On behalf of all of the co-authors, I would like to thank all of the reviewers for their extremely thoughtful and comprehensive reviews. Unless specifically indicated, table and figure numbers refer to the ACPD verison. The reviewers' comments are reproduced in black; our responses are detailed below in red:

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Review of “Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets” by S.A. Epstein et al.

While aqueous oxidation of organic compounds dissolved in water droplets has been extensively studied and understood with good confidence, the level of scientific understanding of aqueous photolysis of similar dissolved organic compounds is much less so. This article attempts to assess the importance of aqueous photolysis for carbonyl species by comparing the branching ratio between aqueous oxidation by OH radicals and aqueous photolysis versus the branching ratio between gaseous photolysis and aqueous photolysis for a number of carbonyl species. The authors find that for most carbonyl compounds, removal via direct photolysis in water droplets can be neglected relative to aqueous reactions with OH. The authors additionally perform experiments to further show that quantum yields can vary dramatically between isomeric compounds, highlighting the overall complexity and ambition of this study.

This paper is well written, the figures and tables are well produced, and the experiments, to a non-experimentalist, seem well designed. However, due to my lack of expertise, I am unable to provide a proper review of the techniques and laboratory methods used in this study (p. 10909, lines 8-26 and p. 10910, lines 1-15) as well as the computational chemistry methods (p. 10914, lines 1-26 and p. 10915, lines 1-15 and Section 3.3). I suggest the editor conscripts another reviewer who can comfortably provide an adequate critique of these lines/sections.

Given the paucity of studies investigating aqueous photolysis of organic compounds, this paper will be an important contribution to the current state-of-the-science. Additionally, similar studies will be needed for assessing the importance of photolysis of multifunctional compounds found in SOA, and this paper appears to be an admirable step towards these future works. I recommend publication with only minor adjustments to the text.

1.1 General Comments:

1. This study’s methods are nicely detailed, however the methods section as a whole is somewhat disorganized. I suggest a more integrated description of the methods used in this study that is

easier for most readers to follow. For instance, it appears that two different methods are given to show how the aqueous extinction coefficient (or molar absorptivity) is calculated to obtain an aqueous photolysis rate constant for carbonyl compounds: (1) assuming the extinction coefficients follow a Gaussian dependence on wavelength (eq. 4 and 5) and (2) using computation chemistry tools (pg. 10914, lines 1-26 and pg. 10915, lines 1-15). It is unclear to me which method was used in this study, or if both were used, in what section was each method applied to? This needs to be addressed.

The TDDFT results were only used to estimate aqueous photolysis for the d-limonene and isoprene SOA products. We clarified this in the methods and results section and added a section addressing this in the introduction. More descriptive section titles will hopefully avoid further confusion. (see #3 below)

2. Sunlight wavelengths below around 290 nm do not appreciably penetrate into the troposphere. Many of the compounds in Table 1 list maximum absorption wavelengths (max) at or below this threshold(e.g. glyceraldehyde, levulinic acid, acetone) raising question to how significant photolysis of these compounds might be in the actual troposphere. Some clear discussion regarding this potential shortcoming should be included in the paper.

λ_{max} (shown in Table 1) is the wavelength of maximum absorption for the carbonyl peak. We changed the caption to read "…wavelength of maximum absorption…" This is not the same as the maximum absorption wavelength. The compound still absorbs at wavelengths above $\lambda_{max.}$ because of the significant widths of the absorption bands, with their tails penetrating significantly into the important wavelength range for the tropospheric photochemistry (λ>290 nm). We changed also modified the text introducing λ_{max} to avoid this confusion. "…where ε_{max} is the maximum extinction coefficient at a wavelength of λ_{max} (the wavelength of maximum absorption) and *w* is the full width at half maximum (FWHM)."

3. Shouldn't the section, "Computational Chemistry Methods" fall under "Modeling Approach"? Aren't "Computational Chemistry Methods" modeling tools? I also think section titles that are less vague would be quite helpful. Instead of "Experimental materials and methods", may be say "Aqueous quantum yield measurements"? Perhaps split the "Modeling Approach" section into, "Comparison between aqueous and gas phase photolysis rates" and "Comparison between aqueous photolysis and aqueous OH oxidation".

Thank you for this suggestion. We used more descriptive section titles such as "Aqueous Quantum Yield Measurements of Glyceraldehyde", "Computational Chemistry Methods for Predictions of d-Limonene and Isoprene SOA Spectroscopic Properties", "Comparison Between Aqueous and Gas-Phase Photolysis Rates", and "Comparison Between Aqueous Photolysis and Aqueous Oxidation by OH Rates"

4. I suggest moving most of Section 3.3 to the methods. As it sits, it doesn't follow the previous section well.

We moved parts of section 3.3 to the methods section.

