

We thank reviewer#1 for the many constructive comments and suggestions which, we think, helped a lot to improve the manuscript. In the following, we provide a point-by-point response to all comments. In order to improve readability, we numbered each reviewer comment and its corresponding response in the style R1-C1 for reviewer comments (C1 means comment 1 of reviewer 1) and R1-A1 for answers to the reviewer comment (A1 means answer to comment 1 of reviewer 1), respectively. Comments by the reviewer are given in black normal font, and our response to the comments is shown in blue. Newly added and modified text in the revised manuscript and supporting information (SI) is given in *italics*. Finally, we would like to mention that the manuscript was checked by an EPA internal review which also caused certain small changes in the revised manuscript (please see the manuscript with tracked changes).

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**RC1:** 'Comment on acp-2021-58', Anonymous Referee #1, 27 Feb 2021

This review article written by Tilgner et al. nicely summarizes the fundamentals and recent literature on how acidity affects chemical partitioning and reactions occurring in the atmospheric aqueous phases. The topic is important and timely. The review covers all the important aspects of this topic, and the manuscript is extremely carefully written. I strongly recommend publication in ACP. I only have a number of minor comments listed below.

Minor comments

**R1-C1:** A class of aqueous-phase reactions that are strongly pH-dependent is hydrolysis. Hydrolysis can be a major fate of many environmental pollutants in aquatic chemistry. While the manuscript contains a few discussions related to hydrolysis (e.g., sections 5.2.3 and 5.3), I suggest the authors considered having a section to systematically discuss hydrolysis. E.g., what functional groups can undergo hydrolysis and how; pH-dependence; the importance of hydrolysis in the atmosphere compared to other reactions already described in the manuscript.

**R1-A1:** We fully agree with the reviewer that hydrolysis processes can be strongly pH-dependent and an important tropospheric multiphase process. Therefore, hydrolysis processes and their pH-dependency were already comprehensively discussed in former reviews, e.g., by Herrmann et al. (2015), Ng et al. (2017) and Brüggemann et al. (2020). As a consequence, hydrolysis processes are not explicitly treated in the present paper and only addressed in sections 5.2 and 5.3. However, according to the reviewer's comment, we have looked again through our manuscript and included some links to the aforementioned papers in sections 5.2 and 5.3. The revised manuscript now refers the reader more directly to the comprehensive reviews for a more detailed overview on this specific topic.

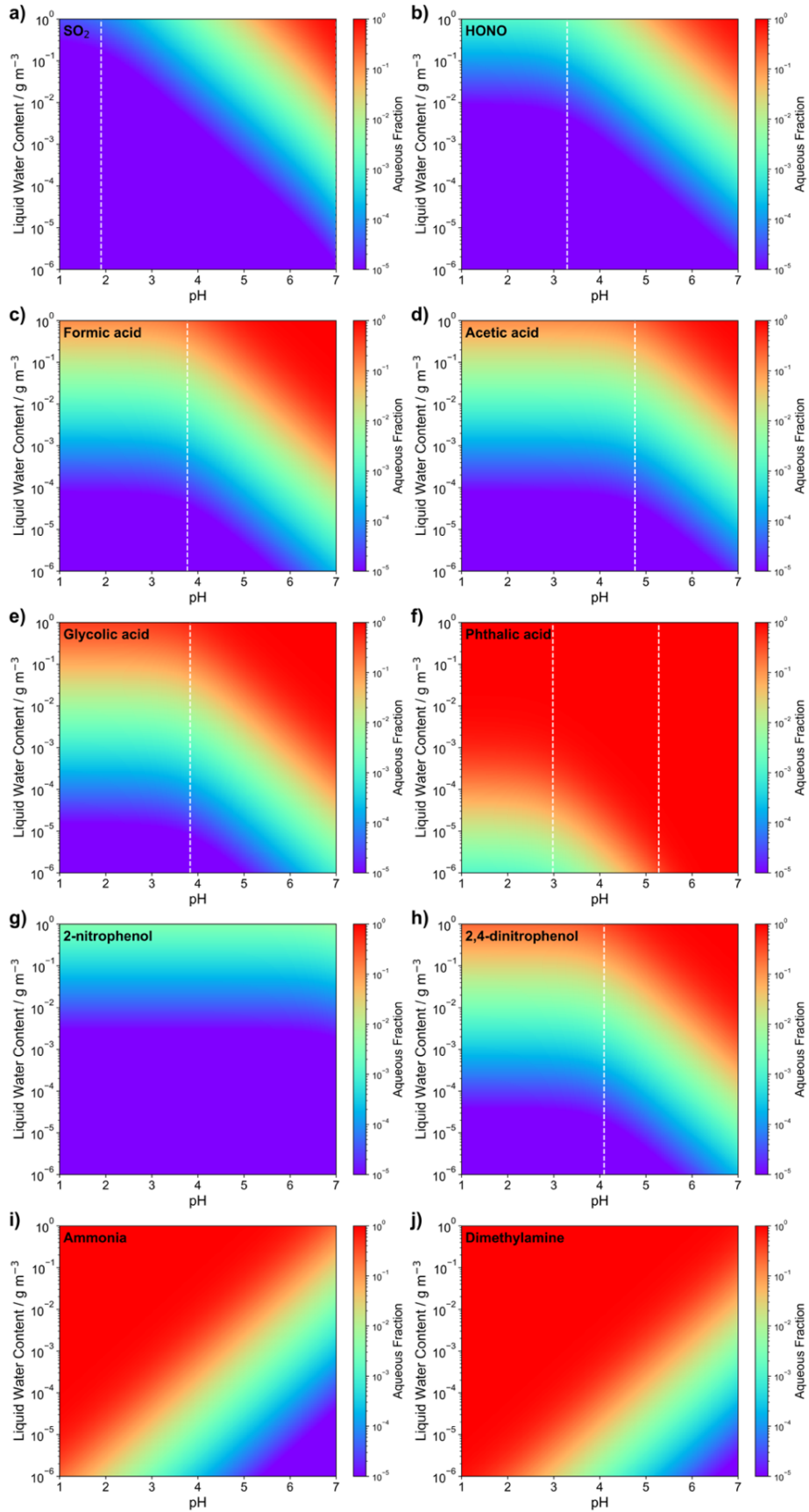
The revised text parts are as follows:

