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Suppression of OH Generation from the Photo-Fenton Reaction in the Presence of α -Pinene Secondary Organic Aerosol Material

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ABSTRACT

Although Fenton and Photo-Fenton chemistry is thought to be an important source of OH in cloud and fog water, a high dissolved organic content, especially of secondary organic aerosol (SOA) material, may affect OH production from this mechanism. The relative production of OH was measured for Fenton and Photo-Fenton reactions with H_2O_2 and Fenton-like and Photo-Fenton-like reactions with α -pinene ozonolysis SOA material, under cloud water relevant conditions (5 μM iron, 45 μM H_2O_2 , and 1500 μM SOA). It is demonstrated that generation of OH radicals from Photo-Fenton chemistry can be significantly suppressed by addition of α -pinene SOA material, where the OH yield for solutions containing H_2O_2 and SOA material together was decreased by a factor of 6 compared to that when only H_2O_2 was present, likely due to complexation by carboxylic acids (such as pinonic acid). When SOA is examined without additional H_2O_2 present, OH is generated by Photo-Fenton chemistry but at a lower rate than for Photo-Fenton chemistry with H_2O_2 alone. Without taking into account this suppression by SOA material, generation of OH by Photo-Fenton chemistry may be overestimated. Furthermore, the suppression of Photo-Fenton chemistry in aqueous organic aerosol may be enhanced with greater SOA material concentration.

INTRODUCTION

Iron and hydrogen peroxide are routinely measured at micromolar to hundreds of micromolar levels in cloud and fog water,^{1–5} and consequently the Fenton reaction between iron(II) and hydrogen peroxide (H_2O_2) can be a significant source of hydroxyl (OH) radicals in the condensed phase.⁶ The Fenton reaction (Reaction 1) has been known since the late 1800's⁷ and has been used for many years as a technology to remove organic contaminants in water,^{8,9} but has only recently been investigated in atmospheric aerosols and cloud droplets.^{10–15} Fenton-like reactions have also been observed with small organic hydroperoxides (ROOH) in place of

H₂O₂¹⁰ under cloud droplet conditions and it has been proposed that larger, more complex organic hydroperoxides will also participate in this chemistry as shown below:

Organic hydroperoxides may produce either hydroxyl (OH) or alkoxy (RO) radicals (Reactions 2a and b). While for small hydroperoxides, methyl- and ethyl-hydroperoxide, the Fenton reaction favours the formation of the alkoxy radical,¹⁰ it is unknown whether larger, more complex hydroperoxides will also favour alkoxy radical formation. The presence of ultraviolet (UV) and visible light drives Photo-Fenton chemistry, which reduces iron(III) to iron(II), catalysing the Fenton reaction as well as producing additional OH radicals.^{16,17}

In ambient cloud droplets and aerosol particles which contain copper, iron(III) may also be reduced through redox coupling with copper(I), thereby providing a dark mechanism for recycling of iron(II) for the Fenton reaction.^{18,19}

Fenton and Photo-Fenton chemistry may also take place in aqueous aerosols as they can also contain the necessary precursors^{20,21} and in some cases may have higher concentrations of iron and hydrogen peroxide than in cloud droplets.²² The production of OH radicals from this chemistry provides an alternate route of oxidation within the condensed phase and can contribute to aerosol aging.

Secondary organic aerosol (SOA) material can be a significant component of ambient aerosol and of the organic content in cloud water.²³ When dissolved in the aqueous phase, SOA material can give rise to H₂O₂ (approximately 3% by mole for α -pinene SOA).²⁴ Peroxide functional groups (ROOR and ROOH) have been proposed to form readily in autoxidation reactions which lead to SOA formation²⁵ and can also form through condensed phase reactions, making them abundant in SOA.^{24,26–30} Fenton chemistry has been observed to occur with laboratory generated SOA material and can be an important source of OH radicals.¹⁴ In addition, SOA contains many carboxylic acid functional groups, which have been reported to complex

with iron and either increase or decrease the rate of Fenton reaction.^{31–33} Further OH production may arise from direct photolysis of iron – acid complexes,^{33,34} or direct photolysis of H₂O₂ and organic hydroperoxides.^{35–37} Recently, production of OH radicals from photolysis of SOA material has been observed, which was attributed to photolysis of hydroperoxides.²⁴ Although these reactions can generate OH radicals under aqueous conditions, the Photo-Fenton-like reaction with SOA has not been explored and has the potential to generate even more OH and result in greater organic oxidation.

This study investigates OH radical formation from Fenton-like and Photo-Fenton-like reactions with α -pinene SOA material under simulated cloud water conditions. OH production was measured using benzoic acid as a radical trap^{38,39} and analysed offline with HPLC. Comparison to the classic Fenton and Photo-Fenton reactions (i.e. with H₂O₂) was used to determine whether SOA material enhances or diminishes the production of OH.

