

Reply to Anonymous Referee #1

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' reply are in black color and modifications to the manuscript are in red color text.

In this work the authors carried out quantum calculations to explore the aqueous-phase reactions of organic peroxides (MHP, PAA and BZP) with dissolved SO₂ or S(IV) species under various pH conditions. The simulated results clearly demonstrated the effects of pH on the major reaction pathways between various organic peroxides with S(IV) species leading to form inorganic sulfate and organosulfate. The potential reaction mechanisms were discussed with details and in general agreed with the existing experimental results. The paper is well written and provide greater mechanistic understanding of the organic peroxides chemistry in aspect of inorganic and organic sulfur formation. I only have a few minor comments

General comments:

For the quantum chemical calculations, what are the concentrations of the reactants used in the calculations? Would the reaction pathways and kinetics potentially affect by the reactant concentrations?

By its principle, quantum chemical (QC) calculations allow to solve for the electronic configuration of the reacting system and provide the reaction energies at all reaction states including the transition states, regardless of the reactants concentrations, and to analyze the reaction mechanisms of the developed reactions. This approach specially focuses on the electronic interaction between the reactants in order to provide atomic level insights into the processes driving the reaction. In this regard, QC calculations are mainly designed to predict and explain unknown reactions and are not affected by the reactants concentrations. Likewise, the transition states obtained from QC calculations are not dependent on the reactants concentrations.

By default, the rate constant of a reaction in aqueous phase (given by Eq. (3) in the main manuscript) is determined from QC calculations at a standard concentration of 1 M, with all other parameters being independent of the reactants concentrations. While the reactants concentrations do not affect the rate constants, they alter the overall kinetics by affecting the reaction rates, which are dependent on the concentrations. The rate constant is a fundamental parameter in kinetics that represents the constant of proportionality relating the reaction rate to the concentrations of reactants, while the reaction rate measures the change in reactant or product concentration per unit time.

The mention of 1 M standard concentration for computing the thermochemistry and the rate constant was already made in Section 2 of the main manuscript.

For the reaction pathways, would there be any other possible reaction pathways between the organic peroxides and S(IV) in addition to the ones discussed and considered in the calculations?

From the average local ionization energy- (ALIE-) mapped molecular van der Waals surfaces of the reactants (shown in **Fig. 2** in the main manuscript), the most probable reaction sites are the -

O-O- functions of OPs and the S atom of dissolved SO₂. According to our QC calculations, the most likely outcome of OPs interacting with S(IV) is the formation of organic and/or inorganic sulfate, depending on the OP structure. Though we did not consider other reaction pathways else than abovementioned ones based on ALIE predictions, we speculate that any potential outcome of OP+S(IV) reaction would be without significance to the atmospheric environment. The following was added in the revised manuscript at page 6.

“In general, based on the ALIE-mapped molecular van der Waals surfaces, the OP+S(IV) reaction is mainly driven by the interaction between the -O-O- function of OP and the sulfur atom of S(IV), while other interactions are considered to be without significance.”

In the atmospheric implications, it is very nice the authors to show and discuss the effective rate constants for different reaction systems under different values of pH and temperature and their corresponding lifetimes. the authors have pointed out such reactions may be important for sulfate formation under oxidant-limiting conditions. Can the authors further elaborate this point? Also, could the authors comment the yield of inorganic sulfate and organosulfates in different reaction systems and environmental conditions.

For decades, there has been considerable debate regarding the mechanisms responsible for atmospheric sulfate formation. Especially, under conditions of low solar radiation such as haze events where there is low production of OH radicals to oxidize SO₂, many studies have observed increasing sulfate formation and suggested alternative pathways for atmospheric sulfate (*Environ. Sci. Technol.*, 2022, **56**(15), 10608-10618; *Proc. Natl. Acad. Sci. U.S.A.*, 2020, **117**(3), 1354-1359; *Sci. Adv.*, 2016, **2**(12), e1601530). Besides sulfate formation mechanisms including ion-mediated and acid-catalyzed mechanisms that have already been elucidated, the current mechanisms can adequately account for sulfate formation under low OH radical conditions. This is further clarified in the revised manuscript. Moreover, to avoid misunderstanding “low OH radical conditions” is used instead of “oxidant-limiting conditions”.

Page 13:

“These pathways can adequately account for sulfate formation under conditions of low solar radiation such as haze events where there is insufficient production of OH radicals.”

Minor comments.

Line 100, “The diffusion coefficient for a reactant is related to its radius in any medium of viscosity η by the Stokes-Einstein approach (Einstein, 1905).” It is not clear what is the viscosity of the aqueous solutions. How the diffusion would affect the reaction pathways if the solutions or aqueous aerosols were highly viscous?

The viscosity used here is the that of water. This is now specified in the revised manuscript:

Page 4:

“For reactants S(IV) and OP in water, the viscosity is that of water and the diffusion coefficients are calculated as:”

The overall rate constants of the studied reactions depend on the diffusion rate constants of the reactants in aqueous solution. According to its expression in Eq. (5) in the main manuscript, the diffusion rate constant is directly proportional to diffusion coefficients of the reactants, while the diffusion coefficient is inversely proportional to the viscosity of the solution (according to Eq. (5) in the revised manuscript). This shows that reactants in solutions with low viscosities will diffuse more easily than in solutions with high viscosities. Although the solution viscosity may not have an impact on the reaction mechanism, it definitely affects the reaction kinetics. We have highlighted the impact of viscosity in the revised manuscript.

