Reply to Anonymous Referee #2

We thank the Referee for their insightful comments on our manuscript. Here, we provide point-to-point response to all the comments. For clarity, the Referee's comments are reproduced in blue color text, authors' replies are in black color and modifications to the manuscript are in red color text.

Manuscript review " Atmospheric fate of organosulfates through gas-phase and aqueous-phase reaction with hydroxyl radicals: implications in inorganic sulfate formation" for EGUSPHERE.

In this manuscript, the authors report on the oxidation of organosulfates, specifically methyl sulfate and glycolic acid sulfate, by OH radicals in the gas phase and in the aqueous phase. The investigations were carried out using DFT calculations with GAUSSIAN, whereby in addition to the electronic structure and thermochemistry, the reaction kinetics of the oxidation reaction and the respective intermediates were also calculated.

The questions and comments on the manuscript are listed below.

In the abstract, the authors should make it clear that they have carried out the DFT calculations.

The second sentence in the Abstract was revised as follows to highlight the use of DFT calculations in this study.
This study uses quantum chemical calculations based on density functional theory to explore the reactions of some prevalent organosulfates, specifically methyl sulfate and glycolic acid sulfate, with hydroxyl radicals (HO•) in the gas-phase and aqueous-phase.

Please check your manuscript for colloquial language, e.g. in line 17 "unfriendly". A molecule does not have these attributes.

In our reply to another comment of the Referee, we conducted more calculations for glycolic acid and based on the results, the sentences at lines 17-19 were deleted.

Line 16: How likely is the reaction of the alkyl radical with ozone (O3) in the presence of oxygen (O2), if we assume that an ozone concentration in the range of 10 to 100 ppb compared to 20% oxygen in the atmosphere?

It is obvious that the reaction of alkyl radicals with O_3 in the presence of O_2 is generally not highly favorable compared to both the reaction with O_2 and the O_3 reaction with other possible radicals. Concisely, under normal atmospheric conditions, alkyl radicals will overwhelmingly react with O_2 to form peroxy radicals rather than reacting with O_3. The later reaction may have some impact, though still limited, under elevated O_3 conditions such as in urban areas, exclusively. Owing to this argument, the related sentence in the revised manuscript has been modified to highlight the preference for alkyl radicals to react primarily with O_2 rather than O_3.

Line 15

Results indicate that all reactions initiate with hydrogen abstraction by HO• from CH_3- in methyl sulfate and from -CH_2- and -COOH in glycolic acid sulfate, followed by the further reaction of the resulting radicals through self-decomposition interaction with O_2 and, possibly, O_3.

Line 20: Why only the rate constant of OH radicals with methyl sulfonate is shown?

For comparison purposes, we initially reported only the rate constant value of the OH reaction with methyl sulfate for which the experimental data is available. In the revised manuscript, we also report the rate constant for the OH reaction with glycolic acid sulfate.

The sentence at line 20 is revised to:

Rate constants of 1.14×10^{-13} cm^3 $molecule^{-1}$ s^{-1} and 6.17×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298.15 K were determined for the gas-phase reaction of methyl sulfate and glycolic acid sulfate, respectively. The former value is consistent with a previous experimental report.

The following sentence is added at line 351

We also report a rate bimolecular rate constant of 6.17×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the gas-phase reaction of HO• reaction with glycolic acid at 298.15 K.

Why does the reader need the text from line 101 to line 113? Because none of the diffusion parameters are discussed later in the manuscript text.

This part of the manuscript provides details for calculating the bimolecular rate constants for aqueous-phase reactions. Numerical details for diffusion parameters are now provided in the revised Supplement and the following text is added in the revised manuscript at line 113:

All numerical values for radii, diffusion coefficients of reactants and the steady-state Smoluchowski rate constants are provided in Tables S1 and S2 in the Supplement.

Line 134: How would the unimolecular rate constant develop if the number of water molecules corresponds to the number of water molecules in the hydration shell in the aqueous phase?

