Reply to Anonymous Referee #3

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.

Review of Tchinda et al for ACP

Tchinda and co-workers study the transformation of glycolic acid sulfate and methyl sulfate both in the gas phase and particle phase using quantum chemical methods. The aqueous phase is modelled using a polarizable continuum model. Up to two explicit water molecules are considered in both the gas phase and aqueous phase calculations. The structure and vibrational frequencies of the stationary points are calculated at the M062X/6-311+g(2df,2pd) level of theory and the single point energies are refined using accurate CCSD(T)-F12/cc-pVDZ-F12 calculations.

This is an interesting topic that shed some further light on the atmospheric fate of organosulfates. However, the presentation is rather messy, and the study appears incomplete. Overall, I do not feel like I got wiser on the fate of organosulfates in the atmosphere and I cannot recommend publication in its current form.

Major Comments

Not all competing pathways are studied. It seems like only some selected pathways were considered. Why were the COOH hydrogen abstraction not considered? Why was the dimer formation only considered for one of the systems, but not the others, ect?

Initially, we explored all hydrogen-abstraction possibilities and while those from CH_3- and -CH_2- favorably formed alkyl radicals whose further chemistry can be assessed, the abstraction from -COOH led to •OC(O)-CH_2-O-SO_3H radical that further decomposes to methylene sulfate radical (H_2C•-O-SO_3H) and CO_2. The chemistry of H_2C•-O-SO_3H radical was assessed in the section dealing with methyl sulfate. We observed that in the aqueous-phase, however, •OH acts as a bridge for hydrogen exchange between the carboxyl group and the sulfate group, making the hydrogen abstraction from -COOH not favorable in the aqueous-phase.

The following sentence is added in the Abstract, line 15
We found that the hydrogen abstraction from the -COOH group in glycolic acid sulfate could lead to decarboxylation and eventually form similar products as methyl sulfate.

The text at lines 295-300 have been modified to the following in the revised manuscript.
Hydrogen abstraction from glycolic acid sulfate could occur both from -CH_2- and -COOH groups according to the following reactions:

$$HOOC\text{-}CH_2\text{-}O\text{-}SO_3H + HO^\bullet \rightarrow H_2O + HOOC\text{-}CH^\bullet\text{-}O\text{-}SO_3H \,, \qquad (R9)$$

$HOOC-CH_2-O-SO_3H$ + HO• → H_2O + •OC(O)-CH_2-O-SO_3H . (R10)

The mechanism of reaction (R9) is similar to that of the hydrogen abstraction from methyl sulfate that forms an alkyl radical. Through this process, glycolic acid sulfate readily undergoes a hydrogen abstraction from the -CH_2- group by HO•, resulting in HOOC-CH•-O-SO_3H formation. The reactant complex in this process lies at 4.65 kcal mol^{-1} at 298.15 K and 1 atm, and the transition state for its conversion is located 2.13 kcal mol^{-1} above the reactant complex. We determined a bimolecular rate constant of the overall reaction is 6.17 $\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for this reaction at 298.15 K. This shows that hydrogen abstraction by •OH from glycolic acid sulfate is more favorable than from methyl sulfate, hereby highlighting the enhancing effect of the carboxyl substituent. The further chemistry of HOOC-CH•-O-SO_3H is examined through reactions with O_3 and O_2. Our calculations show that contrary to the reaction with H_2C•-O-SO_3H, O_3 hardly reacts with HOOC-CH•-O-SO_3H as the O_3···HOOC-CH•-O-SO_3H formation is highly endergonic at standard conditions. However, the reaction with O_2 is seen to be fast, proceeding through formation of the reactant complex that is readily converted to HOOC-CH(OO)•-O-SO_3H. The observed negative Gibbs free energy barrier (-9.02 kcal mol^{-1} below the reactant complex) in this conversion indicates that the formation of HOOC-CH(OO)•-O-SO_3H is almost instantaneous at standard conditions. Two molecules of HOOC-CH(OO)•-O-SO_3H develop into a tetroxide that then decomposes to HC(O)-O-SO_3H and HOOC-CH(O)•-O-SO_3H. The energetics of this reaction are provided in **Figure 6** and **Table S5**.