MATERIALS AND METHODS

Dark-Fenton and Photo-Fenton Reactions

All Fenton reactions (referred to as Dark-Fenton) were conducted in amber glass vessels to reduce ambient light from impacting the reaction. Photo-Fenton reactions were conducted in 10 mL quartz reaction vessels in a Suntest CPS solar simulator (Atlas) with a xenon lamp, which has an emission spectrum in the actinic range (~290–800 nm) (See **Figure S1**), to initiate photocatalyzed reactions. Iron was supplied from a stock solution of iron (II) sulfate heptahydrate (FeSO₄·7H₂O, Sigma Aldrich) to obtain a concentration of 5 μ M in the reaction vessel. Either H₂O₂ ($\geq$ 30% wt, Sigma-Aldrich), cis-pinonic acid (98%, Sigma Aldrich), or water soluble α -pinene SOA material (described in supporting information) was added as the reaction partner. SOA constituents were assumed to have an average molecular weight of 200 g mol⁻¹^{24,40} to convert mass concentration to mole concentration of SOA. The final concentration of H₂O₂, pinonic acid, and SOA were 45 μ M, 1500 μ M, and 1500 μ M respectively. It is reported that aqueous α -pinene SOA contains up to 3% by mole H₂O₂²⁴ (such that 1500 μ M SOA would give rise to as much as 45 μ M H₂O₂). Concentrations were chosen to be within the range of realistic cloud water conditions, where dissolved iron concentrations are generally measured at low micromolar levels (0.1 – 10 μ M)⁵ and H₂O₂ concentrations range from 1 – 100 μ M.⁴ SOA concentrations in cloud water are difficult to estimate, but using a similar estimation as Badali *et*

*al.*²⁴, if the SOA concentration is 1500 μM the approximate corresponding cloud water dissolved organic carbon (DOC) concentration would be on the order of 100 mg L^{-1} . Although on the high end of measured DOC concentrations in cloud water, 100 mg L^{-1} DOC would be representative of a polluted environment.⁴¹ The pH of reaction solutions was unbuffered, but remained approximately constant over the course of the reaction between 3.5 – 4.5.

The reaction solutions were sampled before reaction and at 30 and 60 minutes after initiating reaction. The reaction was considered initiated once all reactants were added to the solution, or once the solutions began irradiation in the case of the Photo-Fenton reactions.

Hydroxyl radical production analysis

Benzoic acid (Sigma-Aldrich) was added to the reaction solution as a hydroxyl radical trap at a concentration of 1 mM. A higher concentration of benzoic acid (3 mM or 5 mM) was tested to ensure all OH radicals were indeed being captured during reaction and that the SOA material or pinonic acid was not scavenging OH (**Figures S3 and S4**). OH production was quantified by the formation of para-hydroxybenzoic acid (PHBA), whose yield is 0.18 from the reaction of benzoic acid with OH.³⁸ Comparing the OH produced after 60 minutes of reaction to the total molar concentration of either H_2O_2 or SOA, we calculated the OH molar yield for each reaction (**Table 1**).

Samples were analysed for benzoic acid and hydroxybenzoic acids with a PerkinElmer Series 200 HPLC with a Shimadzu UV-Vis detector similar to the method in Badali et al.²⁴ The complete instrumental parameters are included in the supporting information.

It should be noted that the photolysis of iron (II) sulfate in the presence of benzoic acid produced a small and reproducible concentration of PHBA, which increased with increasing iron concentration. The production of PHBA from this process was accounted for and subtracted from the measured concentration of PHBA from Photo-Fenton reactions (< 30% of total signal). Formation of PHBA from direct photolysis of H_2O_2 and/or SOA material (i.e. no iron present for Fenton chemistry) was also accounted for (< 13% of total signal).

RESULTS AND DISCUSSION

Dark-Fenton and Photo-Fenton reactions were confirmed to occur with hydrogen peroxide under our experimental conditions. As expected, the Dark-Fenton reaction (**Figure 1**) produced fewer OH radicals than the equivalent Photo-Fenton reaction with H₂O₂ (**Figure 2**), where the OH yield (in terms of H₂O₂) at 60 minutes for the Photo-Fenton reaction was 6 times greater than the Dark-Fenton reaction (**Table 1**). Notably, the OH production from both the Dark-Fenton and Photo-Fenton chemistry appears to behave non-linearly as a function of time, although we have a limited number of measured time points. This suggests that there is a reduction in the rates of these reactions as the concentrations of Fe(II) and H₂O₂ decrease over time. This is expected in the Dark-Fenton reaction where the reaction is limited by reduction of Fe(III) back to Fe(II), as well as loss of H₂O₂ over time. The Photo-Fenton reaction can similarly be limited by reduction of Fe(III) if iron complexes that form are not photo-active, to participate in the Photo-Fenton reaction (Reaction 3).^{2,11,31}

The Dark-Fenton-like reaction with SOA material produced the lowest amount of OH (**Figure 1**) (0.06% molar yield, relative to SOA), which suggests that this is not an important source. This OH yield is significantly smaller than what was concluded by Tong et al.,¹⁴ who found an OH molar yield of 1% from the Dark-Fenton reaction with a similar amount of α -pinene SOA material (1500 μ M). However, the relative iron concentration used was much higher (15 to 50 times higher iron concentrations than this study), which could explain the observed differences in OH production.