From our calculations, the studied organosulfates would rarely bind with more than two water molecules in the gas-phase at ambient conditions. For methyl sulfate for example, we have reported unimolecular rate constants of 1.15×10^{8} s^{-1}, 7.89×10^{7} s^{-1} and 1.59×10^{10} s^{-1}, for the unhydrated, monohydrated and dehydrated reactions, respectively. These values exhibit a non-uniform trend, with a moderate decrease from the unhydrated reaction to the monohydrated reaction, followed by an increase from the monohydrated reaction to the dehydrated reaction. Although the possibility of the number of binding water molecules in the gas-phase reaching the number of water molecules in the hydration shell in the aqueous-phase is highly improbable under relevant atmospheric temperature, pressure and humidity, if such scenario would occur, then the organosulfate would be deprotonated and its reaction would be comparable to the reaction in the aqueous-phase. In this regard, the aqueous-phase reaction was fully explored in **Section 3.1.2.**

Line 134: “Unimolecular rates constants” should read “Unimolecular rate constants”

This has been corrected.

Line 144: Could the authors show the rate constants instead of the lifetimes?

The lifetimes have been replaced by rate constants, and the related text at lines 144-148 has been further revised as follows:

Line 144

The stability of $H_2C•-O-SO_3H\cdots(H_2O)_{n+1}$, examined relative to decomposition through the reverse reaction back to the $HO•\cdots CH_3-O-SO_3H\cdots(H_2O)_n$ complex, reveals barriers heights of 28.64, 24.92 and 24.55 kcal mol^{-1} for n = 0, 1, and 2, corresponding to unimolecular rate constants of 6.16×10^{-9} s^{-1}, 3.30×10^{-6} s^{-1} and 6.14×10^{-6} s^{-1}, respectively. These low-rate constants indicate that once formed, $H_2C•-O-SO_3H\cdots(H_2O)_{n+1}$ would not react back to form initial reactants before possible collision with atmospheric oxidants have occurred.

Beside the uni-molecular decay rate, what would be the rate constant for the alkyl radical - alkyl radical recombination reaction in the absence of any other reaction partner? That would be interesting to know?

We assessed the radical-radical interaction both for $H_2C•-O-SO_3H$ and HOOC-CH•-O-SO_3H, and found that the recombination occurs through C-C bond formation via a barrierless process. Respective resulting products are shown in **Figure R1** below. This recombination can be assumed to occur at collision rate, and would be the most likely fate of $H_2C•-O-SO_3H$ and HOOC-CH•-O-SO_3H in the absence of other reaction partners such as O_2, O_3, or NO_2. Although the direct relevance of the resulting products is not clearly identified, their fate would mostly depend on reactions initiated by hydrogen abstraction from -CH_2- group for methylene sulfate and -CH- and/or -COOH groups for the radical resulting from glycolic acid sulfate.

The following text is added in the revised manuscript to highlight the outcome of radical-radical recombination at Line 222:

Considering the recombination of two $H_2C•-O-SO_3H$ molecules as another likely fate of $H_2C•-O-SO_3H$ the absence of other reaction partners such as O_2, O_3, or NO_2 besides self-decay, our preliminary calculations indicate that this recombination would occur fast and would proceed through C-C bond formation via a barrierless process. However, the relevance of the resulting product is not clearly established and its fate may mostly depend on reactions initiated by a hydrogen abstraction from the -CH_2- group.

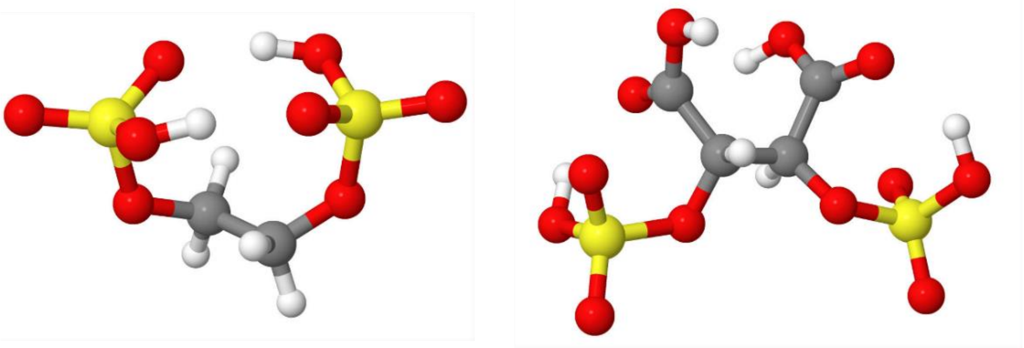

Figure R1: Alkyl radical recombination products from methyl sulfate (left) and glycolic acid sulfate (right). The sulfur atom is in yellow, the oxygen atom in red, the carbon atom is in grey and the hydrogen atom is in white.

