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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets" *by* S. A. Epstein et al.

D. Rasmussen

dmr@ucdavis.edu

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1 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.

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 (λ_{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.
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”.
4. I suggest moving most of Section 3.3 to the methods. As it sits, it doesn't follow the previous section well.
5. It is understandable that there is limited information about K_H, K_{Hyd}, ε_{max} and λ_{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%).

1.2 Minor and Line-by-line comments:

- 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.
- pg. 10906, line 24: Should be “Low volatility products **may** partition into the particle phase…”
- pg. 10906, line 26: Should be “…water-soluble gas and particle phase compounds **can** partition…”
- 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).

- pg. 10907, line 28: What direction is this 10 nm hypsochromic shift in upon dissolution? (i.e. up or down?)
- 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?
- 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?
- 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?
- pg. 10911, lines 18-20: Please explain why this is the case.
- pg. 10911, line 24: Just use Hilel et al. No need to mention all authors.
- In equation 2, indicate J is the aqueous photolysis rate constant with a subscript.
- 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.
- pg. 10913, line 7: Please define the acronym "FWHM" (full width at half maximum) here rather than on line 26, pg. 10914.
- In equation 6, indicate J is the aqueous photolysis rate constant with a subscript.
- pg. 10914, line 10: Please define the acronym "SVP".

- pg. 10914, line 15: Should be a dash between "exchange correlation".
- pg. 10914, line 16: Please define the acronym "PBE".
- 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.
- pg. 10914, line 26: Just use FWHM here as the acronym should be defined earlier (see above comments)
- pg. 10915, line 8: Italicize all Latin phrases.
- 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.
- 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.
- 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..."
- pg. 10917, lines 25-26: "As in the previous analysis..." should reference Section 2.1
- 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..."?
- pg. 10918, lines 9-10: Don't all compounds in Fig. 4 have the same quantum yield ($\Phi = \Phi_{max} = 1$)? Shouldn't this say, "...compounds with large ε_{max} and large λ_{max} will have appreciably short, atmospheric relevant photolysis lifetimes..."?

- 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.
- 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.
- pg. 10920, line 11: TDDFT is already defines in Section 2. No need to redefine it here.
- pg. 10922, line 16: Inset commons before and after "…but few hydrogen atoms for abstraction by OH…"
- pg. 10923, line 6: Remove the " in Ref." before "…in Vione et al. (2006)"
- pg. 10935, Fig. 5 caption: Mention that the OH concentration given here is typical for the daytime
- 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.