To explore the effect that SOA has on OH generation from the Photo-Fenton reaction, a known amount of SOA (1500 μ M) was added to the H₂O₂ solution (45 μ M). Indeed, OH was observed to form from Photo-Fenton chemistry with both H₂O₂ and SOA material present (**Figure 2**). However, the OH molar yield (in terms of H₂O₂ concentration) is 6 times less than that of the Photo-Fenton reaction with H₂O₂ alone (**Table 1**). Additionally, the OH produced does not appear to increase any further between 30 and 60 minutes of reaction time. This indicates that the SOA material acts to suppress OH formation from the Photo-Fenton reaction. Carboxylic acids, which are commonly found in aqueous SOA material, are known to complex readily with both Fe(II) and Fe(III) species and possibly alter the rate of the Photo-Fenton reaction.³¹ While certain carboxylic acids, like oxalic acid, can increase the effectiveness of Photo-Fenton chemistry through photo-reduction of iron and production of additional H₂O₂,

others, like malic, malonic, or formic acid, can inhibit photo-reduction of iron and reduce the amount of free iron available for reaction with H_2O_2 .^{31–33,42,43} Major products in α -pinene SOA (and other terpene derived SOA) are complex carboxylic acids^{44,45}, whose effect on Fenton chemistry has not previously been investigated.

To investigate the effect of a major carboxylic acid present in α -pinene SOA, pinonic acid (1500 μM) was used in place of the SOA material in the Photo-Fenton reaction with H_2O_2 . A similar suppression of the total OH production is observed compared to the case with H_2O_2 alone (**Figure 2**). The OH molar yield (in terms of H_2O_2 concentration) after 60 minutes of reaction with pinonic acid added is 3 times less than that of the reaction with H_2O_2 alone (**Table 1**). Although the OH suppression by pinonic acid is not as large as with the α -pinene SOA, it indicates that this one component can have a similar suppression effect on the Photo-Fenton reaction as can a more complex mixture. It also gives evidence for iron complexation that leads to a reduction in the rate of the Photo-Fenton reaction. Further evidence of pinonic acid complexation by measurement of the UV-Vis spectrum is shown in **Figure S5**. It is likely that other carboxylic acids found in α -pinene SOA, such as pinic or norpinonic acid,⁴⁵ may behave similarly.

Interestingly, the Photo-Fenton-like reaction with SOA material showed an enhanced production of OH compared to the Photo-Fenton reaction with H_2O_2 and SOA material together, however still approximately 3 times less than the Photo-Fenton reaction with H_2O_2 alone (**Figure 2**). The chemistry of these systems is complex and when H_2O_2 and SOA are added together, their individual OH production is apparently not additive perhaps resulting from competition for available iron or aqueous chemistry between the SOA material and H_2O_2 , for example reaction of H_2O_2 with aldehydes to form α -hydroxyhydroperoxides.⁴⁶

The reduced OH production in the Photo-Fenton-like reaction with SOA material compared to the Photo-Fenton reaction with H_2O_2 could arise from the SOA material complexing the iron species, as discussed above. Another possibility is that the H_2O_2 concentration is overestimated in aqueous SOA, with the assumption that 3% of water soluble SOA material would give rise to H_2O_2 .²⁴ This 3% value is likely an upper limit, which may also include response from dissolved organic hydroperoxides that do not participate significantly in

the Photo-Fenton chemistry and/or do not generate significant OH, as was observed to occur for methyl- and ethyl-hydroperoxides which give rise to alkoxyl radicals (RO[•], reaction 2b).¹⁰

We note that the SOA material or pinonic acid could in theory also quench OH production by providing a reactive sink for any OH radicals produced. However, this effect was ruled out by increasing the benzoic acid concentration to confirm that it was the major sink for OH (**Figures S3 and S4**). No significant increase in OH production was observed at higher benzoic acid concentration verifying that 1 mM sufficiently captures OH production from this reaction.

An overall conclusion from this work is that, α -pinene SOA material does not participate significantly in the Dark-Fenton and Photo-Fenton reactions to act as an additional source of OH radicals in the condensed phase. It appears instead that SOA reduces the yield of OH from Photo-Fenton reactions due at least in part to the presence of carboxylic acids like pinonic acid.

Atmospheric Implications

Generation mechanisms of OH in cloud droplets have traditionally included photolysis of H₂O₂, nitrate, and nitrite, and Dark-Fenton and Photo-Fenton chemistry with H₂O₂.² Photolysis of organic hydroperoxides has also been identified as an OH source.²⁴ Recently, Tong et al. suggested that decomposition of SOA material and Dark-Fenton-like chemistry with SOA material may also be significant sources of OH in cloud droplets.¹⁴ This work shows that Photo-Fenton-like chemistry with α -pinene SOA material can also generate a significant amount of OH, more than Dark-Fenton-like chemistry with SOA and direct photolysis of SOA alone. The overall OH production will therefore depend greatly on the chemical composition of the cloud droplets as well as the degree of illumination. This has implications for the oxidizing capacity of the droplets, notably for aging of organic species.

