

Interactive comment on “Heterogeneous Interactions between SO₂ and Organic Peroxides in Submicron Aerosol” by Shunyao Wang et al.

Anonymous Referee #1

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The authors studied the uptake coefficients of sulfur dioxide on particles containing three model organic peroxides (tert-butyl hydroperoxide, cumene hydroperoxide, and 2-butanone peroxide) as a function of (a) relative humidity (as proxy for particle liquid water), (b) particle acidity, and (4) composition of the particles (e.g., with malonic acid, or ammonium sulfate, or various model SOA material generated under dry conditions). The SO₂ was measured by a commercial analyzer and the particles were measured by SMPS. The pH was modeled by E-AIM. The methods are sound, and the paper is well written, and the discussion is fairly thorough. Moreover, the results are likely important for global modeling to better understand the atmospheric sulfur cycle. I request minor revisions based on the specific comments below.

Specific comments (line number precedes comment)

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12 The terminology is a bit confusing. As I understand it “multifunctional” means multiple different functional groups (e.g., an alcohol and a hydroperoxide on the same compound) not multiple peroxide groups. Perhaps multiple peroxide groups on a compound would be better described as poly-peroxide (similarly to polyol) or just multiple peroxide. Please clarify this throughout the text. Also please be specific throughout the text whether you are referring to hydroperoxide moieties or all peroxides.

12 As the authors only studied three peroxides, and they are not analogues in the way that would make the hydroperoxide moiety dependence clear, I would suggest against generalizing with this statement. At least the authors should add “in this study” to the statement to avoid overly broad generalizations, or revise in another way.

39 Mauldin et al 2012 did not positively identify stabilized Criegee, they suggested that it was a “Compound X” or “Unexplored oxidant X” that they believe to be SCIs. However, kinetic competition studies between SCI and water vapor vs SO₂ found that SCI + SO₂ is not competitive in the atmosphere for the dominant SCI CH₂OO (Newland et al, ACP 2015, Nguyen et al, PCCP 2016). It is not clear which rates are used in Liu but that study seems to back up the previous lab work, as Nguyen et al estimated that CH₂OO alone would be responsible for <6% SO₂ oxidation at a Southeast US site. I suggest to change this sentence to “sCIs were hypothesized to oxidize...” and please acknowledge the works before Liu 2019 that have already shown this pathway to be non-competitive at realistic RH using lab studies. <https://core.ac.uk/download/pdf/267289280.pdf> <https://pubs.rsc.org/en/content/articlepdf/2016/cp/c6cp00053c>

115 (and elsewhere) The authors should insert the SI table number explicitly after the Experiment numbers so the reader can know where to look up the experiments.

127 Please state the “different amounts” of HCl added for each experiment and the estimated particle pH that the different amounts of HCl correspond to. The authors say later that they estimate particle pH using E-AIM but this is worth mentioning in methods

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briefly first.

184 Where the losses of SO₂ and growth of particles corrected for chamber wall loss in the control experiments? Were the wall loss controls done at different RH? How were the corrections performed? What are the uncertainties associated with correcting or not correcting for wall effects?

Methods – how was the SO₂ analyzer calibrated? Did the authors have a NIST-traceable SO₂ standard? What is the uncertainty in SO₂ concentration that propagates into γ_{SO_2} ?

205 In the iodometric test using H₂O₂ as a standard, it is known that the reaction between H₂O₂ and KI might be complete after one hour but the reaction of organic peroxides and KI may take several hours up to a day (depending on the structure of the organic peroxide). As the authors have organic peroxide standards – I am curious why the authors decide to use H₂O₂ instead of organic peroxides? For future works, I suggest the authors to see for themselves how long the reaction takes to come to completion for their organic peroxides by following it after several hours. Another problem is the notorious difficulty of reproducing results – were replicates performed?

236 Can the authors discuss aerosol liquid water trends vs RH for the types of malonic/AS aerosols they are studying? There are also several hygroscopicity studies for SOA pure and mixed.

