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Manuscript Submission

Dear Prof. Keutsch:

Please find attached a revised manuscript “Hydroxyl radicals from secondary organic aerosol decomposition in water” by Tong et al. that we would like to submit for publication in ACP.

Two referee comments and one short comment were very helpful in improving the manuscript. All comments were addressed in detailed point-by-point response and implemented in the revised manuscript. In response to one comment by Referee 1 on isoprene SOA, we have conducted additional experiments with isoprene SOA, in collaboration with Prof. William Brune, who is added as a co-author. Upon extraction of isoprene SOA, we detected OH yields of around ~0.1%. An EPR spectrum of isoprene SOA has been added in Fig. 2, and data points for isoprene SOA has been also added in Fig. 4a and Fig. 7. The concentration dependence of OH production by isoprene SOA was also modelled (Fig. 4a).

We are confident that the revised manuscript meets the quality standards of ACP. In view of the very positive referee comments and discussion published in ACPD, we look forward to positive response from you.

Sincerely,

M. Shiraiwa

Manabu Shiraiwa

Response to the comments of Anonymous Referee #1

In this work the authors report OH radical observations in aqueous solutions of secondary organic aerosol in the absence of radiation. They postulate that organic hydroperoxides (ROOH) can decompose in water and form OH radicals. The formation rate of OH was enhanced in the presence of Fe^{2+}, following a Fenton-like mechanism to catalyze radical production. The manuscript is well written, and the experiments were carefully performed. I have a few minor comments, and recommend publication in ACP after these concerns are addressed.

Response:

We thank the referee for reviewing this manuscript and for providing positive comments. We respond to each comment in detail below.

Major comments:

How is the concentration of OH quantified? Since the major finding of this work is OH radical formation, it seems that the quantitation method should be clearly described and justified. It seems to me that the OH is estimated by fitting the EPR data (Supplement Figure S1). What is the sensitivity of the fitting to quantification? What are the detection limits, limit of detection, limit of quantification etc.? Are there standards for quantification? It is acceptable if no standards are available (since OH is very difficult to measure), but perhaps there are other methods (e.g. tracer method used by the Abbatt group in Toronto) for comparison? Given that OH is so difficult to measure, the authors should provide more evidence that their quantitation method is sound.

Response: We have described the method for radical quantification in section '2.2 CW-EPR spectroscopy' and in lines 10-22 of pg. 30022. We will add a paragraph giving details of the quantification method and the detection limit for clarification in the supplement:

"Briefly, peaks and a baseline of spectra were selected, followed by double integration of the peak intensity. Spin concentrations were calculated through the following equation (Eaton et al., 2010):

$$\mathrm{DI} = \mathrm{c} \cdot [G_R \cdot C_t \cdot \mathrm{n}] \cdot \left[\frac{\sqrt{P} \cdot B_m \cdot Q \cdot n_B \cdot S \cdot (S+1) \cdot n_S}{f(B_1, B_m)}\right]$$

where c = constant determined by a standard sample with known number of spins, G_R = Receiver gain, C_t = Conversion time, n = Number of scans, P = Microwave power (W), B_m = Modulation amplitude (Gauss), Q = Quality factor of resonator, n_B = Boltzmann factor for temperature dependence, S = Total electron spin, n_s = Number of spins, $f(B_1, B_m)$ = Spatial distribution of the microwave field and the modulation field, experienced by the sample. We calibrated this method using the stable radical TEMPOL and obtained a difference < 5% between the calculated and measured concentrations, confirming the reliability of the spin counting method. The absolute detection limit of number of spins in an EPR cavity (~20 μL) is estimated to be ~10^{12} spins, which translates to a detection limit of spin concentration of ~100 nM under our experimental conditions."

It was noted in the manuscript that the pH of SOA solution was in the range of of 4.8 – 6.4. In Fenton reaction, Fe^{2+} reacts with hydrogen peroxide to yield OH radical:
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH$
Can OH radical or OH ion generation be quenched under acidic condition? e.g.
$2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2\ H_2O$
What would be the pH effect for OH production from SOA? Will OH production be underestimated or overestimated in this paper, especially when the particle is inhaled into the lung where pH is around 7? (Richard and Francis, J Clin Invest. 1969)
Response: The referee is correct. Indeed the OH radical production can be influenced by the pH of solvent. We found that the formation of OH radicals was increased by ~20% at a pH of 7.4 using a phosphate-buffered saline solution. We have clarified this point and the potential role of pH in the revised manuscript. We intend to investigate pH effects on OH formation in more detail in follow-up studies.