The abstraction from -COOH led to •OC(O)-CH_2-O-SO_3H (**reaction (R10)**) that further decomposes to methylene sulfate radical (H_2C•-O-SO_3H) and CO_2. The structures and energetics of all intermediate states of this reaction are given in **Figure S5** and **Table S6** in the Supplement. At the same level of theory, we determined a biomolecular rate constant of 3.86 $\times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, two orders of magnitude lower than the hydrogen abstraction from the -CH_2- group. This indicates hydrogen that abstraction from glycolic acid would follow two competitive pathways although the hydrogen abstraction from the -CH_2- group preferred. It can be inferred that for organosulfates with -COOH at β-position to the sulfate group, decarboxylation would be a possible outcome of their decomposition initiated by •OH. The chemistry of H_2C•-O-SO_3H was assessed in Section 3.1 above.

We further investigated the HO•-initiated reaction of glycolic acid sulfate in the aqueous-phase, where the deprotonated state, HOOC-CH_2-O-SO_3^-, is predominant.

Line 362

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.

Concerning the dimer formation from other systems, we previously focused on •OO-CH_2-O-SO_3^- and HOOC-CH(OO•)-O-SO_3^- (resulting from •OH-initiated oxidation of methyl sulfate and glycolic acid, respectively), exclusively, as we were unable to determine the transition states in the transformation of electrically neutral dimers, probably due to the effect of the complexed water. However, given that water is known to evaporate fast from gas-phase atmospheric species, we have re-considered the dimer formation without additional water and the results are now included in the revised manuscript.

The following text is added at Line 222

Contrary to the self-decomposition of H_2C•-O-SO_3H and reactions with NO_2 and O_3 that are favorable with H_2C•-O-SO_3H hydrates, we were unable to fully optimize the O_2 reaction with H_2C•-O-SO_3H hydrates but with the unhydrated system, instead. This led to exergonic formation of the •OO-CH_2-O-SO_3H peroxyl radical with 45.98 kcal mol^{-1} Gibbs free energy gain. 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). Following the above reasoning, our calculations indicate that two molecules of •OO-CH_2-O-SO_3H recombine to form a tetroxide that can further decompose to generate two alkoxyl radicals •O-CH_2-O-SO_3H clustered to molecular oxygen. Then, the two •O-CH_2-O-SO_3H radicals quickly interact with O_2 to form H_2O_2 and formic sulfuric anhydride (HC(O)-O-SO_3H) (**reaction (R5)**). The latter product has been identified to enhance new particle formation (An, 2024). Energetics and structures of all intermediates in this reaction are given in **Figure 3**.

Why are reactions with NO_2 and O_3 taken into account, but addition of O_2, which traditional tropospheric chemistry would dictate to be the most important, just neglected?

The fate of the radical (H_2C•-O-$SO_3H\cdots H_2O$) resulting from •OH reaction with the organosulfate was examined based on its estimated atmospheric lifetime relative to the self-decomposition process. As explained in the manuscript, the estimated atmospheric lifetimes based on our calculations indicated that H_2C•-O-SO_3H would live enough to experience collisions with most atmospheric oxidants (including O_2, O_3 and NO_2) before self-decomposition could occur. However, despite previous attempts to investigate O_2 reaction with H_2C•-O-$SO_3H\cdots H_2O$ failed, this system has been re-considered without additional water molecule. Our calculations indicate that H_2C•-O-

SO_3H would react fast with O_2 to form a peroxy radical (•OO-CH_2-O-SO_3H). Thereafter, two molecules of this radical would combine to form a tetroxide, which can further decompose to generate formic sulfuric anhydride (HOC-O-SO_3H). The following changes have been made in the revised manuscript to highlight the outcome of the O_2 + H_2C•-O-SO_3H reaction.

The sentence at line 19 is modified to the following:
The primary reaction products are inorganic sulfate, carbonyl compounds and formic sulfuric anhydride.

The sentence at Line 21 is modified to the following:
Additionally, while prior studies suggested O_2 as primary oxidant in the fragmentation of organosulfates, this study unveils O_3 as a complementary oxidant in the intermediate steps of this process.