α -pinene SOA material also acted to suppress OH production from Photo-Fenton chemistry with H₂O₂. If this process is not considered, OH production from Photo-Fenton chemistry may be overestimated. Given that our reaction conditions are within the range relevant to cloud water, it is likely that Photo-Fenton chemistry is suppressed in cloud droplets that contain terpene-derived SOA material, or in aqueous SOA particles with an even higher organic concentration. Therefore, the Dark-Fenton and Photo-Fenton reactions may be of greater

importance for cloud water with lower organic content. More concentrated aqueous aerosols may have greater contribution of OH production from the Fenton and Photo-Fenton reactions compared to cloud water, but may also have greater suppression effects if significant SOA material is present. While suppression by SOA material occurs, the production rate of OH (assuming linear production of OH) from Photo-Fenton and Photo-Fenton-like reactions measured here (10^{-9} M s^{-1}) is of similar order of magnitude to those measured for the total OH production rate in cloud and fog water (10^{-9} M s^{-1}).⁴⁷ And so, Photo-Fenton reactions may still be significant, despite the suppression effects, with other condensed phase OH sources in cloud water.

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ASSOCIATED CONTENT

Supporting Information

Supporting Information Available: Additional text and figures showing the solar simulator spectrum, SOA generation method, reaction of benzoic acid with OH radicals, HPLC analysis method, and supplementary results including increased benzoic acid concentration and UV-Vis spectrum of iron and pinonic acid complexation.

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REFERENCES

- (1) Sakugawa, H.; Kaplan, I. R.; Tsai, W.; Cohen, Y. Atmospheric hydrogen peroxide. *Environ. Sci. Technol.* **1990**, *10* (10), 29–32.
- (2) Arakaki, T.; Faust, B. C. Sources, sinks, and mechanisms of hydroxyl radical (OH) photoproduction and consumption in authentic acidic continental cloud waters from Whiteface Mountain, New York: The role of the Fe(r) (r = II, III) photochemical cycle. *J.*

- 230 *Geophys. Res.* **1998**, *103*, 3487–3504.
- 231 (3) Siefert, R. L.; Pehkonen, S. O.; Erel, Y.; Hoffmann, M. R. Iron photochemistry of aqueous
232 suspensions of ambient aerosol with added organic acids. *Geochim. Cosmochim. Acta*
233 **1994**, *58* (15), 3271–3279.
- 234 (4) Jackson, A. V.; Hewitt, C. N. Atmosphere Hydrogen Peroxide and Organic
235 Hydroperoxides: A Review. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29* (2), 175–228.
- 236 (5) Deguillaume, L.; Leriche, M.; Desboeufs, K.; Mailhot, G.; George, C.; Chaumerliac, N.
237 Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive
238 parameters. *Chem. Rev.* **2005**, *105* (9), 3388–3431.
- 239 (6) Deguillaume, L.; Leriche, M.; Chaumerliac, N. Impact of radical versus non-radical
240 pathway in the Fenton chemistry on the iron redox cycle in clouds. *Chemosphere* **2005**, *60*
241 (5), 718–724.
- 242 (7) Fenton, H. J. H. Oxidation of Tartaric Acid in presence of Iron. *J. Chem. Soc. Trans.*
243 **1894**, *65*, 899–910.
- 244 (8) Ebrahiem, E. E.; Al-Maghrabi, M. N.; Mobarki, A. R. Removal of organic pollutants from
245 industrial wastewater by applying photo-Fenton oxidation technology. *Arab. J. Chem.*
246 **2013**, *10*, S1674–S1679.
- 247 (9) Kavitha, V.; Palanivelu, K. The role of ferrous ion in Fenton and photo-Fenton processes
248 for the degradation of phenol. *Chemosphere* **2004**, *55* (9), 1235–1243.
- 249 (10) Chevallier, E.; Jolibois, R. D.; Meunier, N.; Carlier, P.; Monod, A. “Fenton-like” reactions
250 of methylhydroperoxide and ethylhydroperoxide with Fe²⁺ in liquid aerosols under
251 tropospheric conditions. *Atmos. Environ.* **2004**, *38* (6), 921–933.
- 252 (11) Nguyen, T. B.; Coggon, M. M.; Flagan, R. C.; Seinfeld, J. H. Reactive uptake and photo-
253 fenton oxidation of glycolaldehyde in aerosol liquid water. *Environ. Sci. Technol.* **2013**,
254 *47* (9), 4307–4316.
- 255 (12) Holmes, B. J.; Petrucci, G. A. Oligomerization of levoglucosan by Fenton chemistry in
256 proxies of biomass burning aerosols. *J. Atmos. Chem.* **2007**, *58* (2), 151–166.