The observation that ROOH (not HOOH or ROOR) decomposition leads to OH formation is interesting. Any speculations as to why ROOH preferentially decomposes? Also, the R group seems to be also important, since b-pinene forms more OH than a-pinene (and they are very similar). Also, why was isoprene SOA not studied? Isoprene SOA is known to contain a large amount of ROOH (Surratt et al., 2006) and is likely more important than terpene SOA.
Response: We speculate that an electron-donating R group within ROOH can promote the homolytic cleavage, as suggested in a previous study (Nam et al., 2000). We will clarify this point in the revised manuscript.
Isoprene SOA was more difficult to generate in our flow tube setup in relatively short reaction time with ozonolysis due to the low yield (Surratt et al., 2006). Recently, we have deployed a potential aerosol mass (PAM) chamber in collaboration with Prof. William Brune (Penn State Univ.; added as a co-author) and formed isoprene SOA from OH photooxidation in the PAM chamber. We found that isoprene SOA can also form OH radicals under dark conditions with a similar yield as terpene SOA. The spectra of isoprene SOA will be added to Fig. 2 and the OH concentrations formed by isoprene SOA will be added to Fig. 4a. First results of ongoing expe-

riments indicate a significant increase of OH yield with Fe^{2+} concentration, in line with the results on previously investigated precursors. The EPR spectra of the isoprene SOA show a dependence on the oxidant concentration level in the PAM chamber. The more complex behaviour of the isoprene SOA from OH photoxidation is under investigation and will be presented in a follow-up study.

The addition of Fe^{2+} leads to elevated OH concentrations, but the concentration of Fe^{2+} seems high relative to SOA for ambient particles. The mass ratios in aerosols are more likely to be around 0.01 to 0.1 (if we assume 10 ng/m3 of Fe and 1 ug/m^3 of SOA). Perhaps in cloud droplets, the ratios would be higher due to higher water content and therefore more soluble iron? I suggest adding some reference of ratio of organic to Fe in cloud droplets to clarify.

Response: Typical dissolved iron concentrations in cloud droplets are 0.1 – 2.5 µM (Deguillaume et al., 2005). The secondary organic compounds in cloud water also varies depending on the pollution levels and can be up to 1-2 mg L^{-1}, which equals to 5-10 µM by using 200 g mol^{-1} as the SOA molar weight. Hence the typical molar ratio between iron ions and secondary organic compounds in cloud water can be 0.01- 0.5, and the concentration ratios used in current study is in the reasonable range of real atmospheric situations.

Pg. 30027 line 7-11: The authors should be careful about making the hypothesis that the OH formation revealed in this study is analogous to autoxidation reactions.

From the cited studies, autoxidation reactions occur as a result of intramolecular reaction in the gas phase. These are favourable in the gas phase because the lifetimes of radicals are longer. The same type of mechanism is unlikely to happen in the condensed phase since the lifetimes of radicals are much shorter due to extensive quenching by other radicals. On the other hand, propagation of radicals is likely promoted by the higher concentrations. The authors should clarify that the hypothesized mechanisms are not similar.

Response: The referee is correct and raises an important point. Indeed, lifetime of radicals in the condensed phase may be shorter compared to the gas phase. However, recent studies have shown that some radicals are long-lived (Shiraiwa et al., 2011; Gehling and Dellinger, 2013) and they can be stabilized in the condensed phase by interacting with transition metals (Truong et al., 2010). It is also well-know that autoxidation can occur in the condensed phase (i.e., an apple turns brown). We will clarify these points in the revised manuscript.

- The link to oxidative stress in the lung lining fluid is very interesting. What is the formation rate of OH compared to clearance rate by the mucus in the airway?

Response: Due to the scavenging effect of antioxidants, the OH radical would have a chemical lifetime on the order of nanoseconds. It is not totally clear whether this lifetime is sufficiently long to cause oxidative damage to cells, but it is well-established that OH radicals play a critical role in oxidative stress and physiological processes despite of very short lifetime (e.g., Winterbourn, 2008).

Minor/Technical comments: Pg. 30026 line 20: "illustrated"

Response: Correction will be made.

Fig. 4: why is there an abrupt change in OH concentration when Fe^{2+}/SOA reaches a certain ratio for a-pinene and b-pinene, but not for limonene?

Response: The decrease of OH radical production with increasing Fe^{2+} concentration is supposedly induced by reaction of the BMPO-OH adduct with Fe^{2+} (Yamazaki and Piette, 1990). Destruction of BMPO-OH can be viewed as iron-catalysed reactions, as Fe^{2+} is constantly recovered in the presence of peroxides. Hence, at high $[Fe^{2+}]$/[SOA], destruction dominates over production. Such behaviour is more prominent for α–pinene and β–pinene SOA, due to higher concentrations of organic hydroperoxides. For limonene SOA, the OH production increased rather gradually with lower abundance of organic hydroperoxides, leading in return to a less prominent destruction of the BMPO-OH adducts by Fe^{2+}. We will clarify this point in the revised manuscript and supplement.