The following is added at line 150:
Considering that water is known to evaporate fast from atmospheric species, H_2C•-O-SO_3H would readily react both in its unhydrated and its hydrated forms.

The following reaction is added at Line 155:
$H_2C{\bullet}\text{-O-}SO_3H\cdots(H_2O)_{n+1} + O_2 \rightarrow \rightarrow HC(O)\text{-O-}SO_3H$. (R5)

The following text is added at Line 222
Contrary to the self-decomposition of H_2C•-O-SO_3H and reactions with NO_2 and O_3 that are favorable with H_2C•-O-SO_3H hydrates, we were unable to fully optimize the O_2 reaction with H_2C•-O-SO_3H hydrates but with the unhydrated system, instead. This led to exergonic formation of the •OO-CH_2-O-SO_3H peroxyl radical with 45.98 kcal mol^{-1} Gibbs free energy gain. 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). Following the above reasoning, our calculations indicate that two molecules of •OO-CH_2-O-SO_3H recombine to form a tetroxide that can further decompose to generate two alkoxyl radicals •O-CH_2-O-SO_3H clustered to molecular oxygen. Then, the two •O-CH_2-O-SO_3H radicals quickly interact with O_2 to form H_2O_2 and formic sulfuric anhydride (HC(O)-O-SO_3H) (**reaction (R5)**). The latter product has been identified to enhance new particle formation (An, 2024). Energetics and structures of all intermediates in this reaction are given in **Figure 3**.

Table 1 was revised to include the energetics of the reaction of the alkyl radical with O_2.

Table 1: Electronic energy changes (ΔE) and Gibbs free energy changes (ΔG at 298.15 K and 1 atm) for all intermediate species in the reaction of methyl sulfate with HO$^•$ radicals. Energy units are kcal mol^{-1}. "RC" stands for intermediate reactant complex, "TS" stands for transition state, "PD" stands for product, "nw" stands for the number of added water molecules to the reaction of methyl sulfate with HO• radicals.

Reaction	ΔG	ΔE
CH_3-O-$SO_3H\cdots(H_2O)_{n=0-2}$ + •OH ↔ RC1-nw → TS1-nw → PD1-nw (H_2C•-O-$SO_3H\cdots(H_2O)_{n+1}$)		
n = 0		
RC1-0w	5.31	-2.57
TS1-0w	11.76	5.66
PD1-0w	-16.88	-26.17
n = 1		
RC1-1w	6.23	-13.38
TS1-1w	12.91	-5.16
PD1-1w	-12.01	-32.34
n = 2		
RC1-2w	7.99	-22.64
TS1-2w	11.53	-18.10
PD1-2w	-13.02	-46.65
H_2C•-O-SO_3^-,$H_3O^+\cdots(H_2O)_2$ → TS1b-2w → PD1b-2w ($H_2CO\cdots SO_3$•$^-$,$H_3O^+\cdots(H_2O)_2$)		
H_2C•-O-SO_3^-,$H_3O^+\cdots(H_2O)_2$	0	0
TS1b-2w	18.79	23.35
PD1b-2w	0.72	7.09
H_2C•-O-SO_3H + O_3 ↔ RC31→ TS31 → PD31 (O_2 + •O-CH_2-O-SO_3H) → RC31b → TS31b → PD31b		
RC31	-18.70	-37.32
TS31	-25.72	-42.17

PD31	-22.48	-34.73
RC31b	-4.48	5.22
TS31b	10.42	26.55
PD31b	-22.24	-7.05
$H_2C^{\bullet}\text{-}O\text{-}SO_3H + O_2 \rightarrow {}^{\bullet}OO\text{-}CH_2\text{-}O\text{-}SO_3H$	-45.98	-65.69
${}^{\bullet}OO\text{-}CH_2\text{-}O\text{-}SO_3H + {}^{\bullet}OO\text{-}CH_2\text{-}O\text{-}SO_3H \rightarrow RC32 \rightarrow TS32 \rightarrow PD32$		
RC32	-99.39	6.28
TS32	-83.49	15.33
PD32	-234.34	-10.68

The sentence at line 205 is updated to:
Optimized structures and energetics of all reactions states in these reactions are given in **Figure 3**, **Figure S2**, **Table 1** and **Table S4**.