*"For further specific details on organic accretion reactions and other linked important pH-dependent reactions of organic compounds, such as hydrolysis reactions, please see Larson and Weber (1994) Herrmann et al. (2015), Zhao et al. (2016), Ng et al. (2017) and Brüggemann et al. (2020) and references therein."*

*"Both the formation and the hydrolysis of esters are slow processes under tropospheric conditions (see Herrmann et al. (2015) for further details). Moreover, the hydrolysis rate of esters will increase with increasing acidity (Mabey and Mill, 1978; Herrmann et al., 2015)."*

**R1-C2:** Figure 2-f. I suggest the authors added pKa2 for phthalic acid. I wonder why the aqueous fraction (XAaq) does not immediately increase at the pKa1 (~3) of phthalic acid? This trend seems to be different from the other monoacids.

**R1-A2:** We thank the reviewer for this careful look at the Figure. In fact, there was a problem in the GNU PLOT script of phthalic acid. Thus, this Figure 2 was revised and for Figure 2-f the missing  $pK_{a2}$  value was added. The revised Figure 2 is now as follows:



**R1-C3:** Figure 7a) and b) - the kinks on the total S(IV) oxidation rates at pH 5 appear very unnatural, and there are no explanations provided. My understanding is that the figure is based on the recommended S(IV) oxidation by Fe(III), as indicated in equation 11. I recommend that the authors explain why the Fe(III) oxidation drastically loses importance at pH > 5.

**R1-A3:** We thank the reviewer for the comment. In fact, the S(IV) oxidation rates appear a bit unnatural. For Figure 7, we have applied the recommended S(IV) oxidation by Fe(III) of Hoffmann and Calvert (1985) reported in equation 11b. This rate expression is only valid for pH conditions < 5 causing this unnatural pattern. However, the efficiency of iron(III)-catalyzed oxidation of S(IV) to S(VI) strongly depends on speciation of iron(III), i.e., the concentration of inorganic and organic complexing agents (Deguillaume et al. (2005)) which was not considered in the rate inter-comparison. At higher pH values, the  $pK_a$  values of important complexing agents are exceeded. So, they are present in their dissociated form enabling to a stronger iron(III) complexation and inhibiting the iron-catalyzed S(IV) oxidation. This strong inhibiting effect on iron(III)-catalyzed S(IV) oxidation is well-known for example for organic acids such as oxalate (see e.g. Grgić et al. (1998)). Thus, the iron(III)-catalyzed S(IV) oxidation drastically loses importance at pH > 5 ( $pK_a$  values of organic acids are typically < 5).

Based on the reviewer suggestion, the manuscript text was extended to better explain the pattern in Figure 7a) & b) and to explain why the iron(III)-catalyzed S(IV) oxidation drastically loses importance at pH values above 5 in atmospheric solutions where substantial amounts of dissolved organic matter are ubiquitous and a stronger partitioning of dissociating organic compounds occurs.