- 257 (13) Daumit, K. E.; Carrasquillo, A. J.; Sugrue, R. A.; Kroll, J. H. Effects of Condensed-Phase
258 Oxidants on Secondary Organic Aerosol Formation. *J. Phys. Chem. A* **2016**, *120* (9),
259 1386–1394.
- 260 (14) Tong, H.; Arangio, A. M.; Lakey, P. S. J.; Berkemeier, T.; Liu, F.; Kampf, C. J.; Brune,
261 W. H.; Poschl, U.; Shiraiwa, M. Hydroxyl radicals from secondary organic aerosol
262 decomposition in water. *Atmos. Chem. Phys.* **2016**, *16* (3), 1761–1771.
- 263 (15) Al-Abadleh, H. A. Review of the bulk and surface chemistry of iron in atmospherically
264 relevant systems containing humic-like substances. *RSC Adv.* **2015**, *5* (57), 45785–45811.
- 265 (16) Daumit, K. E.; Carrasquillo, A. J.; Hunter, J. F.; Kroll, J. H. Laboratory studies of the
266 aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution. *Atmos.*
267 *Chem. Phys.* **2014**, *14*, 10773–10784.
- 268 (17) Faust, B. C.; Hoigné, J. Photolysis of Fe (III)-hydroxy complexes as sources of OH
269 radicals in clouds, fog and rain. *Atmos. Environ. Part A, Gen. Top.* **1990**, *24* (1), 79–89.
- 270 (18) Mao, J.; Fan, S.; Jacob, D. J.; Travis, K. R. Radical loss in the atmosphere from Cu-Fe
271 redox coupling in aerosols. *Atmos. Chem. Phys.* **2013**, *13* (2), 509–519.
- 272 (19) Mao, J.; Fan, S.; Horowitz, L. W. Soluble Fe in Aerosols Sustained by Gaseous HO₂
273 Uptake. *Environ. Sci. Technol. Lett.* **2017**, *4* (3), 98–104.
- 274 (20) Hoffmann, P.; Dedik, A. N.; Ensling, J.; Weinbruch, S.; Weber, S.; Sinner, T.; Gütlich, P.;
275 Ortner, H. M. Speciation of iron in atmospheric aerosol samples. *J. Aerosol Sci.* **1996**, *27*
276 (2), 325–337.
- 277 (21) Dedik, A. N.; Hovvmannt, P.; Ensling, J. Chemical Characterization of Iron in
278 Atmospheric Aerosols. *Atmos. Environ.* **1992**, *26* (14), 2545–2548.
- 279 (22) Arellanes, C.; Paulson, S. E.; Fine, P. M.; Sioutas, C. Exceeding of Henry’s Law by
280 Hydrogen Peroxide Associated with Urban Aerosols. *Environ. Sci. Technol.* **2006**, *40*
281 (16), 4859–4866.
- 282 (23) Zhao, Y.; Hallar, A. G.; Mazzoleni, L. R. Atmospheric organic matter in clouds: Exact
283 masses and molecular formula identification using ultrahigh-resolution FT-ICR mass

- spectrometry. *Atmos. Chem. Phys.* **2013**, *13* (24), 12343–12362.
- (24) Badali, K. M.; Zhou, S.; Aljawhary, D.; Antiñolo, M.; Chen, W. J.; Lok, A.; Mungall, E.; Wong, J. P. S.; Zhao, R.; Abbatt, J. P. D. Formation of hydroxyl radicals from photolysis of secondary organic aerosol material. *Atmos. Chem. Phys.* **2015**, *15* (14), 7831–7840.
- (25) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; et al. A large source of low-volatility secondary organic aerosol. *Nature* **2014**, *506* (7489), 476–479.
- (26) Docherty, K. S.; Wu, W.; Lim, Y. Bin; Ziemann, P. J. Contributions of Organic Peroxides to Secondary Aerosol Formed from Reactions of Monoterpenes with O₃. *Environ. Sci. Technol.* **2005**, *39* (11), 4049–4059.
- (27) Chen, X.; Hopke, P. K. Secondary organic aerosol from α -pinene ozonolysis in dynamic chamber system. *Indoor Air* **2009**, *19* (4), 335–345.
- (28) Chen, X.; Hopke, P. K. A chamber study of secondary organic aerosol formation by limonene ozonolysis. *Indoor Air* **2010**, *20* (4), 320–328.
- (29) Wang, Y.; Kim, H.; Paulson, S. E. Hydrogen peroxide generation from α - and β -pinene and toluene secondary organic aerosols. *Atmos. Environ.* **2011**, *45* (18), 3149–3156.
- (30) Mertes, P.; Pfaffenberger, L.; Dommen, J.; Kalberer, M.; Baltensperger, U. Development of a sensitive long path absorption photometer to quantify peroxides in aerosol particles (Peroxide-LOPAP). *Atmos. Meas. Tech.* **2012**, *5* (10), 2339–2348.
- (31) Baba, Y.; Yatagai, T.; Harada, T.; Kawase, Y. Hydroxyl radical generation in the photofenton process: Effects of carboxylic acids on iron redox cycling. *Chem. Eng. J.* **2015**, *277*, 229–241.
- (32) Ma, J.; Ma, W.; Song, W.; Chen, C.; Tang, Y.; Zhao, J.; Huang, Y.; Xu, Y.; Zang, L. Fenton degradation of organic pollutants in the presence of low-molecular-weight organic acids: Cooperative effect of quinone and visible light. *Environ. Sci. Technol.* **2006**, *40* (2), 618–624.
- (33) Kwan, C. Y.; Chu, W. Photodegradation of 2,4-dichlorophenoxyacetic acid in various