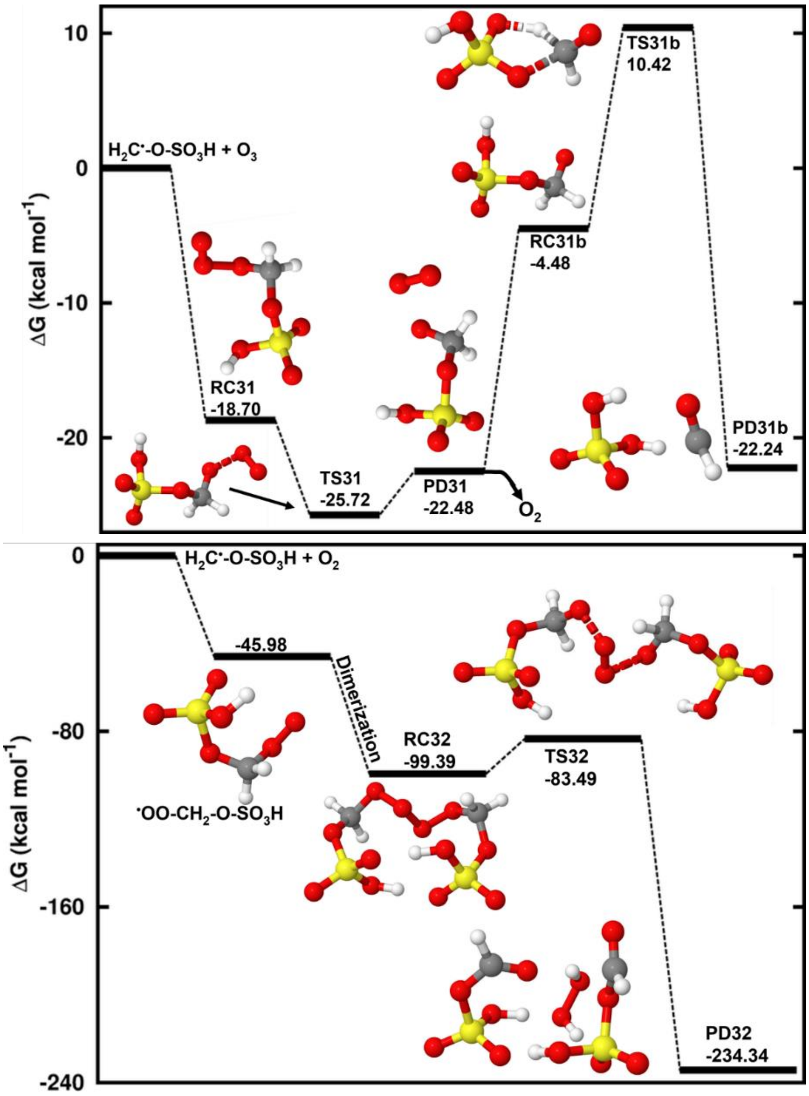

Figure 3: Gibbs free energy changes (in kcal mol^{-1}) and optimized structures for all intermediates in the reaction of H_2C•-O-SO_3H with O_3 (top) and O_2 (bottom). The sulfur atom is in yellow, the oxygen atom is in red, the carbon atom is in grey and the hydrogen atom is in white.

Gas-phase bimolecular kinetics are well-established, and the reactant complex normally does not enter the rate constant calculation. Hence, I find it curious that the authors treat the reactions as unimolecular and just start from the RC.

Section 2.2 of the manuscript provides details on how the reaction rate constants are calculated. Although in the manuscript we mostly report unimolecular rates constants (given by Eq. (3)) that describe how fast the reactant complex develops into the products, the bimolecular rate constant (given by Eq. (1)) fully describes the kinetics from the separate reactants to the product complex. The bimolecular rate constant takes into account both the formation of the reactant complex from separate reactants (expressed by the equilibrium constant) and the transformation of the reactant complex (expressed by the unimolecular rate constant).