5. It is understandable that there is limited information about K_H, K_{Hyd}, "λ_{max} and ε_{max} in the literature. However, calculations performed in this study all still seem to be very generous upper estimates of the importance of aqueous photolysis of carbonyl compounds (e.g. quantum yields are all assumed to be unity when experiments show actual quantum yields to be less than 1%). Comparison between glyceraldehyde and dihydroxyacetone quantum yields indicate that even for structural isomers, quantum yields can vary between 0 and 1. Therefore, we use an upper-bound value of quantum yield (QY) = 1 to pick molecules that do not have competitive aqueous photolysis rates. The goal of the analysis was to be very generous when implementing uncertain values as to prove that even when using these upper-bound values, for the majority of carbonyl compounds, aqueous photolysis is not competitive.

There are multiple instances where a citation is given in the text, but the reference does not appear in the references section. For instance:
– pg. 10907, line 10: The "Sander, 2011" citation does not appear in the references.
– pg. 10908, line 26: The "EPA, 2013" citation does not appear in the references.
– pg. 10911, line 5: The "Sander, 1999" citation does not appear in the references.
– pg. 10911, line 13: The "Sander, 2011" citation does not appear in the references.
– pg. 10911, line 23: The "Karickoff et al., 2011" citation does not appear in the references.
Please correct these, and possibly other, instances of in text citations not appearing in the references section of this paper.
Thank you for catching this issue. We added these references to the Reference section.

- pg. 10906, line 24: Should be "Low volatility products may partition into the particle phase… "
Corrected.

- pg. 10906, line 26: Should be ". . . water-soluble gas and particle phase compounds can partition. . . "
Corrected.

- pg. 10907, lines 7-8; Since little to no radiation at wavelengths <290 nm reach the troposphere, I wonder how significant photolysis of carbonyls is, especially if these compounds are known to only weakly absorb radiation at wavelengths around 280 nm. Furthermore, one can suspect that aqueous photolysis would be even less likely to occur given the reasons the authors mention previously (pg. 10907, lines 26-29 and pg. 10908, lines 1-6).
Agreed.

- pg. 10907, line 28: What direction is this 10 nm hypsochromic shift in upon dissolution? (i.e. up or down?)
A hypsochromic shift is a shift towards shorter wavelengths. We changed the text to the more colloquial "blue shift."

- pg. 10908, lines 8-9: the reaction $O_3 + HO_2/O_2^- \rightarrow OH$ is likely not a significant source of aqueous OH in non-marine environments (see Fig. 4 of Deguillaume et al., 2004; ACP) Maybe cite a more important source of aqueous OH such as Fe(III) or HOOH photolysis?

We eliminated the reaction $O_3 + HO_2/O_2^-$ from the text. Fenton chemistry encompasses Fe(III) production of OH.

- pg. 10908, line 28: Only 5% of glyceraldehyde remains un-hydrated in the aqueous phase, where as 77% of dihydroxyacetone remains un-hydrated. Does the former small fraction inhibit accurate measurements of aqueous photolysis?

The small fraction of free glyceraldehyde has been accounted for in the kinetic photolysis measurements. The small fraction of un-hydrated glyceraldehyde does lower the photolysis rate, but does not inhibit accurate measurements.

- Do you mean effective Henry's law here (pg. 10910, line 19) and here (pg. 10911, line 3) and here (pg. 10911, line 5)? Or is it assumed all acids are in their undissociated form?

All mentions of Henry's law in the paper have been changed to read "effective Henry's law"

- pg. 10911, lines 18-20: Please explain why this is the case.

We modified this sentence to read, "However, prediction with group contribution methods may not be possible for small compounds containing multiple functional groups as the specific arrangement of molecules was not present in the training data"

- pg. 10911, line 24: Just use Hilel et al. No need to mention all authors.

Changed to Hilel et al.

- In equation 2, indicate J is the aqueous photolysis rate constant with a subscript.

Photolysis rate constants are typically represented with the variable J. We prefer to keep it consistent with previous work.

- pg. 10912, lines 14-16: Please give an educated guess as to how the OH rate constants might change if important compounds like alkenes and cyclic compounds (e.g. aromatics) were included.