Line 152: How meaningful is the investigation of the reaction of the alkyl radical with ozone and NO2 in term of their solubility in water? Considering the self-decay reaction as well as the reaction with O2.

NO_2 dissolves effectively in water and it is known that gaseous NO_2 reacts with water to produce nitric acid, which is highly soluble in water (Ford and Miranda, 2020; Tan and Piri, 2013; Lee and Schwartz, 1981; England and Corcoran, 1974). In this regard, to explore the alkyl radical reaction with NO_2 in aqueous-phase would be equivalent to explicitly assessing the reaction with NO_3^-. This reaction was not investigated in the aqueous-phase in the present study. Considering O_3, it is highly soluble in water and this solubility plays an important role in various processes although its stability can be readily affected by various factors including ozone concentration, pH and ultraviolet light (Lovato et al., 2009). Considering its behavior as a prospective oxidant, ozone can react via a direct reaction pathway involving molecular ozone or by an indirect route involving various highly reactive intermediates that arise from its decomposition (Buehler et al., 1984; Buhler et al., 1984; Staehelin et al., 1984; Staehelin and Hoigne, 1982). Although we did not focus on reactions from indirect routes involving reactive intermediates that arise from O_3 decomposition, based on the above, the reaction of the alkyl radical with molecular O_3 is a likely process that would be of relative significance besides self-decay reaction and the reaction with O_2.

The sentence at lines 238-239 is modified to the following in the revised manuscript to justify the relevance of the reaction of alkyl radicals with O_3 and O_3.

While NO_2 dissolves effectively in water and is known to react with molecular water to produce nitric acid which is highly soluble in water (Ford and Miranda, 2020; Tan and Piri, 2013; Lee and Schwartz, 1981; England and Corcoran, 1974), the stability of O_3 solubility in water is readily affected by various factors including ozone concentration, pH and ultraviolet light (Lovato et al., 2009). Depending on environmental conditions, ozone can react via a direct reaction pathway involving molecular ozone or by an indirect route involving reactive intermediates that arise from its decomposition (Buehler et al., 1984; Buhler et al., 1984; Staehelin et al., 1984; Staehelin and Hoigne, 1982). Moreover, O_3 is known to be 13 times more soluble in water than O_2 (Seinfeld and Pandis, 1998). Hence, besides the self-decay reaction, the fate of $H_2C\bullet\text{-}O\text{-}SO_3^-$ was examined via reactions with O_2 and O_3:

Figure 1: How reliable are the decimal places in the DFT calculations?

It is generally adopted in the quantum chemistry community that energy values from DFT calculations can be truncated to two decimal places.

Line 170: This statement depends on the ambient conditions, e.g. the concentration of organic substances in an aerosol particle. This is because the SO3.- could also react with organic substances. What are the intermediate steps in the formation of SO42- from SO3.-? Is there a difference in the gas phase or in the aqueous phase?

It is clear that the intermediate steps in sulfate formation from $SO_3^{\bullet-}$ in the gas-phase are different from those in the aqueous-phase. In the aqueous-phase, the mechanism of $SO_3^{\bullet-}$ conversion is relatively understood, with the major fate being its reaction with organic compounds to form sulfonates (Lv et al., 2021; Lv et al., 2024; Lai et al., 2024) while the gas-phase mechanism is clearly established. Several experimental studies showed that $SO_3^{\bullet-}$ would quickly hydrate in the gas-phase to form $SO_3^{\bullet-}\cdots(H_2O)_n$ cluster wherein the oxidation to sulfuric acid can occur according to the following reactions (Enghoff and Svensmark, 2008; Bork et al., 2013; Fehsenfeld and Ferguson, 1974; Svensmark et al., 2007; Tsona and Du, 2019).

