Heterogeneous OH Oxidation of Isoprene Epoxydiol-Derived Organosulfates: Kinetics, Chemistry and Formation of Inorganic Sulfate

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Abstract

Acid-catalyzed multiphase chemistry of epoxydiols formed from isoprene oxidation yields the most abundant organosulfates (i.e., methyltetrol sulfates) detected in atmospheric fine aerosols. This potentially determines the physicochemical properties of fine aerosols in isoprene-rich regions. However, chemical stability of these organosulfates remains unclear. As a result, we investigate the heterogeneous oxidation of aerosols consisting of potassium 3-methyltetrol sulfate ester ($C_5H_{11}SO_7K$) by gas-phase hydroxyl (OH) radicals through studying the oxidation kinetics and reaction products at a relative humidity (RH) of 70.8 %. Real-time molecular composition of the aerosols is obtained by using a Direct Analysis in Real Time (DART) ionization source coupled to a high-resolution mass spectrometer. Aerosol mass spectra reveal that 3-methyltetrol sulfate ester can be detected as its anionic form ($C_5H_{11}SO_7^-$) via direct ionization in the negative ionization mode. Kinetic measurements reveal that the effective heterogeneous OH rate constant is measured to be $4.74 \pm 0.2 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} with a chemical lifetime against OH oxidation of 16.2 ± 0.3 days. Comparison of this lifetime with those against other aerosol removal processes, such as dry and wet deposition, suggests that 3-methyltetrol sulfate ester is likely to be chemically stable over atmospheric timescales. Aerosol mass spectra only show an increase in the intensity of bisulfate ion (HSO_4^-) after oxidation, suggesting the absence of functionalization processes~~ that is likely attributable to the steric effect of substituted functional groups (e.g. methyl, alcohol and sulfate groups) on peroxy peroxy radical reactions~~. Overall, potassium 3-methyltetrol sulfate ester likely decomposes to form volatile fragmentation products and aqueous-phase sulfate radial anion ($SO_4^{\bullet-}$). $SO_4^{\bullet-}$ subsequently undergoes intermolecular hydrogen abstraction to form HSO_4^-. These processes appear to explain the compositional evolution of 3-methyltetrol sulfate ester during heterogeneous OH oxidation.

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1 Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8), emitted from terrestrial vegetation to the atmosphere, is the largest atmospheric source of non-methane volatile organic compounds. Apart from enhancing urban ozone levels via photochemical oxidation initiated by gas-phase hydroxyl (OH) radicals (Chameides et al., 1988), isoprene-derived oxidation products can also significantly contribute to the formation of secondary organic aerosol (SOA) (Carlton et al., 2009). Gas-phase photochemical oxidation of isoprene by OH radicals can produce isoprene-derived hydroxyhydroperoxides (ISOPOOH) in yields greater than 70% under low-nitrogen oxide (NO_X) conditions (Paulot et al., 2009). Further reactions of ISOPOOH with OH radicals yield large quantities of isomeric isoprene epoxydiols (IEPOX), which partition into aqueous sulfate aerosols through acid-catalyzed ring-opening reactions. This multiphase chemical pathway is a key for the substantial production of isoprene-derived SOA constituents (e.g. 2-methyltetrols, C_5-alkene triols, organosulfates, 3-methyltetrahydrofuran-3,4-diols and oligomers) within atmospheric fine particulate matter ($PM_{2.5}$) (Carlton et al., 2009; Froyd et al., 2010; Surratt et al., 2010; Lin et al., 2012).

Among these SOA constituents, IEPOX-derived organosulfates (e.g. methyltetrol sulfates) have been widely detected in atmospheric aerosols and are estimated to account for 0.3–1.7 % of the total organic carbon (Chan et al., 2010; Froyd et al., 2010; Hatch et al., 2011; Lin et al., 2012; Stone et al., 2012; He et al., 2014; Budisulistiorini et al., 2015; Rattanavaraha et al., 2016; Meade et al., 2016; Hettiyadura et al. 2017). While the formation mechanisms of organosulfates have been extensively studied (Surratt et al., 2007, 2008; Minerath et al., 2009; Cole-Filipiak et al., 2010; Nozière et al., 2010; Lin et al., 2012; Nguyen et al., 2014), their chemical transformations and stability remain unclear. These low-volatility organosulfates are preferentially present in particle phase and can be oxidized by gas-phase oxidants (e.g., OH radicals, ozone, and nitrate radicals) at or near the aerosol surface throughout their atmospheric lifetimes. The heterogeneous oxidative processes can change the size, composition and physicochemical properties (e.g., light scattering and absorption, water uptake and cloud condensation nuclei activity) of both laboratory-generated and atmospheric organic aerosols (Rudich et al., 2007; George and Abbatt, 2010; Kroll et al., 2015). However, the extent of heterogeneous oxidation of organosulfates has not been clearly examined to date. Therefore, a better understanding of particle-phase transformations of isoprene-derived organosulfates can provide more insights on their potential impacts on human health, air quality and climate.

In this work, we investigate the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester ($C_5H_{11}SO_7K$, **Table 1**), as a single-component aerosol system by using an aerosol flow tube reactor at 70.8 % RH in order to gain a more fundamental understanding of the kinetics and chemistry. The molecular composition of the aerosols before and after oxidation is characterized in real-time using a soft atmospheric pressure ionization source (Direct Analysis in Real Time, DART) coupled to a high-resolution mass spectrometer. The 3-methyltetrol sulfate ester investigated in this study is one of the isomers of the methyltetrol sulfates found in atmospheric aerosols, which are collectively the most abundant particulate organosulfates (Budisulistiorini et al., 2015). On the basis of aerosol mass spectra and previously reported reaction pathways, oxidative kinetics and reaction products resulting from the heterogeneous OH oxidation of 3-methyltetrol sulfate ester are discussed. We acknowledge that although 3-methyltetrol sulfate ester derived from the reactive uptake of gas-phase δ-IEPOX onto sulfate seed aerosols is not the sole contributor to IEPOX-derived organosulfates (Cui et al., 2018), the findings of this work provide a basis for understanding better the heterogeneous OH reactivity of other IEPOX-derived organosulfates (e.g. 2-methyltetrol sulfate esters) that predominate in atmospheric aerosols.

2 Experimental Methods

The heterogeneous OH oxidation experiments were carried out in an aerosol flow tube reactor at 70.8 % RH. The synthesis of potassium 3-methyltetrol sulfate ester has been described in the literature (Bondy et al., 2018). The experimental details of the oxidation experiment have been explained elsewhere (Chim et al., 2017a, 2017b, 2018). Briefly, 3-methyltetrol sulfate ester aerosols were generated by an atomizer (TSI, model 3076) and mixed with nitrogen, oxygen, ozone and hexane before entering the reactor. Inside the reactor, the aerosols were oxidized heterogeneously by gas-phase OH radicals, which were generated by the photolysis of ozone under ultraviolet light at 254 nm in the presence of water vapor. The RH within the reactor was controlled by varying the dry/wet gas ratio. A water jacket was used to maintain a stable temperature of 20 ^{o}C inside the reactor. The OH concentration was controlled by varying the ozone concentration. By measuring the decay of hexane using a gas chromatograph coupled with a flame ionization detector, the OH exposure, which is an integral of gas-phase OH radical concentration and reaction time, can be calculated (Smith et al., 2009):

