

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

This new contribution explores theoretically the aqueous condensed phase chemistry of organic peroxides (Ops) with dissolved sulfur in its (+IV) oxidation state as a function of pH. It especially simulates the chemistry of three selected OPs (methyl hydroperoxide (MHP), peracetic acid (PAA) and benzoyl peroxide (BZP)) with dissolved SO_2 . This is certainly an important topic as organic peroxides and SO_2 are key components of aerosols and hydrometeors, that fits the scope of the journal.

Nevertheless, I would recommend that authors comments (and eventually modify their manuscript) to address the following comments, in addition to polishing the use of the English language.

We have addressed the Referee's comments and further polished the English in the whole manuscript.

While this reviewer is not an expert in the theoretical calculations reported here, the experimental section seems nevertheless short and not necessarily providing the level of information required to really assess the quality of the calculations.

We agree with the Referee that little is reported about experimental work. Originally, the paper is based on a theoretical study, exclusively, and we only referred to experimental results to support our findings. More has been added on the comparison with experiments in the revised manuscript.

Page 13:

“The branching ratios estimated from the obtained kinetics of MHP + S(IV) reaction are 99.92% and 0.08% for inorganic sulfate and organic sulfate, respectively. This favored formation of inorganic sulfate relative to methyl sulfate is in agreement with the experimental results that observed that inorganic sulfate is the major product while methyl sulfate is the second product in MHP+HOSO₂⁻ reaction (Lind et al., 1987).”

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 study that found inorganic sulfate to be the sole product of the the reaction of PAA with dissolved SO_2 (Lind et al., 1987).”

The core content of this study concerns the effect of pH on the chemistry between the selected OPs and dissolved SO₂. This seems to be mainly (or even uniquely) simulated through the change of S(IV) species in presence at the selected pH. However, pH is known to catalyze the chemistry, and even the degradation, of OPs. This would certainly also affect the nature of reported transition states. But this not mention and corresponding papers not cited. Enami reported several studies, on different OPs, describing their acid catalyzed degradation (<https://doi.org/10.1002/ejoc.202100343>) or their overall fate in the condensed phase (<https://doi.org/10.1021/acs.jpca.1c01513>); while Krapf et al discussed their overall stability (<https://doi.org/10.1016/j.chempr.2016.09.007>).

The aim of this study was indeed the pH effect on the reaction of OPs with dissolved SO₂ towards sulfate formation, using quantum chemical (QC) calculations. By its principle, (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 concerned about how the electronic structures of the system evolve from the reactants to the products along the reaction process. While OPs do not dissociate with the change of pH, dissolved SO₂ adopts different protonated states depending on the pH and QC calculations allow to examine how each protonated state of dissolved SO₂ interacts with the OP to form the products. The average local ionization energy- (ALIE-) mapped molecular van der Waals surfaces of the reactants (shown in **Fig. 2** in the main manuscript) indicated that the most probable reaction sites for the reactants are the -O-O- functions of OPs and the S atom of dissolved SO₂. While hydronium ions have been shown to catalyze the degradation of hydroperoxides with α -hydroxyalkyl, α -alkoxyalkyl and α -acyloxyalkyl substituents (Environ. Sci. Technol. 2020, 54, 10561-10569; J. Phys. Chem. A 2020, 124, 10288-10295; J. Phys. Chem. A 2021, 125, 4513-4523), the available proton is unlikely to play a similar role in the degradation of OPs investigated in this study, due to unavailable α -substituent. In the series of Enami's studies on this topic, including theoretical calculations, the degradation of α -substituted hydroperoxides is guaranteed by the presence of the hydroperoxide group (-OOH) and the α -substituent with the oxygen atom (-O-) at the β -position so as to enable the formation of a ring structure and further facilitate the decomposition. These two requirements are not met for OPs considered in this work. Nevertheless, in our future investigations, we will minutely examine the potential role of available proton in the degradation of OPs that have no substituents at the α -position. The following was added in the revised manuscript to highlight our reasoning.

Pages 10-11:

“Besides reactions with dissolved SO₂, other recent studies showed that hydronium ions effectively catalyze the decomposition of organic peroxides at acidic pH (Qiu et al., 2020; Hu et al., 2020; Enami, 2021). It should be noted that in these studies, the catalytic effect of the available proton was examined on specific classes of OPs, namely hydroperoxides with α -hydroxyalkyl, α -alkoxyalkyl and α -acyloxyalkyl substituents. The presence of the hydroperoxide group (-OOH) and the α -substituent with the oxygen atom (-O-) at the β -position in these hydroperoxides enable the formation of a hydrogen-bonded ring structure involving the two functions and further facilitate their decomposition. Although these two requirements are not met for OPs considered in this work,

the potential role of the available proton in the degradation of OPs that have no substituents at the α -position is worth of thorough analysis in our future investigations.”