The revised description and discussion of Figure 7 in the text now reads as follows:

*“For diluted aqueous solution (cloud) conditions, the S(IV) oxidation by dissolved  $H_2O_2$ ,  $O_3$ ,  $HNO_4$  and potentially the iron-catalyzed pathway are the most important oxidation pathways (see Fig. 7c and 7d). The reaction with dissolved  $H_2O_2$  is the major oxidation pathway under acidic cloud conditions. Under less acidic cloud conditions (pH > 5), the other reaction pathways are able to contribute significantly to the S(VI) formation. Fig. 7 also displays that the oxidation rates of other oxidants such as  $NO_2$ , excited triplet states of photosensitizers ( $PS^*$ ) and organic hydroperoxides ( $CH_3COOH$ ,  $CH_3C(O)OOH$ ) are unimportant under cloud conditions mainly because of their low in-cloud concentrations.*

*Differently, under more concentrated aqueous solution conditions (haze and deliquesced aerosol), the molar concentrations of TMIs are significantly higher. Thus, the contributions of TMI-catalyzed S(IV) oxidation pathways are elevated against cloud conditions. From the calculation output in Fig. 7a and 7b, it can be seen that the S(IV) oxidation by dissolved  $H_2O_2$  is still predominant below pH  $\leq$  3. However already at quite low acidity conditions with pH  $\approx$  3.5, the TMI-catalyzed pathways can become the main oxidation route for S(IV). Note that the synergistic rate of Ibusuki and Takeuchi (1987) (Eq. 13) were not included in the current study, so even higher contributions of TMI-catalyzed S(IV) oxidation pathways can be possible. Moreover, it should be noted that the S(IV) oxidation rates in Fig. 7a and 7b appear a bit unnatural because of the applied constants of the S(IV) oxidation by Fe(III) (Hoffmann and Calvert, 1985) reported in Eq. 11b. This rate expression is only valid for pH conditions < 5. However, the efficiency of iron(III)-catalyzed oxidation of S(IV) to S(VI) strongly depends on speciation of iron(III), i.e., the concentration of inorganic and organic complexing agents (Deguillaume et al. (2005)) which is not considered in the rate inter-comparison. At higher pH values, the  $pK_a$  values of important complexing agents are exceeded. Accordingly, these compounds will be present in their dissociated forms enabling to a stronger iron(III) complexation and inhibiting the iron-catalyzed S(IV) oxidation. This strong inhibiting effect on iron(III)-catalyzed S(IV) oxidation is well-known for example for organic acids such as oxalate (see e.g. Grgić et al. (1998)). Thus, the iron(III)-catalyzed S(IV) oxidation becomes less important at pH > 5 as many  $pK_a$  values of organic acids are typically < 5.*

*Fig. 7a and 7b shows that besides the TMI-catalyzed S(IV) oxidation pathways, also S(IV) oxidations by dissolved  $HNO_4$  and  $O_3$  as well as, to some extent,  $PS^*$  can be important under polluted haze and rural aerosol conditions when pH is above pH > 5, respectively. Importantly, the current comparison clearly shows that the  $NO_2$ -driven S(IV) oxidation route even under very high  $NO_x$  conditions (66 ppb) applied*

*in the urban haze case still remains of minor importance. Only by the combination of applying unusually high aerosol pH values, artificially low H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> concentrations as well as unrealistically fast kinetic parameters from earlier studies by Clifton et al. (1988) (see subsection 4.5 above), NO<sub>2</sub> rates can fall into the range of other key oxidants discussed here (see (Cheng et al., 2016)). In detail, the used H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> concentrations of 0.01 ppb and 1 ppb used by (Cheng et al., 2016) for urban haze conditions are far too low. Recent measurements of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> concentrations under haze conditions in the North China Plain (Ye et al., 2018a; Ye et al., 2021) showed substantially higher values of about 0.5 ppb and 10 ppb, respectively.*

*In conclusion, the outcomes of this comprehensive comparison are in agreement with findings of isotope field investigations (see e.g., Harris et al. (2013); Au Yang et al. (2018); He et al. (2018); Shao et al. (2019); Li et al. (2020)) which have implicated that mainly H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and TMI-catalyzed pathways are responsible for the S(IV) to S(VI) conversion in atmospheric aqueous-phase cloud and aerosol solutions. However, due to the uncertainties still existing with regard to kinetics and mechanisms further acidity-dependent investigations appear warranted. "*

**R1-C4:** Line 1207 "The deprotonation likely leads to a reduction in the electron density at the carbon-carbon double bond enabling an easier O<sub>3</sub> addition, i.e. a more rapid oxidation. From inductive effect theory, it is known that the COOH group is electron-withdrawing and COO<sup>-</sup> is electron-donating. Thus, the obtained behavior is feasible." - This couple of statements seem to be conflicting with each other. Please clarify.