~~By measuring the decay of hexane using a gas chromatography coupled with a flame ionization detector, the OH exposure, which is an integral of gas phase OH radical concentration and reaction time, can be calculated (Smith et al., 2009):~~

$$\text{OH exposure } = \int_0^t [\text{OH}]\text{dt} = -\frac{\ln\left(\frac{[\text{Hex}]}{[\text{Hex}]_0}\right)}{\text{k}_{\text{Hex}}} \qquad (1)$$

where $[\text{Hex}]_0$ and [Hex] are the hexane concentration before and after OH oxidation, respectively, t is the reaction time (or aerosol residence time), which was measured to be 1.3 min, k_{Hex} is the rate constant for gas-phase OH reaction with hexane, and [OH] is the time-averaged OH radical concentration. The OH exposure varied from 0 to ~ 1.4×10^{12} molecules cm^{-3} s. An annular Carulite catalyst denuder and an activated charcoal denuder were used to remove ozone and gas-phase species from the aerosol stream leaving the reactor, respectively. As a result, only particle-phase products are detected. A fraction of the aerosol stream was sampled by a scanning mobility particle sizer (SMPS, TSI, CPC Model 3775, Classifier Model 3081) to measure the aerosol size and number distribution. The surface-weighted diameter of the aerosols was measured to be 225.9 ± 1.4 nm before oxidation. The remaining flow was then directed into a stainless steel tube heater at 380–400°C, where the temperature and aerosol residence time in the heater were sufficient to completely vaporize the aerosols~~An annular Carulite catalyst denuder and an activated charcoal denuder were used to remove ozone and gas phase species from the aerosol stream leaving the reactor, respectively. A fraction of the aerosol stream was sampled by a scanning mobility particle sizer (SMPS, TSI, CPC Model 3775, Classifier Model 3081) to measure the aerosol size and number distribution. Before oxidation, the surface-weighted diameter of the aerosols was 225.9 ± 1.4 nm. The remaining flow was directed into a stainless steel tube heater at 380–400°C, where the temperature and aerosol residence time in the heater were sufficient to~~

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~~completely vaporize the aerosols~~. The gas-phase species were then directed into the ionization region, an open narrow space between a DART ionization source (IonSense: DART SVP) and an atmospheric inlet of a high-resolution mass spectrometer (ThermoFisher, Q Exactive Orbitrap) for real-time chemical characterization (Chan et al., 2013). The DART ionization source was operated in a negative ion mode, with helium as the ionizing gas (Cody et al., 2005). Metastable helium atoms generated were responsible for ionizing the gas-phase species in the ionization region. 3-methyltetrol sulfate ester can be ionized via direct ionization (Block et al., 2010; Hajslova et al., 2011). Most recently, Kwong et al. (2018) have detected the ionic form of two organosulfates (sodium salts of methyl sulfate (CH_3SO_4Na) and ethyl sulfate ($C_2H_5SO_4Na$)) using the DART ionization source in negative ionization mode. Mass spectra were scanned over a range of *m/z* 70–700. Each mass spectrum was averaged over a 2–3 minute sampling time with a mass resolution of about 140,000. The mass spectra were analyzed using Xcalibar software (Xcalibar Software, Inc., Herndon, VA, USA).

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Particle phase state (e.g. solid or aqueous droplet) is known to play an important role in governing the heterogeneous kinetics and chemistry of organic aerosols (McNeil et al., 2008; Renbaum and Smith, 2009; Chan et al., 2014; Slade and Knopf, 2014; Zhang et al., 2018). ~~Hygroscopicity~~ The hygroscopicity of potassium 3-methyltetrol sulfate ester aerosols has not been experimentally determined. Recently, Estillore et al. (2016) have measured the hygroscopicity of a diverse set of organosulfates, including potassium salts of glycolic acid sulfate, hydroxyacetone sulfate, 4-hydroxy-2,3-epoxybutane sulfate and 2-butenediol sulfate as well as sodium salts of methyl sulfate, ethyl sulfate, propyl sulfate and benzyl sulfate. According to Estillore et al. (2016), these organosulfate aerosols did not show a distinct phase transition but absorbed or desorbed water reversibly when the RH increased or decreased, suggesting that these organosulfate aerosols were likely to be aqueous when RH was above 10%. Based on the literature results, we assume that potassium 3-methyltetrol sulfate ester exhibits hygroscopicity similar to the potassium salts of organosulfates reported by Estillore et al. (2016) (e.g. potassium 4-hydroxy-2,3-epoxybutane sulfate, $C_4H_7SO_6K$) and remains aqueous prior to oxidation.

Volatilization of 3-methyltetrol sulfate ester and the impact of ozone and UV light on the aerosol composition were investigated in the absence of OH. The intensity of parent ions with aerosols removed from gas stream was less than 5% of that measured in presence of 3-methyltetrol sulfate ester aerosols, suggesting that the volatilization of 3-methyltetrol sulfate ester is insignificant. No reaction product was observed in the presence of ozone without UV light or in the absence of ozone with the UV light, suggesting that 3-methyltetrol sulfate ester is not likely to be photolyzed or react with ozone under our experimental conditions.

3 Results and Discussions

3.1 Aerosol Mass Spectra

Figure 1 shows the data measured before and after oxidation at 70.8% RH. Before oxidation (Fig. 1a), a dominant ion peak at *m/z* 215 is observed, which corresponds to the ionic form of potassium 3-methyltetrol sulfate ester ($C_5H_{11}SO_7^-$) (Table 1). After oxidation (Fig. 1b), the parent ion remains the most dominant ion peak at the maximum

OH exposure of ~1.4×10^{12} molecules cm^{-3} s. There is no significant change in the ion intensity except for bisulfate ion (HSO_4^-; *m/z* 97). Figure 2 shows the evolution of HSO_4^- against OH exposure at 70.8% which indicates that the intensity of HSO_4^- increases with the OH exposure. In the following sections, the kinetics and chemistry will be discussed based on the aerosol mass spectra and aerosol-phase reactions previously proposed in the literature.

3.2 Oxidation Kinetics

Oxidation kinetics can be quantified by analyzing the parent decay of 3-methyltetrol sulfate ester against the OH exposure. Figure 3 shows the normalized decay of 3-methyltetrol sulfate ester against OH exposure. At the maximum OH exposure (~ 1.4×10^{12} molecules cm^{-3} s), ~ 45% of 3-methyltetrol sulfate ester is oxidized. The decay of the 3-methyltetrol sulfate ester can be fitted with an exponential function to obtain an effective second order heterogeneous OH rate constant (*k*) through Eq. (2) (Smith et al., 2009):

$$ln\frac{I}{I_0} = -k \cdot [OH]\, t \qquad (2)$$

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where *I* is the ion signal at a given OH exposure, I_o is the ion signal before oxidation, [OH] is the concentration of gas-phase OH radicals, and *t* is the reaction time. The *k* is determined to be $4.74 \pm 0.2 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (Table 1). Based on the fitted *k* value, the chemical lifetime of 3-methyltetrol sulfate ester against heterogeneous OH oxidation (τ) can be estimated by Eq. (3):

$$\tau = \frac{1}{k[OH]} \qquad (3)$$

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where [OH] is the 24-hour averaged OH radical concentration of 1.5×10^6 molecules cm^{-3}. The chemical lifetime against oxidation is calculated to be 16.2 ± 0.3 days. The estimated timescales are longer than those of other important aerosol removal processes, such as dry and wet deposition (~ 7–10 days) (Seinfeld and Pandis, 2016). In addition to heterogeneous oxidation, organosulfates can undergo hydrolysis to form polyols and sulfuric acid with rates depending on their molecular structure and aerosol acidity (Darer et al., 2011; Hu et al., 2011). According to Darer et al. (2011), primary isoprene-derived organosulfates are stable against hydrolysis, even at low pH while secondary and tertiary organosulfates are less thermodynamically stable than primary organosulfates. Since 3-methyltetrol sulfate ester is a primary organosulfate (Table 1), it is unlikely to hydrolyze. With reference to the literature results and our new experimental observations, 3-methyltetrol sulfate ester may possibly be considered chemically stable against heterogeneous OH oxidation and hydrolysis over atmospheric timescales.