I do not buy the presented argument that glycolic acid sulfate does not react with OH in the gas phase.

We thank the Referee for raising this. Our previous statement was based on the fact that our attempts to assess the outcome of HOOC-CH•-O-$SO_3H\cdots H_2O$ reaction with O_3/O_2 failed since we were neither able to determine the different transition states nor to obtain barrierless formation of products. This is probably due to the stabilizing effect of complexed water. Given that water is known to evaporate fast from gas-phase atmospheric species, we have re-considered the investigations of O_3/O_2 reactions with HOOC-CH•-O-SO_3H without additional water molecule. Please, refer to our reply to the Referee's first comment for our full response to this query.

What is the concentration of the organosulfates in the gas-phase compared to the condensed phase? Would they partition to the particle phase faster than they can react with OH radicals?

Despite we do not recall the report of specific organosulfates concentrations in the gas-phase, a study reported that out of measured organosulfates in Beijing, the contribution from the gas-phase was up to 11.6 % of the total organosulfates (Le Breton et al., 2018), suggesting that a significant fraction of organosulfates would always be retained in the gas-phase. This study showed that partitioning of organosulfates to the particle-phase depends on relative humidity and temperature. While increased relative humidity promotes partitioning into the particle-phase, high temperatures favor retention in the gas-phase. Another study showed that gas-to-particle partitioning is regulated by particle hygroscopicity (Ohno et al., 2022). It is then likely that a non-negligible fraction of organosulfates would react with OH in the gas-phase while another fraction would react in the particle-phase. We added the following in the revised manuscript.

Line 51 is revised to:
Organosulfates primarily exists in the particulate phase due to their low volatility (Estillore et al., 2016; George and Abbatt, 2010), although a non-negligible fraction has been shown to always be present in the gas-phase (Ehn et al., 2010; Le Breton et al., 2018) where they can react continuously with gas-phase oxidants (e.g., HO• radicals, O_3, and NO_3 radicals) at or near particle surfaces.

Line 65:
Both organosulfates have been detected at various locations around the world at concentrations in the ranges 1.08×10^{6}-5.01×10^{7} molecule cm^{-3} for methyl sulfate (Hettiyadura et al., 2015; Peng et al., 2021) and 1.16×10^{7}-4.71×10^{8} molecule cm^{-3} for glycolic acid sulfate (Huang et al., 2018; Hettiyadura et al., 2015; Wang et al., 2021; Hughes and Stone, 2019; Cai et al., 2020; Liao et al., 2015).

Specific comments

Line 96: In equation (3) quantum mechanical tunnelling is neglected. However, for hydrogen abstraction reactions tunnelling would be expected to be important. Please include the role of tunnelling for the calculated rates.

We have included the tunneling correction in Eq. (3) and the following is added at line 100.

$$k_{\mathrm{uni}} = \kappa \frac{k_B T}{h} \times \exp\left(-\frac{\Delta G^{\#}}{RT}\right). \tag{3}$$

κ is the Eckart tunnelling coefficient (calculated by solving the Schrodinger equation for an asymmetrical one-dimensional Eckart potential (Eckart, 1930)).

Line 104: Equation (4)-(6) does not appear to be used in the manuscript.

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: It would assume that the HO• + CH_3-O-SO_3H···(H_2O)n to H_2C•-O-SO_3H···(H_2O)n+1 reaction should be considered as a bimolecular reaction. Any particular reason why the reaction is treated as a unimolecular reaction starting from the reactant complex? Will this not misleading make it look like the reaction is more favourable than it is? Same analysis is made in line 211.

Indeed, CH_3-O-SO_3H···$(H_2O)_{n=0-2}$ reaction with HO• to H_2C•-O-SO_3H···$(H_2O)_{n+1}$ is bimolecular. Although in the manuscript we mostly report the unimolecular rate constant of the decomposition of the reactant complex that constitutes the limiting step, the overall hydrogen abstraction from the organosulfate is bimolecular and the rate constant for this process is given by Eq. (1). In the revised manuscript, we will make more reports of bimolecular rate constants when appropriate.

Line 139

The bimolecular rate constant for this reaction is determined to be 1.14×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298.15 K.

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.

