Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-58

Anonymous Referee #2

Referee comment on "Acidity and the multiphase chemistry of atmospheric aqueous particles and clouds" by Andreas Tilgner et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-58-RC2, 2021

The paper at hand by Tilgner and co-workers is a review on acidity in the atmosphere, focusing on aspects of multiphase chemistry in aerosols and clouds. The comprehensive review is for the most part well-written and explains basic and complex concepts well. The author line comprises experts in the field. The topic of this review paper is ever-topical and relevant for the Atmospheric Sciences and thus a great fit for ACP. I can recommend publication after the below comments, provided together with some editing suggestions, are addressed.

Specific Comments

- l. 62, 64 – “phosphorus”
- l. 67-70 – Sentence structure is a bit unclear.
- Figure 1 – Use of the arrow labels “+H^+” and just “H+” does not seem consistent. SOA reactivity should be acid-catalyzed, so without “+”, phosphates should react quantitatively, so “+H^+”. RCOO- protonation should be “+H^+” etc.
- l. 81 – “typical” should be written with lower case t.
- l. 82 - consider using different dashes or the word "to" for the indicated pH ranges
- l. 89-91 – sentence has too many “and”, please revise for readability
- l. 97-99 – partitioning is a two-way process, so it’s not clear why evaporation / back transfer is singled out here.
- l. 102 – “aqueous phase”
- l. 152 – I suggest “on” should be “for”
- l. 156 – “acidity-dependent”
- l. 165 – please clarify use of the word “efficient”, which usually means high outcome for low effort/expense
- l. 166 – “as long as the LWC does not limit the uptake”: it is unclear what “limiting” means here. This should probably mean “solely limiting”? From Fig. 2, it seems that the parameter LWC is always influential, unless X is already 1. In turn, it is never uninfluential (which would be marked by vertical isolines), thus always “limiting”? Same with “restrict” in line 172.

- l. 172 – Please define "typical aerosol conditions" in analogy to your definition of cloud/fog conditions.
- l. 222-223 – The use of different significant digits for pKa and pH here is rather confusing.
- l. 234-234 – "very high and very low acidity conditions show significantly increased buffering capacities": I am not entirely sure what is referred to here. I think it might be worthwhile explaining the black dashed and solid lines in Fig. 3 here (and why they are dashed or solid, respectively).
- Figure 5 – This figure is very busy and difficult to disentangle for the reader. I believe the mention of "blue text" for microphysical processes is missing from the caption. The distinction of molecules (small grey spheres) and particles (small light red spheres) is somewhat difficult to spot. What happens to the small spheres inside the bottom large cloud droplet, labelled "aqueous phase acid production"? What is indicated by the different colors of arrows?
- l. 302 – "anthropogenic primary sources of acidic and alkaline aerosols (see Fig. 5)": where can this be seen in Fig. 5?
- l. 316 – It might be beneficial to briefly explain the concept of "less acid displacement" or at least add "due to" and omit parenthesis.
- Figure 6 – "Total S(IV) rate with and without taking into account ionic strength at the maximum reported limit is shown": Please indicate which line corresponds to which number. The complex figure is overall not much discussed in the text, panels b and c seem not mentioned. Please make clear how and why this figure is different to Fig. 7 and why it is needed in this complexity. What is the dashed line in panel b? Why do lines not add up to the black dashed line in panel c?
- l. 409 – Please clarify what k' refers to.
- l. 414 – "kinetics"
- l. 468 – It seems there is a word missing before "of".
- l. 498-502 – Please revise overly long and complex sentence with multiple sub clauses, missing commas and maybe missing words ("of" in line 500?).
- l. 535 – "thus" is superfluous here.
- l. 586 – It is not clear what "artifact HONO" is, please clarify.
- l. 590-591 – "via this mechanism": I think this has to be explained in slightly more detail. I presume adduct formation effectively reduces the concentration of SO2, hereby limiting potential for S(VI) formation? Please also state how "under environmental conditions" are important here, which is not clear to the reader.
- l. 594 – The reduction potential of HSO3- needs to be referenced to another compound, I assume this is the SO3- radical here. Would this reduction potential not be pH-dependent and lower at higher pH, thus confirming a fast reaction rate at high pH? Thus, please add reduction potentials for the SO3-*/SO3^(2-) pair for comparison. In which pH range would the SO3-*/SO3^(2-) potential be important? See also next comment.
- l. 598 - "which is not supported by thermodynamic models". Please give a reference or clearly state inputs/outputs, model etc. How much of a difference are we talking here? Can you state the numbers that Cheng et al. assume, the numbers that models return and potentially provide measurement data?
- Figure 7 – The colors of CH3C(O)OOH and HNO4 are indistinguishable in my digital version of the manuscript.
- l. 645: "artificially low H2O2 concentrations" – I might have missed this in the paper, but can you provide references for more appropriate H2O2 concentrations? What exactly is "artificial" about the concentration used in that paper?
- l. 645: Why can the Clifton et al. (1988) data not be used, what is "unrealistically fast" and why?
- l. 673-675 – This sentence is not clear. I suppose reactive halogens are a sink for nitrogen oxides? That is hard to understand here, please revise.
- l. 731 – "constants" (plural)
- l. 758 – Please define "DOM".