$$SO_3{\bullet}^- + nH_2O \rightarrow SO_3{\bullet}^-\cdots(H_2O)_n\,, \qquad \text{(R-R1)}$$

$$SO_3{\bullet}^-\cdots(H_2O)_n \rightarrow H_2SO_4\cdots(H_2O)_{n-1} + e\,, \qquad \text{(R-R2)}$$

It was demonstrated from these studies that the free electron is involved in the stabilisation and formation of a cluster with at least one sulfuric acid molecule, wherein it acts as catalyst. These reactions are ion reactions with rate constants that are close to the time-scales of gas kinetic collision.

In the revised manuscript, the related text is modified to the following, to reinforce the understanding of the fate of $SO_3^{\bullet-}$ in the gas-phase

Line 170
Several experimental and theoretical studies showed that $SO_3^{\bullet-}$ would quickly hydrate in the gas-phase to form $SO_3^{\bullet-}\cdots(H_2O)_n$ cluster wherein the oxidation to sulfuric acid occurs in a mechanism stabilized and catalyzed by a free electron (Enghoff and Svensmark, 2008; Bork et al., 2013; Fehsenfeld and Ferguson, 1974; Svensmark et al., 2007; Tsona and Du, 2019). Considering this outcome for $SO_3^{\bullet-}$ in the gas-phase, H_2CO and inorganic sulfate are expected products of the gas-phase reaction of methyl sulfate with HO• at ambient conditions.

Line 234: Do the authors have an explanation, why the obtained rate constant is approx. an order of magnitude lower compared to the measured value by Gweme and Styler, 2024 (doi: 10.1021/acs.jpca.4c02877) and the references therein?

While environmental factors such as pH, temperature and ionic strength can effectively alter the rate constants of aqueous-phase reactions from experimental studies, it is generally accepted that errors of 2-3 kcal mol^{-1} in reaction energies may arise from DFT calculations (Bogojeski et al., 2020). These errors can induce up to 10^2 increase or decrease in the reaction rate constants. Hence, it is likely that the difference between rate constants obtained from our calculations and experimental values from Gweme and Styler (Gweme and Styler, 2024) arise from computational error besides possible experimental errors. The following text is added to the revised manuscript to justify the difference between the rate constant from our calculations and the experimental data.

Line 234

This value is about 13 times lower than a previous experimental value (Gweme and Styler, 2024), and the difference can be attributed both to computational errors and environmental factors.

Line 278: What would be the reaction barrier of the decomposition of the alkoxy radical to SO42- and formaldehyde?

The energy barrier of this decomposition is 7.92 kcal mol^{-1}. The sentence dealing with this decomposition is updated in the revised manuscript to include the reaction barrier.

Line 278

The alkoxy radical •O-CH$_2$-O-SO$_3^-$ can readily decompose to form HSO$_4^-$ and HCO•, by overcoming a barrier of 7.92 kcal mol^{-1} and as explained above and exemplified in **Figure 5**, its formation from H$_2$C•-O-SO$_3^-$ reaction with O$_2$ is less thermodynamically favorable than with O$_3$, despite the overall rate of the former can be higher than that of the latter due to the high concentration of O$_2$.

What is the authors' opinion regarding the decomposition of the peroxy radical similar to the decomposition of alkyl and alkoxyl radicals? Would that be possible?

Believed to be key intermediates in the oxidation of organic compounds, several mechanisms for the decomposition of peroxyl radicals are presented in the literature (Goldman et al., 2021; Salo et al., 2022; Tomaz et al., 2021). These radicals may undergo termination reactions or further autoxidation processes, which can yield a plethora of multifunctional products with low or extremely low saturation vapor pressures. In this study, we specifically investigated the pathway of two peroxy radicals recombining to for a tetroxide intermediate that further decomposes to form alkoxyl radicals.

To through more light on the outcome of peroxyl radicals, we added the following text in the revised manuscript.