Line 185: Could you clarify what you mean with "… while attempts to optimize the reaction with O2 did not succeed due to electronic constraints to form chemically stable species." Are you referring to the spin states? Usually, this reaction occurs very fast and will therefore be more important than the reaction with O3.

The Referee is right that the reaction with O_2 should occur fast. In our previous calculations, we treated the reaction by considering the direct product complex (H_2C•-O-SO_3H···H_2O) from the methyl sulfate reaction with HO•. This reaction did not lead to a successful optimization of all the reaction states. Considering that water would evaporate fast from this product complex, we have performed a re-assessment of the fate of H_2C•-O-SO_3H in its unhydrated state and the H_2C•-O-SO_3H + O_2 reaction has been successfully investigated, along with the H_2C•-O-SO_3H + O_3 reaction.

We find that O_2 addition to H_2C•-O-SO_3H proceeds through formation of the peroxyl radical •OO-CH_2-O-SO_3H with 45.98 kcal mol^{-1} Gibbs free energy gain. The fate of •OO-CH_2-O-SO_3H was further investigated.

The reaction with O_3 also proceeds through formation of the O_3···H_2C•-O-SO_3H complex, following by an oxygen atom transfer to form the alkoxyl radical •O-CH_2-O-SO_3H and release O_2. •O-CH_2-O-SO_3H further undergoes intramolecular decomposition to form H_2SO_4 and HCO•.

In the revised manuscript, the sentence at line 185 has been modified to the following: Besides the self-decomposition of H_2C•-O-SO_3H, we further examined its reactions with NO_2 (**reaction (R3)**), O_3 (**reaction (R4)**), and with O_2 (**reaction (R5)**).

The following text is added at Line 222

Contrary to the self-decomposition of H_2C•-O-SO_3H and reactions with NO_2 and O_3 that are favorable with H_2C•-O-SO_3H hydrates, we were unable to fully optimize the O_2 reaction with H_2C•-O-SO_3H hydrates but with the unhydrated system, instead. This led to exergonic formation of the •OO-CH_2-O-SO_3H peroxyl radical with 45.98 kcal mol^{-1} Gibbs free energy gain. 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). Following the above reasoning, our calculations indicate that two molecules of •OO-CH_2-O-SO_3H recombine to form a tetroxide that can further decompose to generate two alkoxyl radicals •O-CH_2-O-SO_3H clustered to molecular oxygen. Then, the two •O-CH_2-O-SO_3H radicals quickly interact with O_2 to form H_2O_2 and formic sulfuric anhydride (HC(O)-O-SO_3H) (**reaction (R5)**). The latter product has been identified to enhance new particle formation (An, 2024). Energetics and structures of all intermediates in this reaction are given in **Figure 3**.

Line 231-232: I assume the 1 M concentration is used to get the aqueous phase units right here. How well justified is it to use 1 M?

With quantum chemical calculations, while Gibbs free energies in the gas-phase are calculated at standard temperature of 298.15 K and standard pressure of 1 atm, in the aqueous-phase, they are obtained by converting the standard pressure of 1 atm to the standard concentration of 1 M.

This is updated in the revised manuscript.

Line 80.
In the aqueous-phase, the Gibbs free energies are calculated at standard temperature of 298.15 K and by converting the standard pressure of 1 atm (in the gas-phase) to the standard concentration of 1 M. Details are provided in Section S1 in the supplement.

Line 280: "its formation from H_2C•-O-SO_3^- reaction with O_2 is less thermodynamically favorable than with O_3,"

Our calculations indicated that the association of H_2C•-O-SO_3^- with O_2 (to form •OO-CH_2-O-SO_3^-) is more thermodynamically favorable than the association with O_3 (to form •OOO-CH_2-O-SO_3^-), with respective formation Gibbs free energies of -54.83 kcal mol^{-1} and -52.05 kcal mol^{-1}. However, we find that •OOO-CH_2-O-SO_3^- can rapidly decompose to form the alkoxyl radical •O-CH_2-O-SO_3^-, with a negative energy barrier of -5.98 kcal mol^{-1}, while •OO-CH_2-O-SO_3^- forms a tetroxide prior to •O-CH_2-O-SO_3^- formation. The 14.12 kcal mol^{-1} Gibbs free energy separating the tetroxide from •O-CH_2-O-SO_3^- indicates a kinetically hindered process. This justifies our affirmation that •O-CH_2-O-SO_3^- formation from H_2C•-O-SO_3^- reaction with O_2 is less favorable than with O_3. In the revised manuscript, we change "thermodynamically" by "kinetically".