- l. 772-785 – Aldehydes and ketones are not the only carbonyl compounds in the atmosphere, please revise.
- l. 811 – "H3O+ ion": This review might benefit from a systematic treatment of H+ / H3O+. Usage of H3O+ here, while in other places "H+" was used, suggests that the water molecule is important here, is that the case?
- l. 820 – Please indicate to what process "hydrolysis" refers to here.
- l. 842 – "The impact of acidity and its feedback […] performed at TROPOS." Please provide references here and in the entire following paragraph unless this is original research conducted for this paper.
- l. 867 – Please clarify for me the difference of "acid-driven" and "require acidity". Does the latter mean that participation of a proton occurs in a reaction that is not rate-limiting?
- l. 885 – I believe there is a redundant instance of "which has been discussed in more detail for acetaldehyde, glyoxal as well as methylglyoxal".
- l. 900 – "occurs"
- l. 920 – It is not clear what is meant with "the nitrogen nucleophile is more important than the acid-catalyzed aldol condensation", because one is functional group/property, the other one is a type of chemical reaction.
- l. 922 – I suppose "conduct" should read "conducted"
- l. 925 – What does "difficulty for ammonium addition" mean here?
- l. 927 – "due to higher concentrations": What species is referred to here? "Higher" compared to what? The entire paragraph is rather condensed and hard to understand. It is not always clear when aldol addition and when aldol condensation is referred to.
- l. 929 – "All in all, aldol condensations are today generally regarded as demanding to drastically acidic conditions to be really important in particle and multiphase chemistry." This un-referenced statement seems out of place as most studies in the paragraph seem to show an increased formation rate with increasing pH and l. 900 "aldol condensation only occur at a pH = 4-5", please clarify.
- l. 972 – Which "oxidation" is referred to here?
- l. 1049 – It is not clear what is meant by "Similar to the gas phase radical (…)", please revise.
- Sect. 5.4.2.2 – Could you give a reason for the increased reactivity of NO3 with deprotonated acids? I presume a higher electron density changes the reduction potential. Can this be proven using tabulated values?
- l. 1200 – "This higher reactivity can be explained by the higher electron-withdrawing properties of the carboxylate." – Should this not be the "less electron-withdrawing properties of the carboxylate" (compared to the carboxylic acid)? I would expect the –I effect to be smaller for the negatively charged group. This is also stated in l. 1208: "From inductive effect theory, it is known that the COOH group is electron-withdrawing and COO- is electron-donating."
- l. 1207-1208 – "The deprotonation likely leads to a reduction in the electron density at the carbon-carbon double bond enabling an easier O3 addition, i.e. a more rapid oxidation." – Should this not read "increase in the electron density"? See argument in the previous comment.
- l. 1368 – The term "aqSOA" is not defined in this manuscript.
- l. 1375 – One occurrence of "organic" seems redundant.