Pg. 30020 line 5: RH for naphthalene experiments is 30%. What about the other experiments?

Response: The other experiments were conducted under dry conditions. This will be clarified in the revised manuscript.

Pg. 30020 line 9: the typical size is 50-400 nm. Is that by number? What is the volume mode or median diameter?

Response: The typical size of the SOA ranged from 50 to 400 nm in the number size distribution. The median diameters of the mass size distribution were 100 – 200 nm. We will clarify it in the revised manuscript.

Pg. 30020 line 15: I assume 0-20 ppb of ozone is what was measured after the ozone denuders. A clarification is needed. Acknowledgements usually include funding information.

Response: A clarification for the '0-20 ppb' ozone is added as follows: Typically 0-20 ppb of ozone was measured after ozone denuders.

The funding information is added.

References:

Eaton, G. R., Eaton, S. S., Barr, D. P., and Weber, R. T.: Quantitative EPR, Springer Science & Business Media, 2010.

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, 2005.

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Gehling, W., and Dellinger, B.: Environmentally Persistent Free Radicals and Their Lifetimes in PM2.5, Environ. Sci. Technol., 47, 8172-8178, 2013.

Winterbourn, C. C.: Reconciling the chemistry and biology of reactive oxygen species, Nature Chem. Biol., 4, 278-286, 2008.

Nam, W., Han, H. J., Oh, S.-Y., Lee, Y. J., Choi, M.-H., Han, S.-Y., Kim, C., Woo, S. K., and Shin, W.: New insights into the mechanisms of OO bond cleavage of hydrogen peroxide and tert-alkyl hydroperoxides by iron (III) porphyrin complexes, J. Am. Chem. Soc., 122, 8677-8684, 2000.

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Truong, H., Lomnicki, S., and Dellinger, B.: Potential for Misidentification of Environmentally Persistent Free Radicals as Molecular Pollutants in Particulate Matter, Environ. Sci. Technol., 44, 1933-1939, 2010.

Response to the comments of Anonymous Referee #2

This paper demonstrates that interaction with water, especially in the presence of iron, leads to production of OH from secondary organic aerosol (SOA). The authors explain that this is reasonable because organic peroxides are a major component of secondary organic aerosol, and OH can be formed by decomposition of organic peroxides in water.

The science is sound and the results are important because they help to explain how condensed phase oxidation can lead to the aging of SOA in the atmosphere (both fragmentation and functionalization of compounds). This can change the O:C ratio and the mass of organic aerosol.

Response:

We thank the referee for review and positive comments. The point-by point responses are given below.

1. The authors discuss several reasons why the formation of OH radicals in wet particles might be important, including in the oxidation of sulfur dioxide to sulfuric acid. However, they miss one: water-soluble gases, such as aldehydes, can be taken up by wet particles and if there is sufficient OH present they can react to form low volatility products and (e.g., organic acids and oligomers). Thus SOA can form from gaseous precursors through aqueous phase reactions in wet aerosols, if sufficient oxidant is present (see work by Ervens, Turpin, Monod, and others). McNeill and Ervens both argue that this chemistry will be OH limited. Thus the availability of OH radicals in the condensed phase will aid that chemistry.

Response: Thanks for raising this important point. We will add a discussion on SOA formed through aqueous phase chemistry into the manuscript as follows:

Water-soluble gases such as aldehydes taken up by deliquesced particles may undergo reactions under presence of OH radicals to form low volatility products, including organic acids, peroxides, peroxyhemiacetals, and oligomers (Lim et al., 2010; Ervens et al., 2011; Liu et al., 2012; Ervens, 2015; Lim and Turpin, 2015; McNeill, 2015). Thus, the formed OH radicals would promote chemical aging of SOA especially in the presence of iron ions (e.g., SOA coated mineral dust particles) (Chu et al., 2014) and may also induce aqueous-phase oxidation of sulfur dioxide forming sulfuric acid (Harris et al., 2013).

2. The authors might also find the following recent ACP reference about organic peroxides and OH helpful: Lim, Y. B., and B. J. Turpin. "Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the aqueous phase and implications for aqueous OH." Atmospheric Chemistry and Physics 15.22 (2015): 12867-12877.

And this one about formation of oligomers from OH oxidation in wet aerosols (relevant to page on page 30027): Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys., 10, 10521– 10539, doi: 10.5194/acp-10-10521-2010, 2010.
Response: Yes, these reference papers are closely related to this work. We will include them in the revised manuscript. Please see the response above.