3.3 Proposed Reaction Mechanisms

Based on the aerosol mass spectra and well-known aerosol-phase reactions previously reported in the literature (George and Abbatt, 2010; Kroll et al., 2015), we tentatively propose reaction mechanisms for the heterogeneous OH oxidation of 3-methyltetrol sulfate ester. The reaction schemes proposed can be found in the supplementary materials (Schemes S1-S5). Briefly, potassium methyltetrol sulfate ester likely dissociates and exists in its ionic form in the droplets. In the first oxidation step, the OH radical abstracts a hydrogen atom to form an alkyl radical which quickly reacts with oxygen to form a peroxy radical. We propose that the formation of alkoxy radical may be favored over the Russell mechanism (Russell, 1957) and Bennett–Summers reactions (Bennett and Summers, 1974) as functionalization products were not detected. Alkoxy radicals, once formed, may tend to undergo fragmentation due to the presence of vicinal hydroxyl groups, which lower the activation energy required for the decomposition of the alkoxy radicals (Cheng et al., 2015; Wiegel et al., 2015; Jimenez et al., 2009; Peeters et al., 2004; Vereecken and Peeters, 2009).

Formation of HSO_4^-. Sulfate radical anion ($SO_4^{\bullet-}$) can be formed through the decomposition of the alkoxy radical and is a strong oxidant in aqueous phase (Neta et al., 1988; Clifton and Huie, 1989; Padmaja et al., 1993). $SO_4^{\bullet-}$ can abstract a hydrogen atom from a neighboring organic molecule (e.g. unreacted 3-methyltetrol sulfate ester) to form HSO_4^- (R1) or react with particle-phase water to yield a HSO_4^- and an OH radical (R2) (Tang et al., 1988) as illustrated below. It is noted that $SO_4^{\bullet-}$ or OH radical recycled from R2 can react with 3-methyltetrol sulfate ester, contributing to the secondary chain reactions.

$$\mathrm{C_5H_{11}O_7}S^- + \mathrm{SO_4}^{\bullet-} \rightarrow \mathrm{C_5H_{10}O_7}S^{\bullet-} + \mathrm{HSO_4}^- \qquad (R1)$$

$$\mathrm{SO_4}^{\bullet-} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH}^\bullet + \mathrm{HSO_4}^- \qquad (R2)$$

Since 3-methyltetrol sulfate ester is unlikely to hydrolyze (Darer et al., 2011), the formation of the HSO_4^- upon OH oxidation could be best explained by the formation and subsequent reactions of $SO_4^{\bullet-}$.

Based on the proposed reaction mechanisms, the decomposition of alkoxy radicals can lead to formation fragmentation products (without sulfate group) and smaller organosulfates. We acknowledge that the ionization efficiency and detection limit of the reaction products are not fully understood. The absence of the potential products might attribute to the DART ionization and detection issues. More work is needed to investigate the formation and abundance of the reaction products formed upon oxidation in order to better understand the reaction pathways. It is also noted that the formation of second or higher generation products are possible due to the high OH concentrations used in this study. While the potential secondary or higher generation products have not detected possibly due to their low concentrations and/or ionization issues, for clarify, the formation and oxidation of second or higher generation products are not further discussed."

~~3.3 Reaction Mechanisms~~

~~Schemes 1–5 show the reaction mechanisms proposed for the heterogeneous OH oxidation of 3-methyltetrol sulfate ester based on the aerosol mass spectra (Figs. 1 and 2) and well-known aerosol-phase reactions previously reported in the literature (George and Abbatt, 2010; Kroll et al., 2015). Potassium methyltetrol sulfate ester likely dissociates and exists in its ionic form in the droplets. In the first oxidation step, the OH radical abstracts a hydrogen atom to form an alkyl radical which quickly reacts with oxygen to form a peroxy radical. No formation of alcohol or carbonyl functionalization product can be observed in aerosol mass spectra (Fig. 1), regardless of initial hydrogen abstraction site. The absence of functionalization products in the aerosol mass spectra may suggest that fragmentation processes are likely to have occurred. One possible explanation is that the multiple functional groups in the 3-methyltetrol sulfate ester (e.g. hydroxyl, methyl and sulfate groups, or a combination of these functional groups, depending on the initial OH reaction site), which are always located at positions vicinal to a peroxyl group, may sterically hinder the association of two peroxy radicals into the cyclic tetroxide intermediate proposed in the Russell mechanism (Russell, 1957) and Bennett-Summers reactions (Bennett and Summers, 1974). As the intermediate is essential for the formation of alcohol and carbonyl functionalization products, the steric effect may in turn favor the formation of alkoxy radicals (Cheng et al., 2015). Alkoxy radicals, once formed, may tend to undergo~~

~~fragmentation due to the presence of vicinal hydroxyl groups, which lower the activation energy required for the decomposition of the alkoxy radicals (Wiegel et al., 2015; Jimenez et al., 2009). To gain more insights into this process, calculations are preformed using a structural activity relationship (SAR) model developed for the decomposition of alkoxy radicals (Peeters et al., 2004; Vereecken and Peeters, 2009). For example, when the β-carbons are methyl groups (isopropoxyl radical), the barrier height E_b for the decomposition is calculated to be 15.6 kcal mol^{-1}. When one β-carbon bears a hydroxyl group (1-hydroxyisopropoxyl radical), E_b is lowered to 8.1 kcal mol^{-1}, implying a faster decomposition rate. However, the effect of vicinal sulfate on the decomposition of an alkoxy radical has not been estimated.~~

~~The fragmentation of alkoxy radicals can yield fragmentation products (without sulfate group), smaller organosulfates and sulfate radical anions ($SO_4^{\bullet-}$), as shown in Schemes 1–5. However, like the functionalization products, these products have not been detected (Fig. 1). Only the intensity of HSO_4^- increases after oxidation (Fig. 2). On the basis of the proposed reaction pathways (Schemes 1–5), one possibility is that fragmentation products are likely to be volatile and partition back to the gas phase. The high volatility of these products may contribute to the absence of fragmentation products in the aerosol mass spectra. Fragmentation processes can also yield smaller organosulfates, which have low volatilities and remain in the particle phase. In our previous study, we have demonstrated that small organosulfates, such as sodium methyl sulfate (CH_3SO_4Na) and sodium ethyl sulfate ($C_2H_5SO_4Na$), the alcohol and carbonyl functionalization products of sodium ethyl sulfate can be detected by the DART ionization source (Kwong et al., 2018). In other words, if these small organosulfates are formed in a significant amount during the oxidation of methyltetrol sulfate, the DART ionization technique should be able to detect them, which is not the case with reference to the aerosol mass spectra (Fig. 1). We postulate that upon oxidation the reaction intermediates may tend to decompose and eventually yield $SO_4^{\bullet-}$. $SO_4^{\bullet-}$ is a strong oxidant in aqueous phase and can react with a variety of organic compounds (e.g. alcohols, ethers, alkanes and aromatic compounds) (Neta et al., 1988; Clifton and Huie, 1989; Padmaja et al., 1993). For the OH reaction with 3-methyltetrol sulfate ester, $SO_4^{\bullet-}$ can abstract a hydrogen atom from a neighboring organic molecule (e.g. unreacted 3-methyltetrol sulfate ester) to form HSO_4^- (R1) or react with particle-phase water to yield a HSO_4^- and an OH radical (R2) (Tang et al., 1988) as illustrated below. It is noted that $SO_4^{\bullet-}$ or OH radical recycled from R2 can react with 3-methyltetrol sulfate ester, contributing to the secondary chain reactions.~~

~~$C_5H_{11}O_7S^- + SO_4^{\bullet-} \rightarrow C_5H_{10}O_7S^{\bullet-} + HSO_4^-$ $(R1)$~~

~~$SO_4^{\bullet-} + H_2O \rightleftharpoons OH^{\bullet} + HSO_4^-$ $(R2)$~~

~~Since 3-methyltetrol sulfate ester is unlikely to hydrolyze (Darer et al., 2011), the formation of the HSO_4^- upon OH oxidation could be best explained by the formation and subsequent reactions of $SO_4^{\bullet-}$. For instance, the OH-initiated oxidation by hydrogen abstraction at the terminal secondary carbon site (Scheme 1) can yield a peroxy radical. The formation of alkoxy radicals through the self reactions of two peroxy radicals is expected to be favored due to the steric effect induced by the presence of methyl and hydroxyl groups near the peroxyl group. The resultant alkoxy radical likely undergoes β-scission, attributing to the hydroxyl group located near the alkoxy group could lower the energy barrier height (Jimenez et al., 2009). It is postulated that an alkyl radical of methyl sulfate ion could be~~