242 This can also be due to the ionic strength effects the authors talked about earlier Fig S7 and General – Vapor pressure considers the partitioning between the gaseous form of a compound and its pure solid/liquid form. As the authors are considering partitioning between gas and water (e.g., Fig S7 plots data/estimations at RH 50%), wouldn't Henry's Law be a more appropriate parameter?

Fig. S7 and throughout the text – I see that 2-butanone peroxide actually has three peroxide (-OO-) moieties from what is shown in figure 1 and from its Sigma Aldrich

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page? Two of those moieties are hydroperoxide (-OOH), and one is an ROOR. So why is the “-OO-” content for 2-butanone peroxide 2 instead of 3. If the authors only consider the hydroperoxide groups (-OOH) then the figure and text (and discussion) should be amended to clarify this and discuss why the interior -OO- isn't important.

304 The authors have an estimation of peroxide content in the particles and an measure of peroxide content in atomizer solution, so can the authors estimate how much of each peroxide stays in the condensed phase instead of assuming it all does? The assumption that all peroxides are nonvolatile seems to be in violation of the authors' statement in line 282 “measured γ_{SO_2} depends both on reactivity and gas-particle partitioning of the organic peroxides.”

325 Can you give some more information about why the H⁺ would be in the organic phase and not in the aqueous/inorganic phase?

348 Something is a bit confusing with Reaction 5 I think. If b is a quantity <1, then perhaps the ROH should also have some (1-b) multiplier? And suggest to limit the equation to ROOH for accounting purposes, and/or denote “ROOR” as ROOR' and show where R' goes too.

364 Is this only a factor of ionic strength? There seems to be some indication that droplets have a gradient in pH with the most acidic part at the interface, even for larger buffered aqueous droplets. Perhaps this discussion can be expanded to include this citation. <https://www.pnas.org/content/pnas/115/28/7272.full.pdf>

Section 3.4. Can the authors add in a discussion of what protons at the air-liquid interface can do to oxidize SO₂ in addition to the Reactions 5-7? For example Hung and Hoffman shows a number of other dark reactions on acidic microdroplet surfaces including proposed radical formation. <https://pubs.acs.org/doi/abs/10.1021/acs.est.5b01658>

396 is it necessary to refer to pH in two different ways “increasing proton concentrations

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(decreasing pH)”? Ions in hydrated aerosol mixtures should be talked about in terms of activity anyway, instead of concentration.

396, 467 and Figure 5. To be honest there does not seem to be much of a trend of γ_{SO_4} with pH that can support the statements (line 396) “The reactive uptake coefficient was found to increase with increasing proton concentrations (decreasing pH), which is consistent with acid-catalyzed reactions between peroxides and dissolved SO_2 as measured in the bulk phase (Lind et al., 1987; Wang et al., 2019)” and in Line 467 “Increasing the condensed-phase acidity enhances the heterogeneous rate constant at low pH range.” The authors agree that there is a “weak dependence on pH” (467) but the statements quoted here read quite strong, so the text then reads somewhat contradictory. From Table S1, I see that the pH experiments are 17, 23-35 has corresponding γ_{SO_2} range of 3.1 – 4.6 e3. Are you sure the margins of error in the γ_{SO_2} measurements and E-AIM modeling (both Y and X direction) are not larger than +/- roughly 20% from the mean? I believe calibration uncertainty in SO_2 alone can get you there, not to mention acid estimations that are notoriously difficult and can be off by orders of magnitude. I don’t doubt that in reality there may be a weak dependence, but I mainly want to see statements backed up by the data. Please (1) add uncertainty bars to figures, (2) temper the statements to say “may enhance” or “was found to weakly increase”, and (3) acknowledge that within uncertainties, there may not be an observable trend here. I applaud the authors for acknowledging that they cannot fully explain pH trends, as there is a lot going in aerosol particles and we don’t know what we don’t know.

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