3. Figure 2 and first paragraph of results. The reader would benefit from more complete explanation of what is shown in Figure 2 and what it means.
Response: As explained in the third paragraph of the results and discussion session, Figure 2 shows EPR spectra of various samples of water extracts of SOA by α-pinene, β-pinene, limonene, and isoprene as well as field fine particles. The four peaks at specified positions are characteristics for OH radicals and the formation of OH radicals can be enhanced by Fe^{2+}. We have revised section 3 by adding more descriptions.

4. Bigger fonts are needed in the figures. The meaning of the shading in Figure 7 should be explained in the figure caption. Figure 8 – implications should include reactive uptake and SOA formation from oxidation of water-soluble gases.
Response: The fonts in most figures were enlarged and more description on the meaning of the shading in Figure 7 was added to the text. Regarding Fig. 8: this study has indeed important implications for reactive uptake and SOA formation from oxidation of water-soluble gases. However, we would like to keep Fig. 8 as simple as possible.

Response to short comment (SC) from Yongchun Liu

This paper investigates the generation of OH radicals when extracting SOA into water with the presence or absence of Fe^{2+} ions. This research is interesting.

Response:

We thank Yongchun Liu for the short comment and the positive evaluation of our work. Our detailed response to each comment will be shown in below.

P30025, l 14-17: The maximum values of OH formation efficiency appeared with similar ratios of $FeSO_4$ to SOA for β-pinene SOA and α-pinene SOA. Is there any explanation for this phenomenon since organic peroxides in the two types of SOA are different? What is the reason that OH formation efficiency decreased with high ratio of $FeSO_4$/SOA in the other two types of SOA? While the OH formation efficiency increased continuously in limonene SOA with increasing ratio of $FeSO_4$/SOA.

Response: Previous studies have shown that α–pinene and β–pinene SOA contain a high abundance of organic peroxides (Docherty et al., 2005; Badali et al., 2015). As shown and explained in the kinetic modelling (Sect. 2.4 and shaded area in Fig. 4), the decrease of OH radical production with increasing Fe^{2+} concentration is supposedly induced by reaction of the BMPO-OH adduct with Fe^{2+} (Yamazaki and Piette, 1990). Destruction of BMPO-OH can be viewed as iron-catalysed reactions, as Fe^{2+} is constantly recovered in the presence of peroxides. Hence, at high $[Fe^{2+}]$/[SOA], destruction dominates over production. Such behaviour is more prominent for α–pinene and β–pinene SOA, due to higher concentrations of organic hydroperoxides. For limonene SOA, the OH production increased rather gradually with lower abundance of organic hydroperoxides, leading in return to a less prominent destruction of the BMPO-OH adducts by Fe^{2+}. We will clarify this point in the revised manuscript and supplement.

P30025, l 26-30: What is the change trend of ([BMPO-OR]+[BMPO-OH]) and ([BMPOOR]/[BMPO-OH]) as a function of the ratio of $FeSO_4$/SOA. Does the pH of the solution affect ([BMPO-OR]/[BMPO-OH])?

Response: The trend of [BMPO-OR]+[BMPO-OH] was similar to that of [BMPO-OH] as shown in Fig. 4. This is because [BMPO-OR] is much smaller than [BMPO-OH], even though [BMPO-OR] increased upon increase of $FeSO_4$/SOA. We did not observe a clear trend in [BMPO-OR]/[BMPO-OH] and did not observe significant effects of pH on the ratio between organic and OH radicals. As quantification of organic radicals is not the focus and beyond the scope of this study, we intend to investigate these aspects in detail in follow-up studies.

P30026, l 12-13: How about the formation efficiency of BMPO-OH adduct by mixtures of tert-Butyl hydroperoxide with Fe^{2+}?

Response: We have not used tert-Butyl hydroperoxide, but tert-Butyl peroxide and cumene hydroperoxide. As shown in Fig. S5, tert-Butyl peroxide did not produce OH radicals even in the presence of Fe^{2+}. The production of the BMPO-OH adducts was similar to behaviour of terpene SOA. It increased up to certain Fe^{2+} concentrations, and decreased afterwards due to reaction of BMPO-OH adduct with Fe^{2+}.

P30027, l 2-4: The paper "Decreasing effect and mechanism of $FeSO_4$ seed particles on secondary organic aerosol in _-pinene photooxidation. Environmental Pollution, 193: 88-93" proposed that "The formed OH radicals would promote chemical aging of SOA especially in the presence of iron ions". This paper is quite relevant to the topic of this study and I urge the authors to compare the results with this paper.

Response: Thanks for pointing out this interesting paper. This work is indeed closely related to our work and we will refer to it in the revised manuscript.

References:

Yamazaki, I., and Piette, L. H.: ESR spin-trapping studies on the reaction of Fe^{2+} ions with H_2O_2-reactive species in oxygen toxicity in biology, J. Biol. Chem., 265, 13589-13594, 1990.