~~formed after multiple reaction steps proposed in the reaction scheme. Our recent work on the heterogeneous OH oxidation of sodium methyl sulfate has demonstrated that further reactions of this alkyl radical can lead to the formation of a formaldehyde and a $SO_4^{\bullet-}$, which subsequently abstract a hydrogen atom to form HSO_4^- (Scheme 5) (Kwong et al., 2018). At the same time, fragmentation products formed during β-scission (e.g. formic acid and acetic acid) are volatile and likely to partition back to the gas phase.~~

4 Conclusions and Atmospheric Implications

This work investigates the kinetics of oxidation and molecular transformations of potassium 3-methyltetrol sulfate ester resulting from the heterogeneous OH oxidation. Kinetic measurements reveal that the chemical lifetime of 3-methyltetrol sulfate ester against heterogeneous OH oxidation and hydrolysis are longer than those against other aerosol removal processes, such as dry and wet deposition. 3-methyltetrol sulfate ester is potentially chemically stable over its atmospheric ~~timescale~~lifetime. In the atmosphere where particles may contain compounds with different surface-active properties, the chemical lifetime could be affected due to the inhomogeneity in surface concentration. If surface-active compounds are present, the chemical lifetime will likely be longer due to a lower surface concentration of the parent molecules. This reduces the collision probability between gas-phase OH radicals and parent molecules at the particle surface, leading to a smaller overall oxidation rate.

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Aerosol mass spectra reveal that only the intensity of HSO_4^- increases after oxidation, suggesting the dominance of fragmentation processes over functionalization processes. During oxidation, alkoxy radials are likely to be formed following hydrogen abstraction of 3-methyltetrol sulfate ester by OH radicals. ~~because the reaction intermediates in the Russell and Bennett–Summers reactions are sterically unfavorable.~~ The alkoxy radicals subsequently fragment into volatile products and $SO_4^{\bullet-}$. $SO_4^{\bullet-}$ undergoes intermolecular hydrogen abstraction to form HSO_4^- in the aerosol phase, while the volatile fragmentation products may tend to partition into gas phase. ~~The alkoxy radicals subsequently fragment into volatile products and $SO_4^{\bullet-}$. The volatile fragmentation products tend to partition into gas phase, while $SO_4^{\bullet-}$ undergoes intermolecular hydrogen abstraction to form HSO_4^- in the aerosol phase.~~ It is also noted that volatile fragmentation products likely contain polar functional groups. They may partition back to the aerosols, for instance aqueous droplets because of their high water solubilities or Henry's law constants. Additionally, they could be reactively uptaken by aerosols which contain reactive nitrogen or oxygen species through reactions. Smaller organosulfates have not been observed, possibly due to the rapid continuous decomposition of the reaction intermediates proposed in Schemes 1–5. The absence of smaller organosulfates suggests that the oxidation of 3-methyltetrol sulfate ester is not a source of smaller organosulfates detected in atmospheric aerosols. Further investigations into whether large organosulfates yield smaller organosulfates upon heterogeneous OH oxidation are desirable. Aerosol mass spectra have revealed that the OH oxidation of 3-methyltetrol sulfate ester can lead to the formation of inorganic sulfate (e.g. HSO_4^-), in accord with our report that the heterogeneous OH oxidation of sodium methyl sulfate and sodium ethyl sulfate can lead to the formation of HSO_4^- (Kwong et al., 2018). Given the high atmospheric abundance of organosulfates in atmospheric aerosols, further study of the contribution and transformation of organosulfates to inorganic sulfate through chemical reactions (e.g. heterogeneous oxidation, aqueous-phase oxidation and hydrolysis) is desirable. Methyltetrol sulfates are the most abundant isoprene-derived organosulfates measured in atmospheric $PM_{2.5}$ samples collected from isoprene-rich regions influenced by anthropogenic emissions (Budisulistiorini et al., 2015; Hettiyadura et al. 2017). Additional studies are required to better understand the role of the molecular structure (i.e., position of the methyl and sulfate group) on the kinetics and chemistry of methyltetrol sulfates and other organosulfates upon heterogeneous OH oxidation; in particular the effect on the formation of smaller organosulfates, volatile fragmentation products and inorganic sulfate, since the 2-methyltetrol sulfate ester and its isomers rather than the 3-methyltetrol sulfate ester investigated in this study predominate in atmospheric aerosols (Cui et al., 2018).

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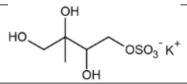
Table 1. Chemical Structure, properties, effective heterogeneous OH rate constant and atmospheric lifetime against OH radical of potassium 3-methyltetrol sulfate ester

Compounds	Potassium 3-methyltetrol sulfate ester
Structural Formula	
Molecular Formula	$C_5H_{11}SO_7K$
Molecular Weight (g mol^{-1})	254.30
Relative Humidity, RH (%)	70.8
Effective Heterogeneous OH Rate Constant, *k* (×10^{-13} cm^3 molecule^{-1} s^{-1})	4.74 ± 0.2
Atmospheric Lifetime against OH Oxidation (Days)[a]	16.2 ± 0.3

[a] using a 24-hour average OH concentration of 1.5×10^6 molecules cm^{-3}

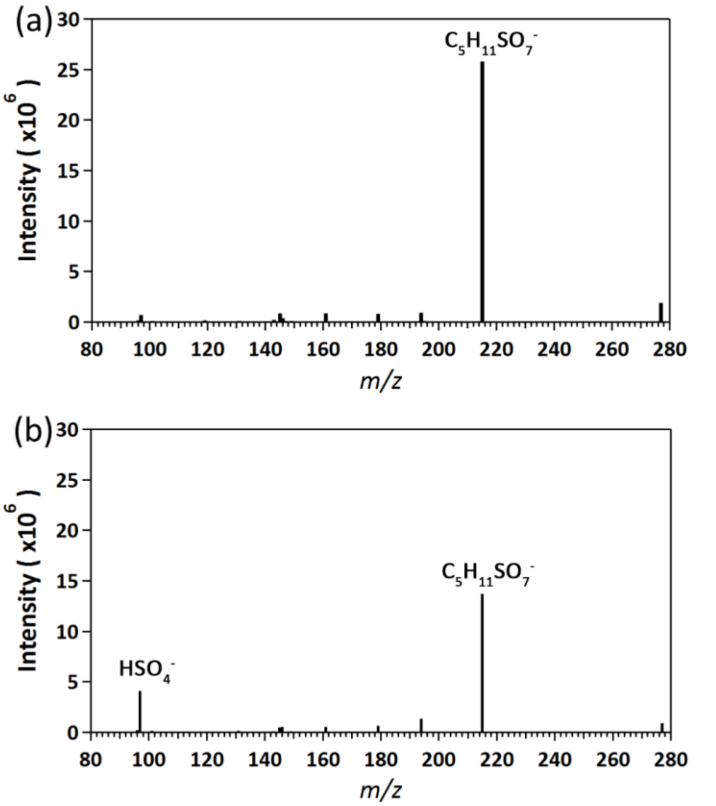


Figure 1. Aerosol mass spectra of potassium 3-methyltetrol sulfate ester before (a) and after (b) OH oxidation at 70.8% RH.

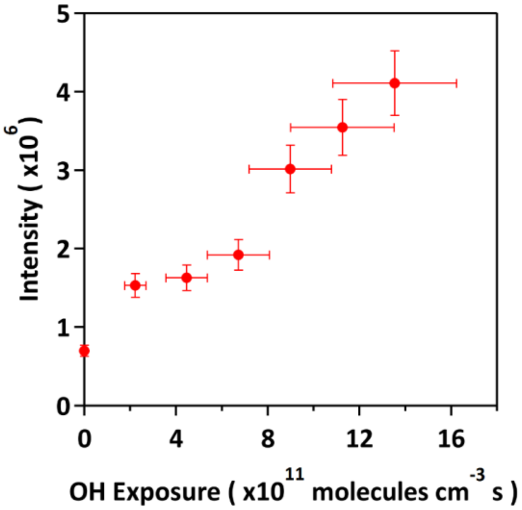


Figure 2. The evolution of the ion intensity of bisulfate ion (HSO_4^-) as a function of OH exposure during the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at 70.8% RH.