Line 296: "… HOOC-CH•-O-SO_3H species was found to be without atmospheric relevance as opposed to the intermediate reactant in the reaction of methyl sulfate."

I do not understand the argument here. The alkyl radical should be able to react barrierlessly with O_2?

We initially assessed the reaction of HOOC-CH•-O-SO_3H with O_2 by considering the direct product complex (HOOC-CH•-O-$SO_3H\cdots H_2O$) of the glycolic acid reaction with HO•. This reaction did not lead to a successful optimization of all the reaction stationary states. Given the known fast evaporation of water from most complexes in the gas-phase, we have re-considered the fate of HOOC-CH•-O-SO_3H in its unhydrated state and the HOOC-CH•-O-SO_3H + O_2 reaction has investigated.

The text at lines 296-301 has been deleted and the following new text is added in the revised manuscript.

Line 295

Hydrogen abstraction from glycolic acid sulfate could occur both from $-CH_2-$ and $-COOH$ groups according to the following reactions:

$HOOC\text{-}CH_2\text{-}O\text{-}SO_3H + HO\bullet \rightarrow H_2O + HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3H$, (R9)

$HOOC\text{-}CH_2\text{-}O\text{-}SO_3H + HO\bullet \rightarrow H_2O + \bullet OC(O)\text{-}CH_2\text{-}O\text{-}SO_3H$. (R10)

The mechanism of **reaction (R9)** is similar to that of the hydrogen abstraction from methyl sulfate that forms an alkyl radical. Through this process, glycolic acid sulfate readily undergoes a hydrogen abstraction from the $-CH_2-$ group by HO•, resulting in $HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3H$ formation. The reactant complex in this process lies at 4.65 kcal mol^{-1} at 298.15 K and 1 atm, and the transition state for its conversion is located 2.13 kcal mol^{-1} above the reactant complex. We determined a bimolecular rate constant of the overall reaction is 6.17×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for this reaction at 298.15 K. This shows that hydrogen abstraction by •OH from glycolic acid sulfate is more favorable than from methyl sulfate, hereby highlighting the enhancing effect of the carboxyl substituent. The further chemistry of $HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3H$ is examined through reactions with O_3 and O_2. Our calculations show that contrary to the reaction with $H_2C\bullet\text{-}O\text{-}SO_3H$, O_3 hardly reacts with $HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3H$ as the $O_3\cdots HOOC\text{-}CH\bullet\text{-}O\text{-}SO_3H$ formation is highly endergonic at standard conditions. However, the reaction with O_2 is seen to be fast, proceeding through formation of the reactant complex that is readily converted to $HOOC\text{-}CH(OO)\bullet\text{-}O\text{-}SO_3H$. The observed negative Gibbs free energy barrier (-9.02 kcal mol^{-1} below the reactant complex) in this conversion indicates that the formation of $HOOC\text{-}CH(OO)\bullet\text{-}O\text{-}SO_3H$ is almost instantaneous at standard conditions. Two molecules of $HOOC\text{-}CH(OO)\bullet\text{-}O\text{-}SO_3H$ develop into a tetroxide that then decomposes to $HC(O)\text{-}O\text{-}SO_3H$ and $HOOC\text{-}CH(O)\bullet\text{-}O\text{-}SO_3H$. The energetics of this reaction are provided in **Figure 6** and **Table S5**.