**R1-A4:** This was an error in the text. Of course, the deprotonation leads to an increase in the electron density. The manuscript was revised and reads now as follows:

*"For saturated carboxylic acids, carboxylates demonstrate roughly a factor of 10 higher reactivity towards O<sub>3</sub> as compared to the protonated acids. This higher reactivity can be explained by the higher electron-donating properties of the carboxylate. Therefore, BDEs of the carbon-bonded H-atoms are smaller making the H atoms more easily abstractable. Furthermore, ETR can also occur."*

*"The deprotonation likely leads to an increase in the electron density at the carbon-carbon double bond enabling an easier O<sub>3</sub> addition, i.e. a more rapid oxidation. From inductive effect theory, it is known that the COOH group is electron-withdrawing and COO<sup>-</sup> is electron-donating. Thus, the obtained behavior is feasible."*

**R1-C5:** Line 1246 "Please note that the overall second order reaction rate constants consider the dissociation speciation of the carboxylic acids but not their effective solubility. Thus, the overall chemical reaction rate will depend on both the aqueous oxidant concentration and on the total aqueous compounds concentration. The latter largely depends on the microphysical conditions present." - I agree with the author's statements. Can they comment on how important O<sub>3</sub> and NO<sub>3</sub> oxidation reactions are, considering their relatively small Henry's law constant? Or may their Henry's law constants are not so small?

**R1-A5:** This subsection was intended to illustrate the pH-dependency of the overall rate constant based on several examples. The reviewer questions regarding the importance of the different radical oxidants is well justified. However, besides the solubility (Henry's law constant) also the gas-phase oxidant concentration is important in order to judge whether an oxidant is crucial or not. Moreover, these concentrations strongly depend on the environment.

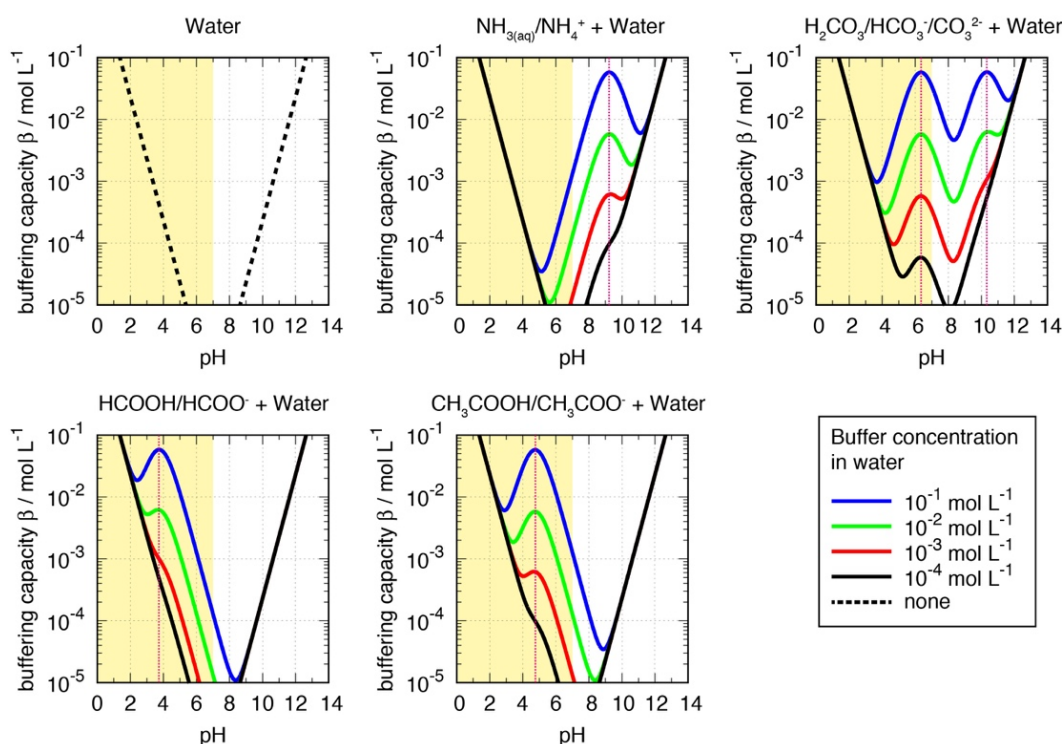
Because of the acidity focus of this review, we have not accentuated on the oxidant importance topic in this review and the comparison of different oxidants. However, former studies did this already, please see Tilgner & Herrmann (2010) and Schöne & Herrmann (2014). Moreover, kinetic reviews by Herrmann et al. (2010) and Herrmann et al. (2015) reported already that aqueous-phase concentrations of OH and NO<sub>3</sub> are quite similar but the aqueous-phase concentration of ozone is typically 5 order of magnitude higher. So, the lower reactivity of ozone can be fully compensated.