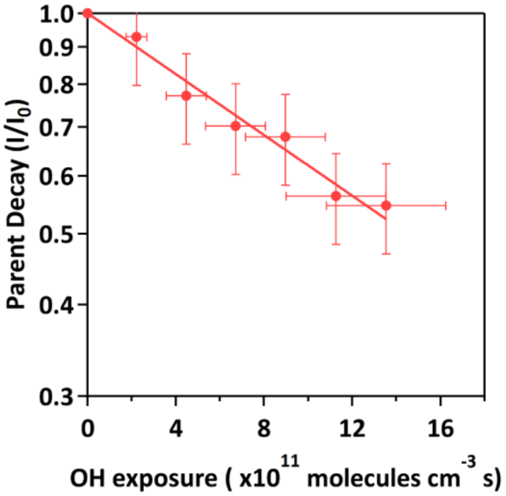
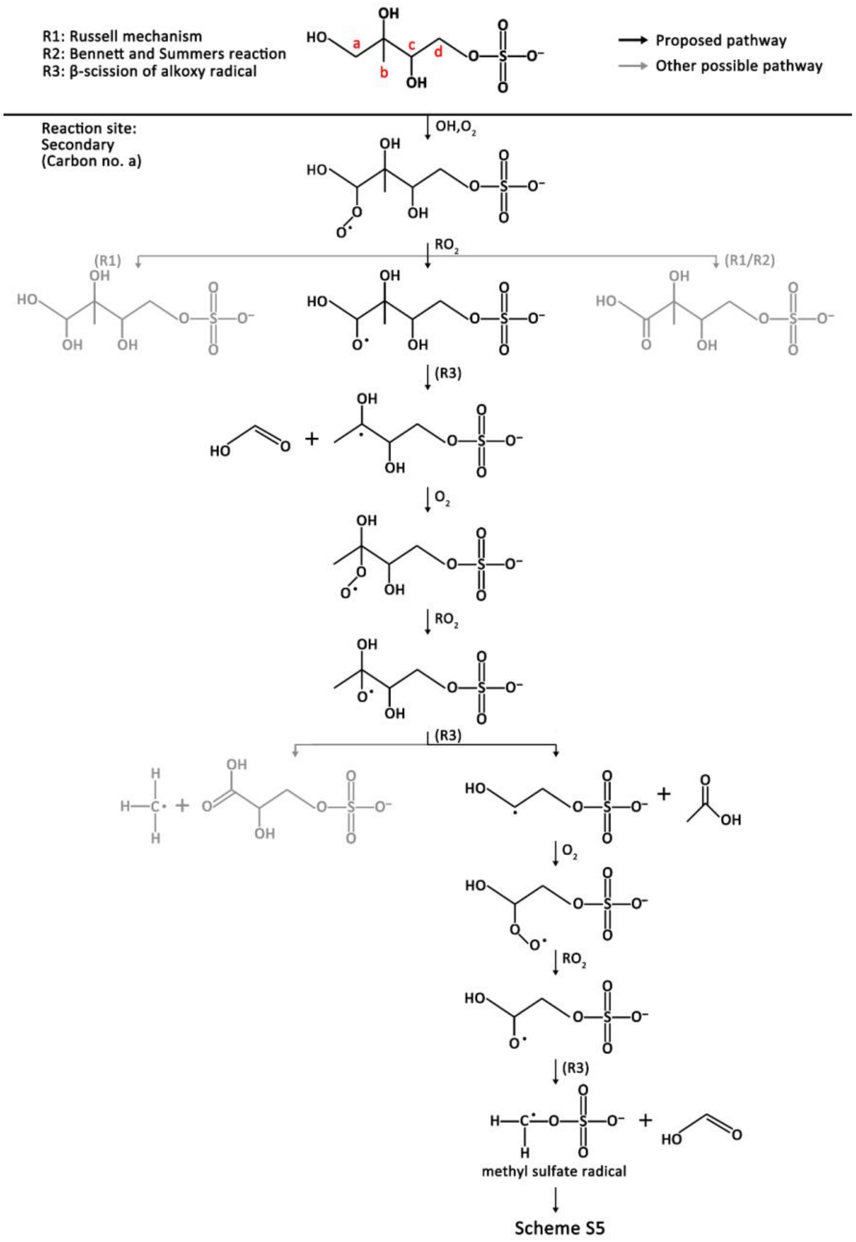
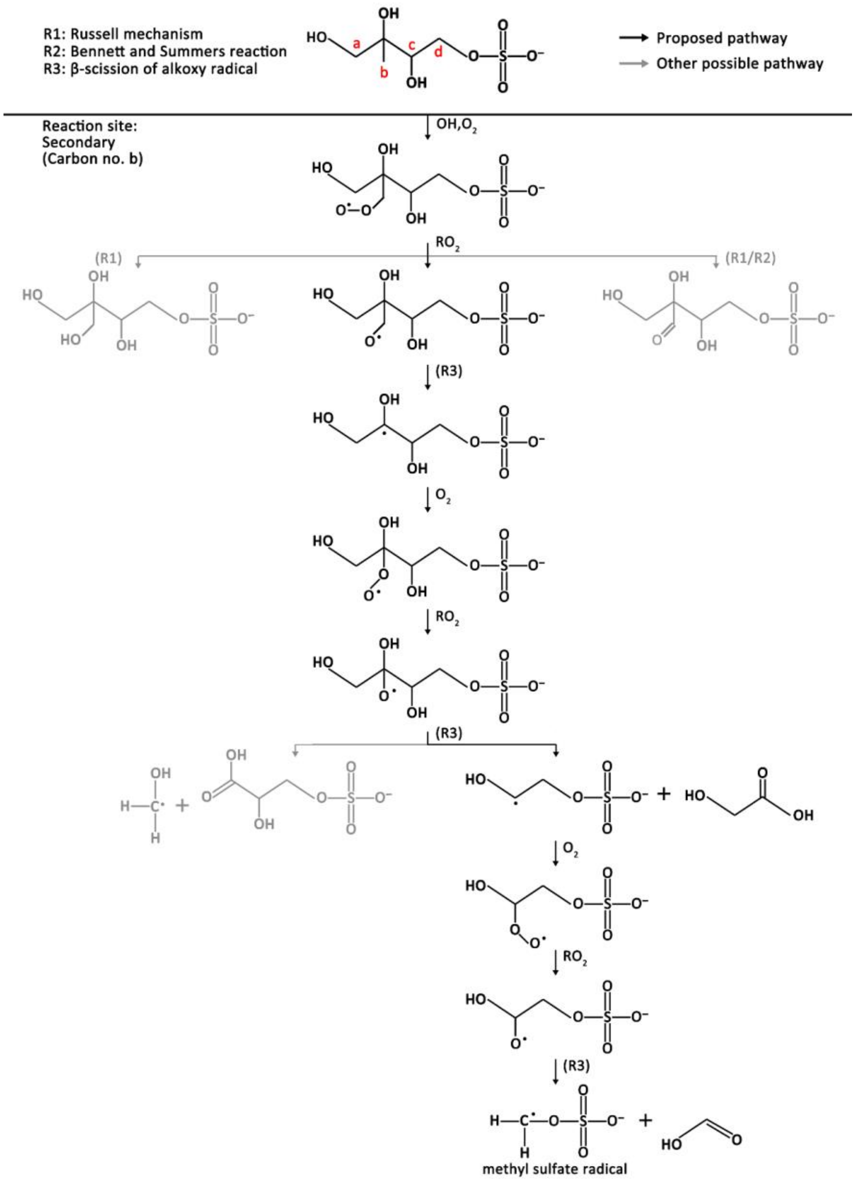


Figure 3. The normalized parent decay as a function of OH exposure during the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at 70.8% RH.