In the opinion of this reviewer, it would be important to explore the effect of available protons on the actual structure of the transition state and not just on the distribution of S(IV) species.

As discussed in our reply to the Referee’s previous comment, the configuration of investigated OPs is not in favor of explicit interaction of available proton. Hence, the transitions states were discussed solely in terms of interaction between the organic peroxide and the protonated state of S(IV) prevailing at the corresponding pH range.

The atmospheric implication is explored over a wide range of temperatures, corresponding even to ice conditions (at 240 K). It does not seem obvious that the temperature dependence of all parameters (such as acid-base equilibrium constants, etc.) have been considered to derive the temperature dependent rate constant. Could this be clarified? Also, this atmospheric significance needs to be compared to the lifetimes of the OPs which is also pH dependent (if the OP self-degrades faster that would limit the reported significance).

The temperature-dependent rate constant was derived by combining the transition state theory approach and the Collins-Kimball theory. The transition state theory is expressed by a temperature-dependent equation which is the product of two temperature-dependent terms: the equilibrium constant and the unimolecular rate constant for the reaction of the reactant complex to the product. Similarly, the Collins-Kimball theory is given by a temperature-dependent equation. These equations were already given in the manuscript and for further clarifications, the following modification was performed in the revised manuscript to highlight the equation for the transition state theory:

Page 3:

“The transition state theory approach to determine the bimolecular rate constant (k) of reaction (R1) under the pseudo-steady-state approximation considers two main terms and it is expressed as

$$k_{\text{bim}} = K_{\text{eq}}k_{\text{reac}} , \quad (1)$$

where K_{eq} is the equilibrium constant of formation of RC and k_{reac} is the unimolecular rate constant for the reaction of RC to the product complex, given respectively by the following equations:

$$K_{\text{eq}} = \frac{1}{c^0} \times \exp\left(-\frac{\Delta G_{\text{eq}}}{RT}\right) , \quad (2)$$

$$k_{\text{reac}} = \frac{k_{\text{BT}}}{h} \times \exp\left(-\frac{\Delta G^{\#}}{RT}\right) , \quad (3)”$$

Due to the simple structure of OPs investigated in this study relative to e.g., hydroperoxides with α -hydroxyalkyl, α -alkoxyalkyl and α -acyloxyalkyl substituents, proton-catalyzed self-degradation

is an unlikely process. Hence, the fate and estimated lifetimes of investigated OPs mainly depend on their reaction with S(IV). The following was added in the revised manuscript at page 11:

“Atmospheric lifetimes of OPs are calculated based on the effective rate constant of Eq. (7) and considering that self-degradation is an unlikely process given the simple structure of investigated OPs relative to those of e.g., hydroperoxides with α -hydroxyalkyl, α -alkoxyalkyl and α -acyloxyalkyl substituents whose self-degradations are catalyzed by the proton (Enami, 2021), these lifetimes are estimated based on S(IV) reactions, exclusively.”

Minor points

The sentence starting line 30 (i.e., “In aqueous media, OPs are produced by the reduction of ROx radicals and from fluorescent dissolved organic matter (DOM) by photogeneration, while other sources include partitioning from gas-phase to particle-phase (O'sullivan et al., 2005; Sun et al., 2021).”) does not provide a sound description of the formation of OPs.

This has been re-written as follows:

“Sources of OPs in aqueous media include self-reaction of photochemically formed organic radicals and partitioning from gas-phase to particle-phase (O'sullivan et al., 2005; Sun et al., 2021; Riemer et al., 2000).”

Line 33: “uptake on water surfaces”, this is not a sink but rather a source.

To remove the confusion, the sentence has been re-written as:

“Primary sinks of OPs include SO₂ oxidation in cloud and rain droplets, mainly forming water-soluble organic compounds and secondary sulfates (Böge et al., 2006; Hua et al., 2008).”

Line 59, change lowly to poorly

This has been changed.

Line 122: the mention to uptake coefficients is unclear as bulk processes are described here.

We agree with the Referee this was not appropriate. The related sentence has been deleted in the revised manuscript.

References

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