- 311 iron-mediated oxidation systems. *Water Res.* **2003**, 37 (18), 4405–4412.
- 312 (34) Zuo, Y.; Holgne, J. Formation of hydrogen peroxide and depletion of oxalic acid in
313 atmospheric water by photolysis of Iron(III)-oxalato complexes. *Environ. Sci. Technol.*
314 **1992**, 26 (5), 1014–1022.
- 315 (35) Walser, M. L.; Park, J.; Gomez, A. L.; Russell, A. R.; Nizkorodov, S. A. Photochemical
316 aging of secondary organic aerosol particles generated from the oxidation of d-limonene.
317 *J. Phys. Chem. A* **2007**, 111 (10), 1907–1913.
- 318 (36) Wong, J. P. S.; Zhou, S.; Abbatt, J. P. D. Changes in Secondary Organic Aerosol
319 Composition and Mass due to Photolysis : Relative Humidity Dependence. *J. Phys. Chem.*
320 *A* **2015**, 119 (19), 4309–4316.
- 321 (37) Epstein, S. A.; Blair, S. L.; Nizkorodov, S. A. Direct Photolysis of α -Pinene Ozonolysis
322 Secondary Organic Aerosol: Effect on Particle Mass and Peroxide Content. *Environ. Sci.*
323 *Technol.* **2014**, 48, 11251–11258.
- 324 (38) Anastasio, C.; McGregor, K. G. Chemistry of fog waters in California's Central Valley : 1.
325 In situ photoformation of hydroxyl radical and singlet molecular oxygen. *Atmos. Environ.*
326 **2001**, 35, 1079–1089.
- 327 (39) Klein, G. W.; Bhatla, K.; Madhavan, V.; Schuler, R. H. Reaction of OH with Benzoic
328 Acid. Isomer Distribution in the Radical Intermediates. *J. Phys. Chem.* **1975**, 79 (17),
329 1767–1774.
- 330 (40) Bateman, A. P.; Nizkorodov, S. A.; Laskin, J.; Laskin, A. Photolytic processing of
331 secondary organic aerosols dissolved in cloud droplets. *Phys. Chem. Chem. Phys.* **2011**,
332 13 (26), 12199–12212.
- 333 (41) Herckes, P.; Valsaraj, K. T.; Collett, J. L. A review of observations of organic matter in
334 fogs and clouds: Origin, processing and fate. *Atmos. Res.* **2013**, 132–133, 434–449.
- 335 (42) Kwan, C. Y.; Chu, W. The role of organic ligands in ferrous-induced photochemical
336 degradation of 2,4-dichlorophenoxyacetic acid. *Chemosphere* **2007**, 67 (8), 1601–1611.
- 337 (43) Thomas, D. A.; Coggon, M. M.; Lignell, H.; Schilling, K. A.; Zhang, X.; Schwantes, R.

- H.; Flagan, R. C.; Seinfeld, J. H.; Beauchamp, J. L. Real-Time Studies of Iron Oxalate-Mediated Oxidation of Glycolaldehyde as a Model for Photochemical Aging of Aqueous Tropospheric Aerosols. *Environ. Sci. Technol.* **2016**, *50* (22), 12241–12249.
- (44) Ma, Y.; Russell, A. T.; Marston, G. Mechanisms for the formation of secondary organic aerosol components from the gas-phase ozonolysis of α -pinene. *Phys. Chem. Chem. Phys.* **2008**, *10* (29), 4294–4312.
- (45) Glasius, M.; Lahaniati, M.; Calogirou, A.; Di Bella, D.; Jensen, N. R.; Hjorth, J.; Kotzias, D.; Larsen, B. R. Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone. *Environ. Sci. Technol.* **2000**, *34* (6), 1001–1010.
- (46) Zhao, R.; Lee, A. K. Y.; Soong, R.; Simpson, A. J.; Abbatt, J. P. D. Formation of aqueous-phase α -hydroxyhydroperoxides (α -HHP): Potential atmospheric impacts. *Atmos. Chem. Phys.* **2013**, *13* (12), 5857–5872.
- (47) Arakaki, T.; Anastasio, C.; Kuroki, Y.; Nakajima, H.; Okada, K.; Kotani, Y.; Handa, D.; Azechi, S.; Kimura, T.; Tsuchioka, A.; et al. A general scavenging rate constant for reaction of hydroxyl radical with organic carbon in atmospheric waters. *Environ. Sci. Technol.* **2013**, *47* (15), 8196–8203.

Figure 1. Para-hydroxybenzoic acid (PHBA) and total OH formation as a function of reaction time from the Dark-Fenton reactions with H₂O₂ (45 μM) and α-pinene SOA (1500 μM). Error bars indicate propagated standard deviation from multiple (≥3) experiments and respective control reactions.

Figure 2. Para-hydroxybenzoic acid (PHBA) and total OH formation as a function of reaction time (time since irradiation) from the Photo-Fenton reactions with H₂O₂ (45 μM), α-pinene SOA (1500 μM), a mixture of H₂O₂ and pinonic acid (45 μM H₂O₂ and 1500 μM pinonic acid), and a mixture of H₂O₂ and SOA (45 μM H₂O₂ and 1500 μM SOA). Error bars indicate propagated standard deviation from multiple (≥3) experiments and respective control reactions.

Table 1. Hydroxyl radical molar yields after 60 minutes of reaction from the Dark-Fenton and Photo-Fenton reactions of H₂O₂ (45 μM), α-pinene SOA (1500 μM), a mixture of H₂O₂ and pinonic acid (45 μM and 1500 μM, respectively), and a mixture of H₂O₂ with SOA (45 μM and 1500 μM, respectively). OH molar yields are calculated from the concentration of OH, using the concentration of PHBA formed after 60 minutes (**Figures 1 and 2**) and the yield of PHBA, compared to the starting molar concentration of either H₂O₂ or SOA. Uncertainties are the standard deviation between multiple (3) experiments.