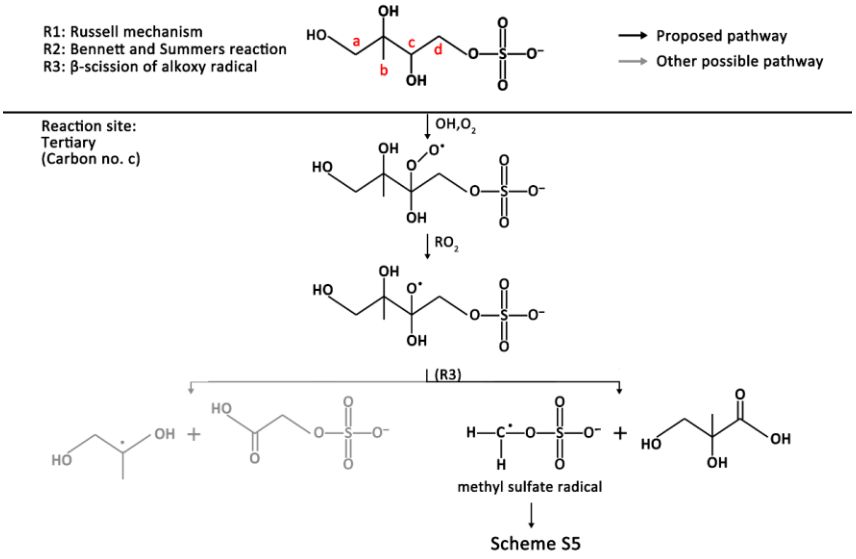


~~**Scheme 1.** Proposed reaction mechanisms for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled a.~~

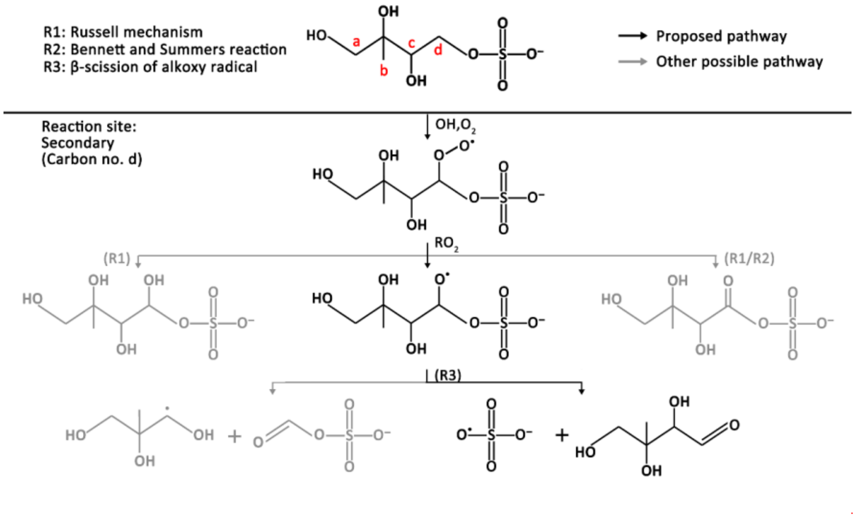


Scheme S5

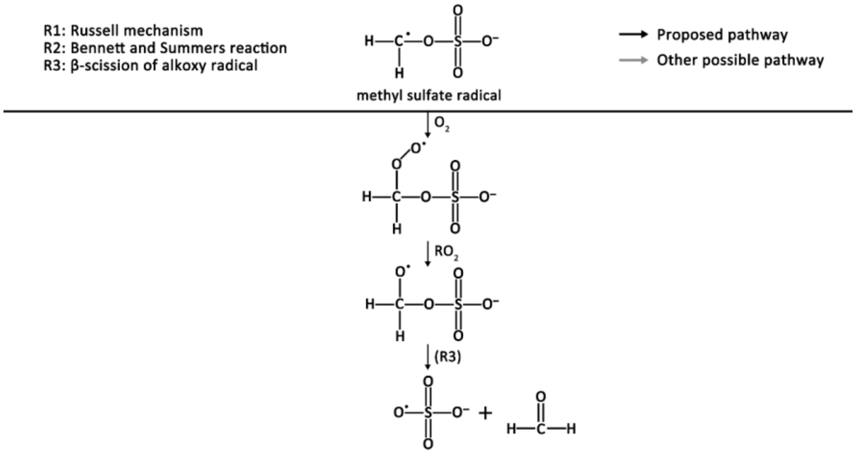
~~**Scheme 2.** Proposed reaction mechanisms for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled b.~~



~~**Scheme 3.** Proposed reaction mechanisms for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled c.~~



~~**Scheme 4.** Proposed reaction mechanism for the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at the carbon labelled d.~~



~~**Scheme 5.** Proposed reaction mechanism for the reactions of alkyl radical of methyl sulfate anion.~~

Reply to Interactive comment on "Heterogeneous OH Oxidation of Isoprene Epoxydiol-Derived Organosulfates: Kinetics, Chemistry and Formation of Inorganic Sulfate" by Hoi Ki Lam et al.

Anonymous Referee #1

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-989-RC2, 2018.

In this paper the authors describe results of a laboratory study of the heterogeneous oxidation of 3-methyltetrol sulfate ester by OH radicals in aqueous aerosol particles. This compound served as a surrogate for organosulfate esters formed from particle-phase reactions of isoprene oxidation products. Understanding the atmospheric fate of these compounds is important because of their potential importance as aerosol components. The reactions were conducted in a flow tube and the concentrations of the parent compound and products were monitored using DART mass spectrometry. The rates of oxidation were quantified using relative rate methods and the measured rate constant used to estimate the lifetime of these and similar compounds in the atmosphere due to this reaction. The only major product observed was bisulfate, and a mechanism was proposed to explain its presence. The paper is clearly and concisely written and the experiments are straightforward. The interpretation is reasonable, although it is challenging to build a believable mechanism when only one of the proposed products was detected. I think the paper should be publishable after some comments are addressed, but there is clearly work to be done to provide more convincing evidence for the proposed mechanism.

We would like to sincerely thank the reviewer for his/her thoughtful comments and suggestions. Please see our responses to reviewer's comments and suggestions below.

Comment #1

Page 2, line 34: The kinetics method assumes that the particles are uniformly mixed, which is probably true here. But in the atmosphere where particles contain numerous compounds with a range of surface-active properties there will be significant inhomogeneities in surface concentrations where the OH reaction occurs, thus affecting estimated lifetimes. Some comments on this are warranted.

Author Response:

We agree with the reviewer that the chemical lifetime could be affected by surface-active compounds in the particle. If surface-active compounds are present, the chemical lifetime will likely be longer due to a lower surface concentration of parent molecules. This reduces the collision probability between gas-phase OH radicals and parent molecules at particle surface, leading to a smaller overall oxidation rate. We have added the following information in the revised manuscript.

Page 6, Line 20, "In the atmosphere where particles may contain compounds with different surface-active properties, the chemical lifetime could be affected due to the inhomogeneity in surface concentration. If surface-active compounds are present, the chemical lifetime will likely be longer due to a lower surface concentration of the parent molecules. This reduces the collision probability between gas-phase OH radicals and parent molecules at the particle surface, leading to a smaller overall oxidation rate."

Comment #2

Page 5, line 20: The authors should justify their decision to ignore decomposition of α-hydroxyperoxy radicals to carbonyl + HO_2, which is the dominant pathway in the gas phase. This should be based on kinetics arguments since the absence of product peaks in the mass spectrum could be influenced by ionization. Relevant rate constants are available [Neta et al., J. Phys. Chem. Ref. Data, 19, 413-513 (1990)].