Page 4:

“It is known that the viscosity of aerosols can be affected by relative humidity, chemical composition, water uptake and temperature (Song et al., 2021). Given that aerosols are mixtures of different proportions of organic and inorganic salts, it is obvious that the actual diffusion coefficients and overall kinetics of the studied reactions in aqueous aerosols will strongly depend on the actual aerosol viscosity.”

Line 115, “The formation of $\text{SO}_2 \cdot \text{H}_2\text{O} \cdot \text{MHP}$ is relatively endergonic at 298.15 K and standard concentration of 1 M.” Can the authors elaborate why the concentration of 1M was chosen for the calculations? Would the concentration of the reactants affect the reaction pathways and kinetics?

In QC calculations, standard conditions to calculate the Gibbs free energy in the gas-phase as defined in Gaussian are 298.15 K and 1 atm. For aqueous-phase reactions, standard conditions are defined in terms of absolute temperature and molar concentration, namely 298.15 K and 1 M. The expression of the Gibbs free energy in aqueous-phase, given in Eq. (S1) in the Supplement, includes a term that converts the standard pressure of 1 atm in the gas-phase to the standard concentration of 1 M in aqueous-phase. This was already given in the Supplement and is further highlighted in the revised manuscript.

Page 2:

“The Gibbs free energy in aqueous-phase is calculated at standard temperature of 298.15 K and molar concentration of 1M. Details are given in Section S1 in the Supplement.”

Moreover, as already explained in our reply to a previous comment of the Referee, while the concentrations of the reactants may not affect the chemical mechanism of the reaction, they will significantly affect the overall kinetics by altering the reaction rates.

Line 155, “The high proportion of sulfate relative to methyl sulfate observed by Lind et al. can further be explained by the demonstrated fast hydrolysis of methyl sulfate at acidic pH (Hu et al., 2011) and its effective oxidation by OH radicals (Kwong et al., 2018) to form inorganic sulfate.” Could the authors comment how significance of these two processes in the formation of inorganic sulfate and organosulfates relative to the reactions between organic peroxides and S(IV) species?

From QC calculations, the two predicted pathways in the reaction of MHP with dissolved SO_2 are the formation of methyl sulfate and inorganic sulfate, with the path for inorganic sulfate being preponderant, in agreement with the experimental observation of Lind et al. (J. Geophys. Res.: Atmos., 92, 4171-4177, 1987). Considering that hydrolysis at acidic pH and OH-initiated reaction

of methyl sulfate are fast, the ultimate outcome of MHP + S(IV) reaction is nothing but inorganic sulfate formation. This implies that the reaction of OPs with dissolved SO₂ will mostly contribute to inorganic sulfate formation and the implication of this reaction in aqueous aerosol will be more pronounced in terms of inorganic sulfate mass loadings. This was already mentioned in Section 4 and is further highlighted at page 7.

Page 7:

“The implication for this is that MHP reaction with S(IV) will contribute to aqueous aerosol mostly in terms of inorganic sulfate mass loading.”

Line 183, “In general, the reaction of PAA is much more favorable to the formation of inorganic sulfate than the reaction of MHP at all pH ranges, while the formation of organosulfate is slightly prevented. This is in line with the experimental observation that the reaction of PAA with dissolved SO₂ almost exclusively forms inorganic sulfate (Lind et al., 1987).” What would be the ratios of the inorganic sulfate to organosulfate formed upon the reaction of PAA and dissolved SO₂ at pH 1.81 – 6.97 and pH > 6.97? Also, what would be ratios for other reaction systems?

The kinetics of the reaction of PAA with S(IV) show that formation of inorganic sulfate is 11 orders of magnitude and 9 orders of magnitude faster than organosulfate formation at pH 1.81 – 6.97 and pH > 6.97, respectively. From the calculated rate constants, the branching ratios can be estimated to be 100% for inorganic sulfate formation and 0% for organosulfate. For the MHP reaction, the branching ratios are 99.92 % and 0.08% for inorganic sulfate and organosulfate, respectively. We have revised the above text and included the branching ratios in the revised manuscript.

Page 8:

“In general, the reaction of PAA is much more favorable to the formation of inorganic sulfate than the reaction of MHP at all pH ranges, while the formation of organosulfate is substantially prevented.”

Page 13:

“The branching ratios estimated from the obtained the kinetics of MHP + S(IV) are 99.92% and 0.08% for inorganic sulfate and organic sulfate, respectively.”

Page 13:

“Despite quantum chemical calculations predict the pathways for the formation of both inorganic sulfate and organosulfate from PAA+S(IV) reaction, the kinetics show that inorganic sulfate formation is more than 9 orders of magnitude faster than organosulfate formation in the whole pH range investigated, simply indicating that organosulfate formation from PAA reaction is insignificant. Regardless of the pH range, the branching ratios estimated from the kinetics are 100% for inorganic sulfate formation and 0% for organosulfate. This is in line with the experimental observation that the reaction of PAA with dissolved SO₂ almost exclusively forms inorganic sulfate (Lind et al., 1987).”