Therefore, Herrmann et al. (2015) concluded already that “O<sub>3</sub> reaction rate constants have to be on the order of about 10<sup>3</sup>–10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup> to be competitive with chemical conversions initiated by OH radicals”. We hope this is addressing this specific well-taken reviewer comment.

Technical comments

**R1-C6:** Figure 4. Can the authors consider adding pK<sub>a</sub> values of each compound, in a similar manner as in Figure 2?

**R1-A6:** We thank the reviewer for this valuable comment and we agree that the addition of the pK<sub>a</sub> values much improves the interpretation and the applicability of the buffering capacity plots. Accordingly, we have included the pK<sub>a</sub> values of each buffer compound with a purple dashed line and updated the caption of Figure 4. The revised Figure 4 and corresponding caption is as follows:



**Figure 4.** Buffering capacity  $\beta$  of water, ammonia/ammonium and carbonate/bicarbonate/carbonic acid (top: from left to right) as well as formic and acetic acid (bottom: from left to right) as a function of pH. The atmospherically relevant range of cloud and aerosol pH is marked in yellow, and the pK<sub>a</sub> values of the corresponding buffers are marked with dotted pink lines.

**R1-C7:** Figure 5 caption. The authors defined the red text and green text in the figure, leaving the blue ones unexplained. Maybe add that blue text describes physical changes of droplets?

**R1-A7:** The reviewer is right. We have added an explanation to the caption which reads now as follows:

“Figure 5. Schematic of sources (red text) and conditions of acidity in different aqueous aerosol particles (green text) together with microphysical and chemical processes that are able to influence the acidity of tropospheric aerosols (Fig. created after Raes et al. (2000) and McMurry (2015)). The blue text describes microphysical processes of CCNs and cloud/fog droplets. The dashed gray line represents an aerosol number size distribution based on McMurry (2015).”

**R1-C8:** Line 358 - "sulfate oxidation" should be "S(IV) oxidation"

**R1-A8:** The reviewer is right. The text has been revised.

**R1-C9:** Line 572 - "newly kinetically analyzed for the present review" sounds awkward. Please rephrase.

**R1-A9:** The sentence was rephrased and reads now as follows:

*"For this review, the kinetic data of Spindler et al. (2003) have been again kinetically analyzed in more detail."*

**R1-C10:** Line 599 - Lee and Schwartz 1983 the citation format is inconsistent.

**R1-A10:** The citation format has been changed.

**R1-C11:** Line 796 - extra "." at the end

**R1-A11:** The extra "." was removed.

**R1-C12:** Line 802 - "substituted organic acid" - should it be "substituted aldehyde"?

**R1-A12:** We thank the reviewer for carefully reading our manuscript and finding this typo. Accordingly, "substituted organic acid" has been replaced by "substituted aldehyde or ketone". The revised sentence reads:

*"In general, the hydration constants  $K_{hyd}$  decrease with decreasing electron-withdrawing power of the substituent in a substituted aldehyde or ketone (Clayden et al., 2012)."*

**R1-C13:** Line 820 - "hydrolysis" should be "hydration"

**R1-A13:** "hydrolysis" was replaced by "hydration".

**R1-C14:** Figure 12 caption - This caption uses "Fig. XX", while others all use "Figure XX"

**R1-A14:** The formatting was revised.

**R1-C15:** Line 886 - the phrase "which was discussed in more detail for acetaldehyde, glyoxal, as well as methylglyoxal" is repeated.

**R1-A15:** The repeated part was removed.

**R1-C16:** Line 908 - "On the one hand"

**R1-A16:** "On the one hand," was replaced by "On one hand,"

**R1-C17:** Line 917 - Li et al. 2019 - citation format is inconsistent.

**R1-A17:** The citation format has been revised.

**R1-C18:** Line 1065 - “Overall, the different contribution of ETR and H-abstraction pathways modify also the product distribution as a function of pH.” Does the author have any references for this statement?