Author Response:

Thanks for the comment. As suggested by the reviewer, the decomposition of α-hydroxylperoxy radical to carbonyl and HO_2 is a dominant pathway in gas phase. In our previous study, we have also found that this intramolecular HO_2 elimination process is an important reaction pathway during the heterogeneous OH oxidation of tartaric acid (Cheng et al., 2016). We do not include this reaction in this study because the carbonyl functionalization products have not been detected. Since the similarity in structures as compared to the parent compound (i.e. methyltetrol sulfate), we thought that the ionization issue might not be the primary reason for the absence of carbonyl products peak. However, as pointed by the reviewer, we agree that the detection of reaction products originated by the intramolecular HO_2 elimination process could be influenced by the ionization since the ionization efficiency and detection limit of the potential products are not fully understood. Further investigations on the ionization efficiency and detection limit of potential reaction products are needed to better understand the reaction pathways and the significance of the decomposition of α-hydroxyperoxy radicals through the HO_2 elimination process. In the revised manuscript, we have discussed and included this reaction pathway in the proposed reaction mechanisms in the supplementary material.

Supplementary material, Page 3, Line 27, "It is noted that decomposition of α-hydroxylperoxy radical to carbonyl and HO_2 is a dominant pathway in gas phase (Neta et al., 1990). In our previous study, we have also found that this intramolecular HO_2 elimination process is an important reaction pathway during the heterogeneous OH oxidation of tartaric acid (Cheng et al., 2016). However, the carbonyl functionalization products have not detected in the aerosol mass spectra. Given the similarity in structures as compared to the parent compound (i.e. methyltetrol sulfate), the ionization issue might not be the primary reason for the absence of carbonyl products in the mass spectra. However, further investigations on the ionization efficiency and detection limit of reaction products are needed to better understand the reaction pathways and the significance of the decomposition of α-hydroxyperoxy radicals through HO_2 elimination process during oxidation."

References

Cheng, C.T., Chan, M. N., Wilson, K.R.: Importance of unimolecular HO2 elimination in the heterogeneous OH reaction of highly oxygenated tartaric acid aerosol", J. Phy. Chem. A, 118, 28978–28992, 2016.

Neta, P., Huie, R. E., and Ross, A. B.: Rate constants for reactions of peroxyl radicals in fluid solutions, J. Phys. Chem. Ref. Data, 19, 413–513, 1990.

Comment #3

Page 6, lines 13–18: I am not yet convinced by the argument that because the authors were able to detect small organosulfates in a previous study that they would have seen them here if they were present. How sensitive is the DART method to matrix effects, concentrations, and other conditions?

Author Response:

We agree with the reviewer's concern. We acknowledge that the detection limits and possible matrix effects are not yet well understood. Further studies on the sensitivity of DART-MS to smaller organosulfates under different conditions are warranted. We have added this information in the revised manuscript.

Supplementary material, Page 2, Line 36, "In our previous study, we have demonstrated that small organosulfates, such as sodium methyl sulfate (CH_3SO_4Na) and sodium ethyl sulfate ($C_2H_5SO_4Na$), the alcohol and carbonyl functionalization products of sodium ethyl sulfate can be detected by the DART ionization source (Kwong et al., 2018). If these small organosulfates are formed in a significant amount during the oxidation of methyltetrol sulfate, the DART ionization technique will likely be able to detect them. We acknowledge that the detection limits and possible matrix effects are not yet well understood. Further studies on the sensitivity of DART-MS to smaller organosulfates under different conditions are warranted."

Comment #4

Page 7, lines 1–2 and elsewhere: Why wouldn't compounds that evaporate also be detected by DART, since the method for analyzing the particles involves first evaporating them at high temperature?

Author Response:

As mentioned in the experimental section, the volatile fragmentation products or gas-phase species were removed by an activated charcoal denuder before entering the heater as well as ionization region, leaving only the particle-phase products (see Page 3, Line 22). We have clarified this point in the revised manuscript.

Page 3, Line 22, "An annular Carulite catalyst denuder and an activated charcoal denuder were used to remove ozone and gas-phase species from the aerosol stream leaving the reactor, respectively. As a result, only particle-phase products are detected. A fraction of the aerosol stream was sampled by a scanning mobility particle sizer (SMPS, TSI, CPC Model 3775, Classifier Model 3081) to measure the aerosol size and number distribution. The surface-weighted diameter of the aerosols was measured to be 225.9 ± 1.4 nm before oxidation. The remaining flow was then directed into a stainless steel tube heater at 380–400°C, where the temperature and aerosol residence time in the heater were sufficient to completely vaporize the aerosols."

Technical Comments

Page 3, line 15: Should be "chromatograph".

Author Response:

We have revised the sentence.

Page 3, Line 15, "By measuring the decay of hexane using a gas chromatograph coupled with a flame ionization detector, the OH exposure, which is an integral of gas-phase OH radical concentration and reaction time, can be calculated (Smith et al., 2009):"

Reply to Interactive comment on "Heterogeneous OH Oxidation of Isoprene Epoxydiol-Derived Organosulfates: Kinetics, Chemistry and Formation of Inorganic Sulfate" by Hoi Ki Lam et al.

Anonymous Referee #3

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-989-RC1, 2018.

This manuscript describes the OH oxidation of small organosulfates derived from atmospheric oxidation of isoprene. Using advanced mass spectrometry of aerosol particles generated in an aerosol flow reactor, it is shown that loss of 3-methyltetrol sulfate ester is slow, with a lifetime for oxidation of more than 2 weeks under likely atmospheric conditions. This suggests that other loss processes (e.g. deposition) may be the main atmospheric loss process for similar organosulfate esters. Lack of detection of smaller oxidation products suggests formation of volatile products upon oxidation. These results are consistent with relatively high observed levels of organosulfates in atmospheric aerosol. This work is a solid contribution to the field, and I recommend this manuscript for publication pending minor revisions.

We would like to sincerely thank the reviewer for his/her thoughtful comments and suggestions. Please see our responses to reviewer's comments and suggestions below.

Comment #1

The experimental setup and data are fairly straightforward, generally giving clear, direct support of the key conclusion of a long atmospheric lifetime for small, oxidized organosulfates, but the detailed and long discussion of mechanistic details is not warranted. Without detection, in either gas or aerosol phase, of any reaction products other than bisulfate, the mechanistic discussion is largely speculative. Nearly all of this discussion should be removed. All reaction schemes presented should be moved to supplementary material and the mechanistic discussion must be reduced significantly. You cannot make such strong claims about a mechanism in which you more or less only observe loss of product with inability to detect products. Table 1 is the crucial result of this paper, not the speculation about the mechanism for oxidation.

Author Response:

We agree with the reviewer's comment. In the revised manuscript, we have reduced the mechanistic discussion and moved the detailed discussion and reaction schemes to the supplementary material. We also address that the reaction pathways (Schemes S1-S5) are tentatively proposed based on the observed aerosol-phase products detected by the DART. To better understand the reaction pathways, more studies are needed to characterize and quantify the reaction products in both aerosol and gas phases with different analytical techniques in order to cross check the aerosol composition data obtained by DART and verify the proposed reaction pathways in this work.

Page 5, Line 20,

" **3.3 Proposed Reaction Mechanisms**

Based on the aerosol mass spectra and well-known aerosol-phase reactions previously reported in the literature (George and Abbatt, 2010; Kroll et al., 2015), we tentatively propose reaction mechanisms for the heterogeneous OH oxidation of 3-methyltetrol sulfate ester. The reaction schemes proposed can be found in the supplementary materials (Schemes S1-S5). Briefly, potassium methyltetrol sulfate ester likely dissociates and exists in its ionic form in the droplets.

In the first oxidation step, the OH radical abstracts a hydrogen atom to form an alkyl radical which quickly reacts with oxygen to form a peroxy radical. We propose that the formation of alkoxy radical may be favored over the Russell mechanism (Russell, 1957) and Bennett–Summers reactions (Bennett and Summers, 1974) as functionalization products were not detected. Alkoxy radicals, once formed, may tend to undergo fragmentation due to the presence of vicinal hydroxyl groups, which lower the activation energy required for the decomposition of the alkoxy radicals (Cheng et al., 2015; Wiegel et al., 2015; Jimenez et al., 2009; Peeters et al., 2004; Vereecken and Peeters, 2009).