Line 222

The chemistry of peroxyl radicals has been the subject of several experimental and theoretical studies. It is widely accepted that the peroxyl radical would predominantly decompose to form alkoxyl radicals or alcohols along with carbonyl compounds through tetroxide intermediates (Russell, 1957). However, although the end products from this decomposition have been verified experimentally, the mechanisms have often been deemed unlikely due to inconsistency between thermodynamic experiments and computational studies (Nangia and Benson, 1980; Zhang et al., 2012; Liang et al., 2011). Moreover, the effort to elucidate alcohols and carbonyl compounds formation from the decomposition of the tetroxide in a previous study could not be achieved due to the impossibility to determine the corresponding transition states (Ghigo et al., 2003), while alkoxyl radical formation was observed to simply correspond to the dissociation of the tetroxide. A most recent theoretical study specifically focusing on the decomposition pathways of the tetroxide intermediate indicated that although substantial uncertainties may exist in their computed energetics, alkoxyl radicals are likely primary products from atmospherically relevant peroxyl radicals (Salo et al., 2022).

Line 291: Since the pKa of methyl sulfate is less than zero on the pH scale, and radicals generally have a lower pKa than the parent compound, how likely the presence of the distinct radical species is to be expect?

Lower pKa values are indicative of higher reactivities, which means that the radicals formed from hydrogen abstraction from organosulfates are expected to be more reactive that the organosulfates themselves. We have examined the possibilities of radicals conversions through many processes including self-decay, radical-radical combination as well as through reactions with O_2 and O_3, and found that radicals from both studied organosulfates react very fast with O_2 to form peroxyl radicals. Moreover, given the high abundance of atmospheric O_2, it is likely that reactions with O_2 will dominate the fate of radicals resulting from hydrogen abstraction from organosulfates. The chemistry of resulting peroxyl radicals has been carefully assessed in the revised manuscript.

Line 294: Why don't the authors give rate constants and lifetimes in the manuscript that are comparable to the discussion in the section on methyl sulfate? Why is there no discussion of the reactivity of similar compounds (glycolic acid) with OH to at least give an order of magnitude for the reactivity for glycolic acid sulfate?

We have now included some literature values of the rate constants both for the reactions of methyl sulfate and glycolic acid sulfate for comparison.

Line 312: How likely would be the decomposition of the alkyl radical to COOH and CHO-SO3-? What would be the energy barrier and the decomposition rate?

The configurational scans performed on $HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3^-$ along the C-C coordinate showed that the decomposition along the C-C bond could not be achieved, probably because the targeted decomposition products (COOH and $HC\text{-}O\text{-}SO_3^-$) are not chemically stable. We found that the C-C bond could elongate from 1.45 Å to more than 3.40 Å, yet the energy of the system kept increasing. We conclude that this decomposition is not a likely fate for $HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3^-$.

Line 317: Why the fate of SO3.- is discussed again?

The statement here was to highlight that one of the ultimate products of HO•–initiated oxidation of glycolic acid sulfate would be inorganic sulfate through $SO_3^{\bullet-}$ intermediate.

Line 334: Could the authors provide information on the contribution of the three different decomposition pathways of tetroxide? It is known from the literature that about 10-20% of tetroxide in the aqueous phase is decomposed by the formation of molecular singlet oxygen and alkoxy radicals, depending on the parent compound. What would be the contribution of the H2O2 + RCRO (ketone) formation pathway and what would be the contribution of the RCROH (alcohol), RCRO (ketone) and O2 formation pathways? What would be the influence of the organic moiety of the molecules discussed here?

The chemistry of peroxyl radicals has been the subject of thorough investigation in many previous studies (Russell, 1957; Salo et al., 2022; Berndt et al., 2018; Tomaz et al., 2021; Goldman et al., 2021). Although no main channel exists for the reactions of peroxyl radicals, it has been established that their most relevant reactions can be categorized into propagating and terminating reactions. Earliest studies of this radical have led to the conclusion that the majority of peroxyl radical self- and cross-reactions either form alkoxyl radicals or alcohols along with carbonyl compounds through tetroxide intermediates according to the following processes (Russell, 1957; Lightfoot et al., 1992):

$$\text{R-OO}\bullet + \text{R'-OO}\bullet \rightarrow \text{R-OOOO-R'} \rightarrow \text{R}_{\bullet\text{H}}\text{=O} + \text{R'-OH} + {}^3\text{O}_2\,, \qquad \text{(R-R3)}$$

$$\rightarrow \text{R-OO-R'} + {}^3\text{O}_2\,, \qquad \text{(R-R4)}$$

$$\rightarrow \text{R-O}\bullet + \text{R'-O}\bullet + {}^3\text{O}_2\,. \qquad \text{(R-R5)}$$