**R1-A18:** This is a very good question. Actually, to the best knowledge of the authors, there is currently no detailed product study available on NO<sub>3</sub>-radical reactions of carboxylic acids that investigated the product distribution under different pH conditions. However, aqueous-phase H-abstraction reactions of an undissociated acid by NO<sub>3</sub> are expected to lead to a functionalization of the acid. This chemical fate is well-known from several OH studies where the H-abstraction channel is predominant (see e.g., Leitner and Doré (1997), Tan et al. (2012), Otto et al. (2017)). On the other hand, ETR reactions by SO<sub>4</sub><sup>-</sup> and NO<sub>3</sub>-radical leads to a decarboxylation of the acid (see Chawla and Fessenden (1975), and Exner et al. (1993)). This means, the ETR leads to a formation of CO<sub>2</sub> and a smaller carbon chain compound with one carboxyl group less. All in all, the products formed via the ETR and H-abstraction pathways are different.

Based on the well-taken reviewer hint, we have extended the discussion in the manuscript which reads now as follows:

*“On one hand, aqueous-phase H-abstraction reactions to leads mostly to a functionalization of the acid (see e.g., Leitner and Doré (1997); Tan et al. (2012); Otto et al. (2017)). On the other hand, ETR reactions of dissociated acids leads to a decarboxylation of the acid (Exner et al., 1994; Chawla and Fessenden, 2002) resulting in a formation of CO<sub>2</sub> and a smaller carbon chain compound.”*

**R1-C19:** Line 1138 - “Therefore, the statements of Zhao et al. (2016) regarding the pH dependence in the reactivity of saturated carboxylic acids are by far too overgeneralized)” - the same authors have a recent paper showing that larger organic acids indeed do not exhibit much pH dependence. Please cite. <https://doi-org.login.ezproxy.library.ualberta.ca/10.1021/acs.est.0c03331>

**R1-A19:** A sentence was added referring to this recent paper. The added sentence reads as follows:

*“For the sake of completeness, a more recent study by the same authors (Amorim et al., 2020) show that larger organic acids indeed do not exhibit much pH dependence.”*

**R1-C20:** Line 1190 - “due to of the”

**R1-A21:** “of ” has been removed.

**R1-C21:** Line 1249 - “depend” should be “depends”

**R1-A21:** “depend” was replaced by “depends”.

**R1-C22:** Line 1386 - Just wanted to double check if the authors have defined “OM”.

**R1-A22:** “OM” replaced by organic matter (OM).

## References:

Amorim, J. V., Wu, S., Klimchuk, K., Lau, C., Williams, F. J., Huang, Y., and Zhao, R.: pH Dependence of the OH Reactivity of Organic Acids in the Aqueous Phase, *Environ. Sci. Technol.*, 54, 12484-12492, <https://doi.org/10.1021/acs.est.0c03331>, 2020.

Au Yang, D., Bardoux, G., Assayag, N., Laskar, C., Widory, D., and Cartigny, P.: Atmospheric SO<sub>2</sub> oxidation by NO<sub>2</sub> plays no role in the mass independent sulfur isotope fractionation of urban aerosols, *Atmos. Environ.*, 193, 109-117, <https://doi.org/10.1016/j.atmosenv.2018.09.007>, 2018.

Brüggemann, M., Xu, R., Tilgner, A., Kwong, K. C., Mutzel, A., Poon, H. Y., Otto, T., Schaefer, T., Poulain, L., Chan, M. N., and Herrmann, H.: Organosulfates in Ambient Aerosol: State of Knowledge and Future Research Directions on Formation, Abundance, Fate, and Importance, *Environ. Sci. Technol.*, **54**, 3767-3782, <https://doi.org/10.1021/acs.est.9b06751>, 2020.

Chawla, O. P., and Fessenden, R. W.: Electron spin resonance and pulse radiolysis studies of some reactions of peroxy sulfate (SO<sub>4</sub>.1,2), *J. Phys. Chem.*, **79**, 2693-2700, <https://doi.org/10.1021/j100591a020>, 2002.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Sci. Adv.*, **2**, e1601530, <https://doi.org/10.1126/sciadv.1601530>, 2016.

Clayden, J., Greeves, N., and Warren, S.: *Organic Chemistry*, 2 ed., Oxford University Press, Oxford, 2012.

Clifton, C. L., Altstein, N., and Huie, R. E.: Rate constant for the reaction of nitrogen dioxide with sulfur(IV) over the pH range 5.3-13, *Environ. Sci. Technol.*, **22**, 586-589, <https://doi.org/10.1021/es00170a018>, 1988.