The abstraction from -COOH led to $\bullet OC(O)\text{-}CH_2\text{-}O\text{-}SO_3H$ (reaction (R10)) that further decomposes to methylene sulfate radical ($H_2C\bullet\text{-}O\text{-}SO_3H$) and CO_2. The structures and energetics of all intermediate states of this reaction are given in **Figure S5** and **Table S6** in the Supplement. At the same level of theory, we determined a biomolecular rate constant of 3.86×10^{-14} cm^3 $molecule^{-1}$ s^{-1}, two orders of magnitude lower than the hydrogen abstraction from the $-CH_2-$ group. This indicates that hydrogen abstraction from glycolic acid would follow two competitive pathways although the pathway leading to the alkyl radical is somewhat preferred. It can be inferred that for organosulfates that have a -COOH substituent at the β-position relative to the sulfate group, decarboxylation would be a possible outcome of their decomposition. The chemistry of $H_2C\bullet\text{-}O\text{-}SO_3H$ was assessed in Section 3.1 above.

We further investigated the HO•-initiated reaction of glycolic acid sulfate in the aqueous-phase, where the deprotonated state, $HOOC\text{-}CH_2\text{-}O\text{-}SO_3^-$, is predominant.

Line 331: Why is the dimer from 2 peroxy radicals only formed for glycolic acid sulfate and only in the aqueous phase? What are the alternative fates of peroxy radicals?

Kindly refer to our reply to the previous question for our reply to this question.

Line 334: "… does not fragment to form in the alkoxyl radical in the singlet state, but rather transits to the triplet state before fragmentation could occur, the energy difference between the two electronic states being as low as 7.60 kcal mol-1 ."

How is it determined that it "transits" to the triplet state here? Did you do the intersystem crossing calculations?

We wanted to express that from our calculations we could not get the fragmentation of O_3^-S-O-CH(COOH)-OOOO-CH(COOH)-O-SO_3^- to happen in the singlet state but rather in the triplet state, the two states being separated by 7.60 kcal mol^{-1} Gibbs free energy.
We have rephrased this sentence as follows:

However, we found that contrary to the case of •OO-CH_2-O-SO_3^- where the tetroxide could readily decompose to form the •O-CH_2-O-SO_3^- radical in the singlet state, the fragmentation of O_3^-S-O-CH(COOH)-OOOO-CH(COOH)-O-SO_3^- to form the alkoxyl radical HOOC-CH(O)•-O-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).

Technical comments

Line 22: Remove either "highlight" or "unveils"

"highlight" has been removed from the sentence.

Additionally, while prior studies suggested O_2 as primary oxidant in the fragmentation of organosulfates, this study unveils O_3 as a complementary oxidant in the intermediate steps of this process.

Line 44: Sentence starting with "Despite organosulfates have generally … " please rephrase.

The indicated sentence has been deleted and the sentence at line 51 is revised to the following to express the idea of line 44:

Organosulfates primarily exists in the particulate phase due to their low volatility (Estillore et al., 2016; George and Abbatt, 2010), although a non-negligible fraction has been shown to always be present in the gas-phase (Ehn et al., 2010; Le Breton et al., 2018) where they can react continuously with gas-phase oxidants (e.g., HO• radicals, O_3, and NO_3 radicals) at or near particle surfaces.

Line 75 and 76: M062X/6-311+g(2df,2pd) -> M06-2X/6-311+G(2df,2pd)

M062X/6-311+g(2df,2pd) has been changed to M06-2X/6-311+g(2df,2pd) in the whole revised manuscript.

Line 175: I find this part of the sentence hard to understand "… and the combination of Russell (Russell, 1957) and Bennett and Summers (Bennett and Summers, 1974) mechanisms we speculated by the authors to explain this formation.". Could you please rephrase.

This sentence has been rephrased and the revised form reads as follows:

The products predicted by our calculations were observed in a previous experimental study by Kwong et al. (Kwong et al., 2018) for the same reaction, and the mechanisms from Russell (Russell, 1957) and Bennett and Summers (Bennett and Summers, 1974) were speculated by the authors to explain this formation.

Line 188: "difficulty breaking" -> "difficulty in breaking"

This has been corrected.

Line 268: "oxygen atom of the alkoxy function" -> "oxygen atom of the alkoxy functional group"

This has been corrected.

Data availability

All coordinates of the studied systems as well as energetic should be available as supporting information. Otherwise, the study is not reproducible.

The cartesian coordinates of all studied systems are now added in the revised Supplement.

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