Reaction	OH Molar Yield (%) (in terms of H ₂ O ₂)	OH Molar Yield (%) (in terms of SOA)
Dark-Fenton H ₂ O ₂	10.1 ± 0.1	-
Photo-Fenton H ₂ O ₂	58.2 ± 29.0	-
Dark-Fenton SOA	-	0.06 ± 0.03
Photo-Fenton SOA	-	0.60 ± 0.22
Photo-Fenton Pinonic acid + H ₂ O ₂	18.4 ± 1.4	-
Photo-Fenton SOA + H ₂ O ₂	10.2 ± 5.4	0.30 ± 0.16

Table of Contents Graphic:

Supporting Information for

Suppression of OH Generation from the Photo-Fenton Reaction in the Presence of α -Pinene
Secondary Organic Aerosol Material

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This Supporting Information provides additional text and figures including:

1. The emission spectrum of the Suntest CPS solar simulator
2. SOA Generation and Collection
3. Details on the oxidation reaction of benzoic acid with OH radicals
4. The effect of increasing benzoic acid concentration
5. Detailed parameters for the HPLC analysis method
6. UV-Visible spectrum of iron and pinonic acid – evidence for complexation

1. Suntest CPS solar simulator emission spectrum

The Suntest CPS solar simulator (Atlas), which was used to initiate Photo-Fenton chemistry, was operated with the internal cooling fan on as well as chilled by a water/ethylene glycol recirculator. The internal temperature of the reaction solutions was approximately 30 - 34°C during Photo-Fenton experiments. The emission spectrum of the solar simulator was measured with a Black-Comet C-50 spectroradiometer (StellarNet Inc.). Spectra were recorded using 10 ms integration time and averaged over 20 scans. **Figure S1** shows the irradiance as a function of wavelength for the Suntest CPS solar simulator, measured at the location of the reaction solutions, compared to that expected of sunlight.

The spectral irradiance of sunlight was calculated over the wavelength range of 250 – 800 nm with the National Center for Atmospheric Research's "Quick TUV Calculator", available here: http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/.

The following parameters were used: SZA = 0°, overhead ozone column = 300 Dobson units, surface albedo = 0.1, and ground elevation = 0 km. The total downwelling radiation is presented.

Figure S1. Irradiance as a function of wavelength for the Suntest CPS solar simulator (measured) and sunlight (calculated).

2. SOA Generation and Collection

SOA was generated at room temperature (293 ± 3 K) from the ozonolysis of gas phase α -pinene in a dark, 3 L glass flow tube reactor under dry conditions (RH <5%). α -pinene was introduced by passing a 1.7 sccm flow of nitrogen through a bubbler containing liquid α -pinene (Sigma-Aldrich) held at -10°C , which was diluted with a 100 sccm flow of purified air before entering the flow tube. Ozone was generated by passing a flow of purified air over a 185 nm mercury pen-ray lamp to reach an approximate mixing ratio of 1.9 ppm in the flow tube, in excess of the α -pinene mixing ratio. The total flow rate in the reactor was 1700 sccm, corresponding to a residence time of 1.76 minutes. No OH scavenger was added. SOA was collected on supported PTFE filters (Zefluor, Pall Life Sciences, 47 mm, 2 μm pore size) for 48 hours, giving rise to approximately 7 mg of material. Immediately after collecting, the water soluble fraction of SOA was extracted in 10 mL of purified water (18 M Ω , Millipore). All reactions were carried out on the same day as collection to reduce any sample storage artefacts. The pH of extracted SOA solutions ranged between 3.5 – 4.5.

3. Details on the oxidation reaction of benzoic acid with OH radicals

The rate constant for the OH oxidation of benzoic acid is $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (under acidic conditions, $\text{pH} = 3.5 - 4.5$).^{1,2} The reaction produces three isomers of hydroxybenzoic acid: ortho-, meta-, and para-hydroxybenzoic acid, shown in **Figure S2**. Para-hydroxybenzoic acid (PHBA) was quantified in our study as it had good sensitivity and reproducible calibrations. In order to calculate OH concentrations produced from reaction, the PHBA concentration was corrected for the yield of PHBA from the reaction below, previously determined to be 18%.²

Figure S2. Reaction of benzoic acid with OH radical to produce ortho-, meta-, and para-hydroxybenzoic acid isomers.

4. The effect of increasing benzoic acid concentration

In order to confirm that all OH formed from the Photo-Fenton-like reaction with α -pinene SOA was captured, the benzoic acid (BA) concentration was increased from 1 mM to 3 mM under the same reaction conditions. **Figure S3** shows that the production of para-hydroxybenzoic acid (PHBA) and total OH production at lower BA concentration is consistent with increased BA concentration, within experimental uncertainty. Taking the concentration of PHBA produced, we convert it to the concentration of OH produced, using the known PHBA yield (18%).² The molar yield of OH from these reactions is calculated from the OH produced at 60 minutes of reaction time, divided by the total starting concentration of SOA material. The OH molar yields (in terms of SOA) for the Photo-Fenton-like reaction with SOA are as follows:

OH Molar Yield from Photo-Fenton SOA (1 mM BA) = $0.60 \pm 0.22 \%$

OH Molar Yield from Photo-Fenton SOA (3 mM BA) = $0.57 \pm 0.31 \%$

As the absolute production of PHBA and the OH molar yields from both reactions agree within experimental uncertainty, we conclude that 1 mM BA is sufficient to capture all available OH produced from the Photo-Fenton reaction with SOA.