Deguillaume, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., and Chaumerliac, N.: Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters, *Chem. Rev.*, **105**, 3388-3431, <https://doi.org/10.1021/cr040649c>, 2005.

Exner, M., Herrmann, H., and Zellner, R.: Rate constants for the reactions of the NO<sub>3</sub> radical with HCOOH/HCOO<sup>-</sup> and CH<sub>3</sub>COOH/CH<sub>3</sub>COO<sup>-</sup> in aqueous solution between 278 and 328 K, *J. Atmos. Chem.*, **18**, 359-378, <https://doi.org/10.1007/bf00712451>, 1994.

Grgić, I., Dovžan, A., Berčič, G., and Hudnik, V.: The Effect of Atmospheric Organic Compounds on the Fe-Catalyzed S(IV) Autoxidation in Aqueous Solution, *J. Atmos. Chem.*, **29**, 315-337, <https://doi.org/10.1023/a:1005918912994>, 1998.

Harris, E., Sinha, B., van Pinxteren, D., Tilgner, A., Fomba, K. W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., and Herrmann, H.: Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO<sub>2</sub>, *Science*, **340**, 727-730, <https://doi.org/10.1126/science.1230911>, 2013.

He, P. Z., Alexander, B., Geng, L., Chi, X. Y., Fan, S. D., Zhan, H. C., Kang, H., Zheng, G. J., Cheng, Y. F., Su, H., Liu, C., and Xie, Z. Q.: Isotopic constraints on heterogeneous sulfate production in Beijing haze, *Atmos. Chem. Phys.*, **18**, 5515-5528, <https://doi.org/10.5194/acp-18-5515-2018>, 2018.

Herrmann, H., Hoffmann, D., Schaefer, T., Brauer, P., and Tilgner, A.: Tropospheric aqueous-phase free-radical chemistry: radical sources, spectra, reaction kinetics and prediction tools, *ChemPhysChem*, **11**, 3796-3822, <https://doi.org/10.1002/cphc.201000533>, 2010.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase, *Chem. Rev.*, **115**, 4259-4334, <https://doi.org/10.1021/cr500447k>, 2015.

Hoffmann, M. R., and Calvert, J. G.: Chemical transformation modules for eulerian acid deposition models, v2, the aqueous-phase chemistry, EPA/600/3-85/017, US Environmental Protection Agency, Research Triangle Park, NC, 1985.

Ibusuki, T., and Takeuchi, K.: Sulfur-Dioxide Oxidation by Oxygen Catalyzed by Mixtures of Manganese(II) and Iron(III) in Aqueous-Solutions at Environmental Reaction Conditions, *Atmos. Environ.*, **21**, 1555-1560, [https://doi.org/10.1016/0004-6981\(87\)90317-9](https://doi.org/10.1016/0004-6981(87)90317-9), 1987.

Larson, R. A., and Weber, E. J.: *Reaction Mechanisms in Environmental Organic Chemistry*, Lewis Publishers CRC Press, Boca Raton, Florida, 1994.

Leitner, N. K. V., and Doré, M.: Mécanisme d'action des radicaux OH sur les acides glycolique, glyoxylique, acétique et oxalique en solution aqueuse: Incidence sur la consommation de peroxyde d'hydrogène dans les systèmes H<sub>2</sub>O<sub>2</sub>/UV et O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, *Water Res.*, **31**, 1383-1397, [https://doi.org/10.1016/s0043-1354\(96\)00122-4](https://doi.org/10.1016/s0043-1354(96)00122-4), 1997.

Li, J., Zhang, Y. L., Cao, F., Zhang, W., Fan, M., Lee, X., and Michalski, G.: Stable Sulfur Isotopes Revealed a Major Role of Transition-Metal Ion-Catalyzed SO<sub>2</sub> Oxidation in Haze Episodes, *Environ. Sci. Technol.*, **54**, 2626-2634, <https://doi.org/10.1021/acs.est.9b07150>, 2020.

Mabey, W., and Mill, T.: Critical-Review of Hydrolysis of Organic-Compounds in Water under Environmental-Conditions, *J. Phys. Chem. Ref. Data*, **7**, 383-415, <https://doi.org/10.1063/1.555572>, 1978.