However, although the end products from the first study of this tetroxide decomposition have been verified experimentally, the mechanism itself has been deemed unlikely as it is inconsistent with thermodynamic experiments and computational studies (Nangia and Benson, 1980; Zhang et al., 2012; Liang et al., 2011).

The effort to elucidate the decomposition of the tetroxide into alcohol and carbonyl compound (**reaction (R-R3)**) was prevented by the impossibility to find the corresponding transition states (Ghigo et al., 2003), while alkoxyl radical formation (**reaction (R-R5)**) simply corresponds to the dissociation of the tetroxide. Furthermore, a most recent theoretical study specifically focusing on the decomposition pathways of the tetroxide intermediate indicated that although substantial uncertainties may exist in the computed energetics, alkoxyl radicals may primarily form from atmospherically relevant primary and secondary peroxyl radicals (Salo et al., 2022). Salo et al. also examined the reactions of peroxyl radicals with different organic moiety and found that although different organic moieties do not alter the nature of expected products, the barrier heights for the decomposition are affected both by the nature of the substituent and the carbon chain length (Salo et al., 2022).

We equally faced difficulties to locate the transition states in the formation of alcohol + carbonyl products, on the singlet surface as well as on the triplet surface, and our presented results are based on alkoxyl radical formation pathway, exclusively.

To clarify this, the sentence at line 222 is modified in the revised manuscript to the following:

The chemistry of peroxyl radicals has been the subject of several experimental and theoretical studies. It is widely accepted that the peroxyl radical would predominantly decompose to form alkoxyl radicals or alcohols along with carbonyl compounds through tetroxide intermediates (Russell, 1957). However, although the end products from this decomposition have been verified experimentally, the mechanisms have often been deemed unlikely due to inconsistency between thermodynamic experiments and computational studies (Nangia and Benson, 1980; Zhang et al., 2012; Liang et al., 2011). Moreover, the effort to elucidate alcohols and carbonyl compounds formation from the decomposition of the tetroxide in a previous study could not be achieved due to the impossibility to determine the corresponding transition states (Ghigo et al., 2003), while alkoxyl radical formation was observed to simply correspond to the dissociation of the tetroxide. A most recent theoretical study specifically focusing on the decomposition pathways of the tetroxide intermediate indicated that although substantial uncertainties may exist in their computed energetics, alkoxyl radicals are likely primary products from atmospherically relevant peroxyl radicals (Salo et al., 2022).

Line 277

Based on the above on the chemistry of peroxyl radicals, two molecules of $\bullet OO\text{-}CH_2\text{-}O\text{-}SO_3^-$ can combine to form a tetroxide, which can further decompose to generate $\bullet O\text{-}CH_2\text{-}O\text{-}SO_3^-$ by overcoming a Gibbs free energy barrier of 14.12 kcal mol^{-1} (see **Figure 5**).

The sentence at line 332 is modified to the following in the revised manuscript.

$HOOC\text{-}CH(OO\bullet)\text{-}O\text{-}SO_3^-$ can recombine with each other to form a tetroxide ($O_3^-S\text{-}O\text{-}CH(COOH)\text{-}OOOO\text{-}CH(COOH)\text{-}O\text{-}SO_3^-$) as shown in **Figure 6**. However, we found that contrary to the case of $\bullet OO\text{-}CH_2\text{-}O\text{-}SO_3^-$ where the tetroxide could readily decompose to form the $\bullet O\text{-}CH_2\text{-}O\text{-}SO_3^-$ radical in the singlet state, the fragmentation of $O_3^-S\text{-}O\text{-}CH(COOH)\text{-}OOOO\text{-}CH(COOH)\text{-}O\text{-}SO_3^-$ to form the alkoxyl radical $HOOC\text{-}CH(O)\bullet\text{-}O\text{-}SO_3^-$ occurred on the triplet state instead. The triplet electronic state was shown from a recent study to be favorable to the decomposition of tetroxides to alkoxyl radicals from some atmospherically relevant peroxyl radicals (Salo et al., 2022).