Figure S3. Para-hydroxybenzoic acid (PHBA) and total OH formation as a function of reaction time (time since irradiation) from the Photo-Fenton-like reaction with α -pinene SOA with 1 mM and 3 mM of benzoic acid (BA) as the OH radical trap. Error bars indicate propagated standard deviation from multiple (≥ 3) experiments and respective control reactions.

Further confirmation that all OH produced from the Photo-Fenton reaction with pinonic acid was captured was carried out to ensure pinonic acid was not competitively reacting with OH. The Photo-Fenton reaction with 45 μM H_2O_2 and 1500 μM pinonic acid was carried out at two benzoic acid concentrations, 1 mM and 5 mM. **Figure S4** shows that PHBA and total OH produced in these two reactions is indistinguishable within the experimental uncertainty. It is concluded that 1 mM benzoic acid is sufficient to capture the total OH production from the Photo-Fenton reaction with H_2O_2 and pinonic acid. The OH molar yields (in terms of H_2O_2) for these two reactions are as follows:

OH Molar Yield from Photo-Fenton H_2O_2 + Pinonic acid (1 mM BA) = $18.4 \pm 1.4 \%$

OH Molar Yield from Photo-Fenton H_2O_2 + Pinonic acid (5 mM BA) = $16.8 \pm 3.5 \%$

Figure S4. Para-hydroxybenzoic acid (PHBA) and total OH formation as a function of reaction time (time since irradiation) from the Photo-Fenton-like reaction with H_2O_2 (45 μM) and pinonic acid (1500 μM) with 1 mM and 5 mM of benzoic acid (BA) as the OH radical trap. Error bars indicate propagated standard deviation from multiple (≥ 3) experiments and respective control reactions.

5. Detailed parameters for the HPLC analysis method

A PerkinElmer Series 200 HPLC with Shimadzu UV-Vis detector with deuterium lamp was used for separation and quantification of benzoic acid and (ortho-, meta-, and para-) hydroxybenzoic acids (HBA). The detector wavelength was set to 256 nm, with a range of 0.01. Separation was achieved with a Phenomenex Gemini 150 mm C18 column. The flow rate was 0.5 mL/min with a 14.3 minute, two-step gradient elution starting with: 87% acidified water (0.13% v/v trifluoroacetic acid in water) and 13% acetonitrile, linearly increasing to 35% acetonitrile from 5 to 8.3 minutes, and then returning to 13% acetonitrile for the remaining 6.5 minutes.

All samples were acidified with one drop of 1 mM H_2SO_4 prior to analysis. Samples were injected manually with a glass syringe, rinsed with both deionized water and acetonitrile. Peak integration was conducted in the provided TotalChrom software. Para-hydroxybenzoic acid (PHBA) eluted as a single peak at a retention time of approximately 3 min.

Calibrations were performed with a five-point calibration ranging from 0 – 1000 μM of each of para-HBA, meta-HBA, ortho-HBA, and benzoic acid (all Sigma-Aldrich). Reported errors were calculated from the standard deviation between triplicate reaction trials.

6. UV-Visible spectrum of iron and pinonic acid – evidence for complexation

The UV-Vis spectrum of equimolar concentrations of Fe(II) and pinonic acid (100 μM) was measured to investigate the possibility for iron complexation. To remove the contribution of absorbance from free pinonic acid, the spectrum for the mixture of iron and pinonic acid was normalized by subtracting the spectrum of only pinonic acid (also at 100 μM). **Figure S5** shows the normalized spectrum of the iron and pinonic acid mixture compared to the spectrum of iron(II) alone (at 100 μM). There is a significant increase in the absorbance of the iron and pinonic acid mixture at lower wavelengths (approximately 230 – 350 nm) which is indicative of complex formation between the iron and acid. The change in the electronic structure when a complex is formed is reflected in the absorbance profile for the iron-acid complex.

The measurements were made with a liquid waveguide capillary UV-Visible system (50 cm path length, World Precision Instruments), with a deuterium tungsten halogen light source (DT-Mini-2, Ocean Optics) and a temperature controlled UV-Vis spectrometer (USB2000+, Ocean Optics).

Figure S5. UV-Visible absorbance spectra of the Fe(II)-pinonic acid complex (corrected for absorbance due to free pinonic acid) and Fe(II) alone.

142 **References**

- 143 (1) Wander, R.; Neta, P.; Dorfman, L. M. Pulse Radiolysis Studies. XII. Kinetics and Spectra
144 of the Cyclohexadienyl Radicals in Aqueous Benzoic Acid Solution. *J. Phys. Chem.* **1968**,
145 72 (8), 2946–2949.
- 146 (2) Anastasio, C.; McGregor, K. G. Chemistry of fog waters in California’s Central Valley : 1.
147 In situ photoformation of hydroxyl radical and singlet molecular oxygen. *Atmos. Environ.*
148 **2001**, 35, 1079–1089.