We added the following paragraph to the discussion: "While the presence of (α,β) unsaturation may increase the rate of aqueous photolysis relative to an unsaturated analog, the rate of oxidation by OH is usually faster in the unsaturated compounds. E.g. k_{OH}(2-propenal) = 7×10^9 $M^{-1}s^{-1}$ and k_{OH}(propanal) = 2.2×10^9 $M^{-1}s^{-1}$; k_{OH}(2-butenal) = 5.8×10^9 $M^{-1}s^{-1}$ and k_{OH}(butanal) = 3.8×10^9 $M^{-1}s^{-1}$; k_{OH}(2-butenone) = 9.8×10^9 $M^{-1}s^{-1}$ and k_{OH}(1-butene-3-one) = 8.5×10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988;Monod et al., 2005)."

Cyclization into a 6-member ring does not significantly affect the k_{OH} (Monod and Doussin, 2008). This is beyond the scope of the text; we do not compare rates between molecules and their cyclic analogues.

- pg. 10913, line 7: Please define the acronym “FWHM” (full width at half maximum) here rather than on line 26, pg. 10914.

Completed.

- In equation 6, indicate J is the aqueous photolysis rate constant with a subscript.

See above.

- pg. 10914, line 10: Please define the acronym “SVP”

Completed.

- pg. 10914, line 15: Should be a dash between “exchange correlation”.

Completed.

- pg. 10914, line 16: Please define the acronym “PBE”.

Completed.

- pg. 10914, line 15 and 16: The first Perdew et al. 1996 citations should be “a” for the first, the second should be “b”. It’s reversed here.

Done.

- pg. 10914, line 26: Just use FWHM here as the acronym should be defined earlier (see above comments)

Done.

- pg. 10915, line 8: Italicize all Latin phrases.

Done.

- pg. 10916, lines 16-18: Given that the quantum yield of glyceraldehyde was found to be so small, this assumption seems quite dramatic to me.

See response to comment 5 above.

- pg. 10916, lines 24-25: Note that this estimate of global average surface albedo does not include cloud cover. If cloud cover is included, albedo is more like .33 (planetary albedo). I assume that this is below clouds.

Since cloud cover is dynamic, we choose the clear sky albedo to serve as an upper estimate for the actinic flux.

- pg. 10917, line 23: I think this should be “However, a low value of Z does not necessarily imply that photolysis is the primary sink in the aqueous phase. . . ”

Changed.

- pg. 10917, lines 25-26: “As in the previous analysis. . . ” should reference Section 2.1

Changed.

- pg. 10918, line 7: A quantum yield of unity is assumed as well as maximum molar absorptivity. Shouldn’t this be “minimum” as in “Markers indicate the predicted minimum photolysis lifetime.”?

  Changed to "minimum".

- pg. 10918, lines 9-10: Don’t all compounds in Fig. 4 have the same quantum yield ($\varphi = \varphi_{max} = 1$)? Shouldn’t this say, “…compounds with large "ε_{max} and large λ_{max} will have appreciably short, atmospheric relevant photolysis lifetimes…”?

  The compounds shown on the graph have established values of ε_{max} and λ_{max}, but not φ. We use $\varphi = \varphi_{max} = 1$ when plotting the compounds to illustrate that when φ is large, photolysis will occur on an atmospherically relevant timescale. The actual value of φ is the largest uncertainty in this calculation, therefore we want to qualify that photolysis happens on atmospherically relevant timescales if φ is large.

pg. 10919, line 14: Should be $Q < 1$ here as Q is the measure of the rate of removal due to aqueous photolysis versus aqueous oxidation with OH.

Changed.

- pg. 10919, line 15: Should be $Z < 1$ here as Z is the measure of the rate of removal due to gaseous photolysis versus aqueous photolysis.

  Changed.

- pg. 10920, line 11: TDDFT is already defines in Section 2. No need to redefine it here.

  We prefer to redefine TDDFT here for readers that may not be completely familiar with computational methods.

- pg. 10922, line 16: Inset commons before and after “…but few hydrogen atoms for abstraction by OH… ”

  Changed.

- pg. 10923, line 6: Remove the “ in Ref.” before “…in Vione et al. (2006)”

  Changed.

- pg. 10935, Fig. 5 caption: Mention that the OH concentration given here is typical for the daytime

  Changed.

- Supplementary Material, pg. 11, Table S2: I don’t think there should there be a “1” in the 2nd column, 1st row of the table.

  Changed.

References Used in the Response

Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B.: Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution, J. Phys. Chem. Ref. Data, 17, 513-886, 1988.

Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H.: Kinetics of oh-initiated oxidation of oxygenated organic compounds in the aqueous phase: New rate constants, structure activity relationships and atmospheric implications, Atmos. Environ., 39, 7667-7688, 2005.

Monod, A., and Doussin, J. F.: Structure-activity relationship for the estimation of oh-oxidation rate constants of aliphatic organic compounds in the aqueous phase: Alkanes, alcohols, organic acids and bases, Atmos. Environ., 42, 7611-7622, 2008.