McMurry, P. H.: AEROSOLS | Observations and Measurements, in: *Encyclopedia of Atmospheric Sciences (Second Edition)*, edited by: North, G. R., Pyle, J., and Zhang, F., Academic Press, Oxford, 53-65, <https://doi.org/10.1016/B978-0-12-382225-3.00048-7>, 2015.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J.,



- and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, *Atmos. Chem. Phys.*, **17**, 2103-2162, <https://doi.org/10.5194/acp-17-2103-2017>, 2017.
- Otto, T., Stieger, B., Mettke, P., and Herrmann, H.: Tropospheric Aqueous-Phase Oxidation of Isoprene-Derived Dihydroxycarbonyl Compounds, *J. Phys. Chem. A*, **121**, 6460-6470, <https://doi.org/10.1021/acs.jpca.7b05879>, 2017.
- Raes, F., Van Dingenen, R., Vignati, E., Wilson, J., Putaud, J. P., Seinfeld, J. H., and Adams, P.: Formation and cycling of aerosols in the global troposphere, *Atmos. Environ.*, **34**, 4215-4240, [https://doi.org/10.1016/S1352-2310\(00\)00239-9](https://doi.org/10.1016/S1352-2310(00)00239-9), 2000.
- Schöne, L., and Herrmann, H.: Kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solutions, *Atmos. Chem. Phys.*, **14**, 4503-4514, <https://doi.org/10.5194/acp-14-4503-2014>, 2014.
- Shao, J. Y., Chen, Q. J., Wang, Y. X., Lu, X., He, P. Z., Sun, Y. L., Shah, V., Martin, R. V., Philip, S., Song, S. J., Zhao, Y., Xie, Z. Q., Zhang, L., and Alexander, B.: Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: air quality model assessment using observations of sulfate oxygen isotopes in Beijing, *Atmos. Chem. Phys.*, **19**, 6107-6123, <https://doi.org/10.5194/acp-19-6107-2019>, 2019.
- Spindler, G., Hesper, J., Brüggemann, E., Dubois, R., Müller, T., and Herrmann, H.: Wet annular denuder measurements of nitrous acid: laboratory study of the artefact reaction of NO<sub>2</sub> with S(IV) in aqueous solution and comparison with field measurements, *Atmos. Environ.*, **37**, 2643-2662, [https://doi.org/10.1016/S1352-2310\(03\)00209-7](https://doi.org/10.1016/S1352-2310(03)00209-7), 2003.
- Tan, Y., Lim, Y. B., Altieri, K. E., Seitzinger, S. P., and Turpin, B. J.: Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal, *Atmos. Chem. Phys.*, **12**, 801-813, <https://doi.org/10.5194/acp-12-801-2012>, 2012.
- Tilgner, A., and Herrmann, H.: Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM, *Atmos. Environ.*, **44**, 5415-5422, <https://doi.org/10.1016/j.atmosenv.2010.07.050>, 2010.
- Ye, C., Liu, P., Ma, Z., Xue, C., Zhang, C., Zhang, Y., Liu, J., Liu, C., Sun, X., and Mu, Y.: High H<sub>2</sub>O<sub>2</sub> concentrations observed during haze periods during the winter in Beijing: Importance of H<sub>2</sub>O<sub>2</sub> oxidation in sulfate formation, *Environ. Sci. Technol. Lett.*, **5**, 757-763, <https://doi.org/10.1021/acs.estlett.8b00579>, 2018.
- Ye, C., Chen, H., Hoffmann, E. H., Mettke, P., Tilgner, A., He, L., Mutzel, A., Brüggemann, M., Poulain, L., Schaefer, T., Heinold, B., Ma, Z., Liu, P., Xue, C., Zhao, X., Zhang, C., Zhang, F., Sun, H., Li, Q., Wang, L., Yang, X., Wang, J., Liu, C., Xing, C., Mu, Y., Chen, J., and Herrmann, H.: Particle-Phase Photoreactions of HULIS and TMI<sub>s</sub> Establish a Strong Source of H<sub>2</sub>O<sub>2</sub> and Particulate Sulfate in the Winter North China Plain, *Environ. Sci. Technol.*, <https://doi.org/10.1021/acs.est.1c00561>, 2021.
- Zhao, R., Lee, A. K. Y., Wang, C., Wania, F., Wong, J. P. S., Zhou, S., and Abbatt, J. P. D.: The Role of Water in Organic Aerosol Multiphase Chemistry: Focus on Partitioning and Reactivity, in: *Advances in Atmospheric Chemistry*, edited by: Barker, J. R., Steiner, A. L., and Wallington, T. J., *Advances in Atmospheric Chemistry*, Volume 1, World Scientific, Singapore, 95-184, [https://doi.org/10.1142/9789813147355\\_0002](https://doi.org/10.1142/9789813147355_0002), 2016.