Line 338: The atmospheric implication appears to be somewhat incomplete with regard to the reaction of glycolic acid sulfate with respect to the rate constants.

We have added the rate constant for the reaction of glycolic acid sulfate in the revised manuscript.

Line 351

In the aqueous-phase, we determined rate constants of 7.87×10^6 $M^{-1}s^{-1}$ and 7.29×10^8 $M^{-1}s^{-1}$ for the reaction of methyl sulfate and glycolic acid sulfate, respectively.

Line 362: What do the authors mean with low reactivity of glycolic acid sulfate relative to methyl sulfate? The rate constant of glycolic acids with OH radicals was measured with k = 5x10^8 L mol-1 s-1 (Buxton et al., 1988). The rate constant of methyl sulfate with OH is in the range of 5x10^7 to 1x10^7 L mol-1s-1 (Gweme and Styler, 2024 (doi: 10.1021/acs.jpca.4c02877)). To what extent can the presence of the SO3 group deactivate the CH2 group of glycolic acid sulfate?

We have re-analyzed our findings based on previous results. As discussed in our reply to a previous comment of the Referee, we speculated that the difference between our reported rate constant for the HO• reaction with methyl sulfate may arise both from computational errors and environmental factors such as pH, temperature and ionic strength. It is generally accepted that DFT calculations can induce up to 2-3 kcal mol^{-1} errors in reaction energies can arise from DFT calculations (Bogojeski et al., 2020), which can induce up to two order of magnitude increase or decrease in reaction rate constants.

For glycolic acid, we determined a rate constant of 7.29×10^{8} M^{-1}s^{-1} in good agreement with the value measured by Buxton et al. (Buxton et al., 1988) and more than two orders of magnitude higher than the rate constant for the reaction of methyl sulfate. The following text is added to the revised manuscript to justify the difference between the rate constant from our calculations and the experimental data.

Line 234

This value is about 13 times lower than a previous experimental value (Gweme and Styler, 2024), and the difference can be attributed both to computational errors and environmental factors.

The sentence at line 304 is modified to include the bimolecular rate constant for the aqueous-phase reaction of glycolic acid sulfate.

A bimolecular rate constant of 7.29×10^{8} M^{-1}s^{-1} is determined for this reaction, in good agreement with the experimental report by Buxton et al. (Buxton et al., 1988).

The sentences at lines 362-365 are modified to:

Overall, the kinetics results show a moderate difference between the rate constants of HO• reactions with methyl sulfate and glycolic acid sulfate. The slightly high rate constant of the reaction of glycolic acid sulfate indicate the enhancing effect of the -COOH group in the hydrogen abstraction by HO•. Moreover, we found that the hydrogen abstraction from the -COOH group in glycolic acid sulfate leads to decarboxylation and eventually forms similar products as methyl sulfate. It can be inferred that for organosulfates with -COOH at β-position to the sulfate group, decarboxylation would be take place, leading to the formation of the corresponding alkyl sulfate radical. This highlights the potential role that chemical substitution on the carbon chain of organosulfates may play during their decomposition.

The sentence at lines 342-345 is updated to the following:

By investigating the decomposition mechanisms of two small atmospheric organosulfates (methyl sulfate and glycolic acid sulfate) by reaction with HO• radicals in this study, it was shown that the reaction of glycolic acid sulfate in the gas-phase is more kinetically favorable than that of methyl sulfate, which can be attributed to the effect of -COOH substitution that stabilizes the intermediate reactant complex from glycolic acid.

To summarise, taking all comments into account, I recommend the major revision of the manuscript. The topic itself is interesting and the manuscript has its merits, but in its current form is not sufficient.

We acknowledge all the valuable comments raised by the Referee. We have addressed all the comments, and we believe that our revised manuscript in its current state satisfactorily meets the standards of *Atmospheric Chemistry and Physics*.

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