$C_8H_{11}SO_7^-$	Isoprene	Methyl vinyl ketone/methacrolein + $SO_4^{\cdot-}$	(Hettiyadura et al., 2019; Nozière et al., 2010; Schindelka et al., 2013)	✓	
$C_8H_{11}SO_8^-$	**Unknown**	**Unknown**	–		✓
$C_8H_{11}SO_9^-$	**Unknown**	**Unknown**	–		✓
$C_9H_{15}SO_5^-$	Monoterpenes	**Unknown**	(Brüggemann et al., 2019)		✓
$C_9H_{13}SO_6^-$	Monoterpenes	Limonene/terpinolene + ·OH + NO + highly acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_9H_{15}SO_6^-$	Monoterpenes/sesquiterpenes	limonene + ·OH + (NO) + (highly) acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_9H_{11}SO_7^-$	Monoterpenes	**Unknown**	(Brüggemann et al., 2019)		✓

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$C_9H_{13}SO_7^-$	Monoterpenes	**Unknown**	(Brüggemann et al., 2019)		✓
$C_9H_{15}SO_7^-$	Isoprene/monoterpenes/ anthropogenic	limonene + •OH + NO + highly acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_9H_{13}SO_8^-$	Monoterpenes	**Unknown**	(Brüggemann et al., 2019)		✓
$C_9H_{15}SO_8^-$	Monoterpenes	α-terpinene + •OH + NO + highly acidic sulfate seed	(Surratt et al., 2008)	✓	
	Previous studies			**This work**	
Formula	**Suggested precursor**	**Suggested formation pathway**	**Ref.**	**Additional formation pathway**	**Suggested new formation pathway**
More oxygenated C_{10} OS products					
$C_{10}H_{15}SO_5^-$	Monoterpenes	α-pinene + •OH/NO_3• + highly acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_{10}H_{15}SO_6^-$	Monoterpenes	β-pinene + •OH + NO + highly acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_{10}H_{17}SO_6^-$	Monoterpenes/anthropogenic	α-pinene/α-terpinene/terpinolene + •OH + (NO) + (highly) acidic sulfate seed	(Surratt et al., 2008)	✓	
$C_{10}H_{13}SO_7^-$	**Unknown**	**Unknown**	–		✓
$C_{10}H_{15}SO_7^-$	Monoterpenes/anthropogenic	α-pinene/β-pinene/limonene/α-terpinene/γ-terpinene + •OH/NO_3•/SO_4•$^-$ + (NO) + (highly) acidic sulfate seed	(Surratt et al., 2008; Nozière et al., 2010)	✓	
$C_{10}H_{17}SO_7^-$	Monoterpenes	α-pinene/β-pinene /limonene/α-terpinene/terpinolene + •OH/SO_4•$^-$ + (NO) + (highly) acidic sulfate seed	(Surratt et al., 2008; Nozière et al., 2010)	✓	
$C_{10}H_{13}SO_8^-$	**Unknown**	**Unknown**	–		✓
$C_{10}H_{15}SO_8^-$	Monoterpenes/anthropogenic	**Unknown**	(Brüggemann et al., 2019; Riva et al., 2016)		✓
$C_{10}H_{17}SO_8^-$	Monoterpenes/anthropogenic	α-pinene/α-terpinene/terpinolene + •OH/SO_4•$^-$ + (NO) + (highly) acidic sulfate seed	(Surratt et al., 2008; Nozière et al., 2010)	✓	
$C_{10}H_{13}SO_9^-$	Monoterpenes	**Unknown**	(Brüggemann et al., 2019)		✓
$C_{10}H_{15}SO_9^-$	**Unknown**	**Unknown**	–		✓
$C_{10}H_{15}SO_{10}^-$	**Unknown**	**Unknown**	–		✓

5 Conclusions

Overall, the aqueous-phase •OH oxidation can serve as an important sink for αpOS-249 with corresponding atmospheric lifetimes ranged from minutes to about 2 days under relevant atmospheric cloud conditions. This efficient oxidation also highlights that the atmospheric abundance of αpOS-249 and potentially other structurally similar OSs (e.g., limonene derived OSs) in field studies may be underestimated if their transformation pathways are not properly considered. Moreover, aqueous-phase •OH oxidation of αpOS-249 can yield a number of more-

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oxygenated C_{10} OS products, smaller OS ($<C_{10}$) products, and inorganic sulfates (e.g., bisulfate (HSO_4^-) and sulfate (SO_4^{2-})). Among these products, most of the OS products have been detected in the atmosphere, with some having previously unknown sources and formation mechanisms. Altogether, this study shows that the transformation pathways of OSs (e.g., *α*pOS-249) via aqueous-phase •OH oxidation can serve as sources for some unclassified OSs in the atmosphere.

Data availability. Data are available upon request from the corresponding author.

Supplement. The supplement related to this article is available online at:

Author contributions. DL and MNC designed the experiments. DL ran the experiments. YB and YW synthesized *α*pOS-249 standard. ZZ and PKS helped with the chemical analysis. DL, YW, and MNC prepared the manuscript. YJL, YLST, YYY, TS, HH, and JZY provided valuable comments and suggestions for the manuscript.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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