Formation of HSO_4^-. Sulfate radical anion ($SO_4^{\bullet-}$) can be formed through the decomposition of the alkoxy radical and is a strong oxidant in aqueous phase (Neta et al., 1988; Clifton and Huie, 1989; Padmaja et al., 1993). $SO_4^{\bullet-}$ can abstract a hydrogen atom from a neighboring organic molecule (e.g. unreacted 3-methyltetrol sulfate ester) to form HSO_4^- (R1) or react with particle-phase water to yield a HSO_4^- and an OH radical (R2) (Tang et al., 1988) as illustrated below. It is noted that $SO_4^{\bullet-}$ or OH radical recycled from R2 can react with 3-methyltetrol sulfate ester, contributing to the secondary chain reactions.

$$\mathrm{C_5H_{11}O_7}S^- + \mathrm{SO_4}^{\bullet-} \rightarrow \mathrm{C_5H_{10}O_7}S^{\bullet-} + \mathrm{HSO_4}^- \qquad (R1)$$

$$\mathrm{SO_4}^{\bullet-} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH}^{\bullet} + \mathrm{HSO_4}^- \qquad (R2)$$

Since 3-methyltetrol sulfate ester is unlikely to hydrolyze (Darer et al., 2011), the formation of the HSO_4^- upon OH oxidation could be best explained by the formation and subsequent reactions of $SO_4^{\bullet-}$.

Based on the proposed reaction mechanisms, the decomposition of alkoxy radicals can lead to formation fragmentation products (without sulfate group) and smaller organosulfates. We acknowledge that the ionization efficiency and detection limit of the reaction products are not fully understood. The absence of the potential products might attribute to the DART ionization and detection issues. More work is needed to investigate the formation and abundance of the reaction products formed in the aerosol and gas phases upon oxidation in order to better understand the reaction pathways. It is also noted that the formation of second or higher generation products are possible due to the high OH concentrations used in this study. While the potential secondary or higher generation products have not detected possibly due to their low concentrations and/or ionization issues, for clarify, the formation and oxidation of second or higher generation products are not further discussed."

Comment #2

You must comment on the potential for side-reactions, such as oxidation of second-generation products, due to the high OH levels used in this study.

Author Response:

We agree with the reviewer that first generation products can be further oxidized to form second or higher generation products due to the high OH levels in this study. However, the potential secondary or higher generation products have not detected possibly due to their low concentration and/or ionization efficiency. For clarity, the formation and oxidation of second or higher generation products are addressed but will not be discussed in details.

Page 6, Line 9, "It is also noted that the formation of second or higher generation products are possible due to the high OH concentrations used in this study. While the potential secondary or higher generation products have not detected possibly due to their low concentrations and/or ionization issues, for clarity, the formation and oxidation of second or higher generation products are not further discussed."

Comment #3

Supplementary materials must include a figure showing time dependent variables during an experiment including: aerosol size distributions, hexane concentration, and product signal. This may be nearly a step function, but it should be clearly shown that your system clearly responds to initiation of oxidation.

Author Response:

We would like to note that oxidation experiments were carried out in a flow tube reactor. We have measured the composition and size of the aerosols leaving the reactor before and after OH oxidation with a fixed reaction time (aerosol residence time is about 1.5 minutes in this study. Hence, the time dependent data (e.g. the time evolved data of aerosol size distributions and product signal) are not available in our study.

Comments #4

It should be noted that volatile products formed in the aerosol used here might remain in other aerosol if the Henry's law constant changes dramatically with composition, particularly if the volatile products are highly reactive with other types of aerosol species not present in your study (e.g. reactive nitrogen species). Comment on precedents available in published literature.

Author Response:

We agree with the reviewer that based on the proposed reaction mechanisms, volatile fragmentation products likely contain polar functional groups. They might partition back to the aerosols, for instance aqueous droplets because of their high water solubilities or Henry's law constants. Additionally, these fragmentation products could be reactively uptaken by the aerosols which contain reactive nitrogen or oxygen species through reactions. We have added this information in the revised manuscript.

Page 6, Line 29, "It is also noted that volatile fragmentation products likely contain polar functional groups. They may partition back to the aerosols, for instance aqueous droplets because of their high water solubilities or Henry's law constants. Additionally, they could be reactively uptaken by aerosols which contain reactive nitrogen or oxygen species through reactions."

Comments #5

Due to the open ionization region, is it possible that you lose volatile products as a result of detection method? This would mean that non-detection of products might be caused by the method of detection rather than evaporation under reasonable atmospheric conditions.

The non-detection of products (particularly from functionalization) using DART would be good information to add to the abstract.

Author Response:

As mentioned in the experimental section, the volatile fragmentation products or gas-phase species were removed by an activated charcoal denuder before entering the heater as well as ionization region, leaving only the particle-phase products (see Page 2 Line 22). We have clarified this point.

Page 3, Line 22, "An annular Carulite catalyst denuder and an activated charcoal denuder were used to remove ozone and gas-phase species from the aerosol stream leaving the reactor, respectively. As a result, only particle-phase products are detected. A fraction of the aerosol stream was sampled by a scanning mobility particle sizer (SMPS, TSI, CPC Model 3775, Classifier Model 3081) to measure the aerosol size and number distribution. The surface-weighted diameter of the aerosols was measured to be 225.9 ± 1.4 nm before oxidation. The remaining flow was then directed into a stainless steel tube heater at 380–400°C, where the temperature and aerosol residence time in the heater were sufficient to completely vaporize the aerosols."

Comments #6

Section 3.3 This should be reduced to a single paragraph that only mentions the proposed mechanism and does not go into details concerning issues such as the sterics of the reaction intermediates.

Author Response:

The reviewer has raised the same concern in **Comment #1.** We agree with the reviewer's comment. In the revised manuscript, we have reduced mechanistic discussion and moved the reaction schemes to the supplementary materials. We also address that the reaction pathways (Schemes S1-S5) are tentatively proposed based on the observed products detected by the DART. Please see our response to **Comment #1**. We have also removed the content about the steric effects on the formation of reaction products from the Abstract.

Comments #7

Page 2, Line 2 Change to read ", the largest atmospheric source"

Author Response:

We have revised the sentence in the manuscript.

Page 2, Line 2, "Isoprene (2-methyl-1,3-butadiene, C_5H_8), emitted from terrestrial vegetation to the atmosphere, is the largest atmospheric source of non-methane volatile organic compounds."

Comments #8

Page 4, Line 6, Change to read "The hygroscpocity"

Author Response:

We have revised the sentence in the manuscript.

Page 4, Line 5, "The hygroscopicity of potassium 3-methyltetrol sulfate ester aerosols has not been experimentally determined."

Comments #9

Page 7, Line 9, Change to read "stable over its atmospheric lifetime."

Author Response:

We have revised the sentences in the manuscript.

Page 6, Line 19, “3-methyltetrol sulfate ester is potentially chemically stable over its atmospheric lifetime.”

Comments #10

7,12-13 Note that this is only a likely mechanism.

In the revised manuscript, we have reduced the mechanistic discussion and do not go into detailed reaction pathways such as the steric effects of functional groups on the formation of the reaction intermediates. We have removed the sentences in the revised manuscript.

Comments #11

Figure 2 Y-axis should note m/z.

Author Response:

Figure 2 illustrates the change in ion intensity detected as a function of OH exposure while *m/z* refers to the mass-to-charge-ratio of ions detected. We have modified the caption of Figure 2.

Figure 2, “The evolution of the ion intensity of bisulfate ion (HSO_4^-) as a function of OH exposure during the heterogeneous OH oxidation of potassium 3-methyltetrol sulfate ester at 70.8% RH.”

Comments #12

Figure 3 Y-axis should note m/z.

Author Response:

Figure 3 illustrates the parent decay, which is the ion signal of 3-methyltetrol sulfate ester at a given OH exposure divided by the ion signal of 3-methyltetrol sulfate ester before oxidation, as a function of OH exposure. Hence, there would be no unit for the parent decay.

Comments #13

Scheme 5. Only 1 pathway is shown, text seems to mention more than one.

Author Response:

Scheme S5 shows the proposed reaction pathway of methyl sulfate anion decomposing into sulfate radical anion, as an extension of both Schemes S1 and S2 (as noted in Schemes S1 and S2).