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Title	Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets

Comments on the manuscript entitled "Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets**" by S.A. Epstein, E. Tapavicza, F. Furche, and S.A. Nizkorodov**

Review by Anne Monod

General comments:

This paper is of high interest, as it provides a thorough analysis of the importance of direct photolysis reactions of carbonyl compounds in cloud and fog droplets, compared to aqueous phase OH-oxidation, and gas phase photolysis and OH-oxidation. This paper can be regarded as the companion paper of the one published in 2012 (Epstein and Nizkorodov, ACP, 2012), but the present one focusses on carbonyl compounds. This class of compounds is in fact of high atmospheric relevance for this investigation as i) they can partly hydrate in the aqueous phase, thus inducing different reactivity compared to the gas phase; ii) they are able to oligomerize in the aqueous phase (Tan et al., 2012; Lim et al., 2010; Renard et al., 2013); iii) their photolysis can initiate totally different chemical mechanisms in the aqueous phase compared to the gas phase (Guzman et al., 2006; Griffith et al., 2013). All these reasons fully justify a new study on the subject, and this should be underlined in the introduction.

The paper highlights the current lack of experimental data concerning aqueous phase photolysis (in particular extinction coefficients and quantum yields), and the results obtained are extremely useful to determine what compounds are of atmospheric relevance for further experimental investigations. The results are significant and fully appropriate for the journal, the paper is well written, and I recommend its publication after minor revisions. I have several specific comments that are mentioned below, among which are my 3 main concerns:

1- For the predictions of aqueous OH rate constants: it would be certainly worth using the up-to-date version of the SAR which is dedicated to carbonyl compounds: Doussin and Monod, 2013.
2- Unsaturated carbonyl compounds are not clearly treated in the manuscript (see detailed comments)
3- Figure 5 could be modified in a much more useful way (see detailed comments)

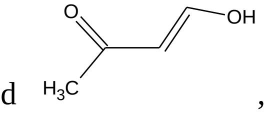
Detailed comments:

- **Abstract**: the last sentence is confusing: the reader may understand that the paper shows that for all α, β conjugated carbonyls, aqueous phase direct photolysis is of importance.
- **Introduction**:
  - p. 10907 line 10: the reference to Sander et al (2011) is missing in the references.
  - p. 10908 lines 19-22: this phrase is too long and confusing. The goal of investigating these 2 compounds in particular should be more clearly explained here. Furthermore, the reader needs a reference to Figure 1 at this point.
  - P. 10909 lines 2-5: same remark as in the abstract
- **Material and methods**:

  - P. 10909 lines 17-19: rephrase “to filter out light outside the actinic wavelength range” as this is not correct for the higher wavelengths.
- **Modelling approach**:
  - The calculation of Z implies that the kinetics of hydration is much faster than that of the studied reactions. The author should mention this, and refer to Doussin and Monod (2013) and Ervens and Volkamer (2010) and possibly the older references included in these papers.
  - P. 10911 line 3: replace “the Henry’s law constant” by “the effective Henry’s law constant”
  - P. 10911 lines 9-12: effective Henry’s Law predictions: how does the HENRYWIN compares to the SAR developed by Raventos-Duran et al. (2010)?
  - P. 10911 lines 22-26: predictions of hydration equilibrium constants: also refer to Gomez-Bombarelli et al. (2009). Also, the reference to Karickoff et al. (2011) is missing in the references.
  - P. 10912 lines 7-11: predictions of aqueous OH rate constants: it would be certainly worth using the up-to-date version of the SAR which is dedicated to carbonyl compounds: Doussin and Monod, 2013.
  - P. 10912 lines 14-16: I fully agree that alkenes or cyclic compounds are potentially important compounds in the authors’ analysis. However, the paper is not quiet consistent on this issue: it states here that these classes of compounds were not included in this study, but some of them are considered further in the results (Figure 3, Figure 4, Figure S11). It should be worth considering the compounds of atmospherically relevance, for which experimental data exist. For instance, for α, β unsaturated carbonyls, aqueous phase extinction coefficients and OH-oxidation rate constants can be found in Liu et al., 2009, Szeremeta et al., 2009, Liu et al., 2012 and Renard et al., 2013 and references therein.
  - P. 10912 lines 17-20: it is true that the relative fraction of anion and undissociated acid is a function of droplet pH, and that the undissociated form is less reactive towards OH-oxidation. However, the photolysis reaction should also be affected, both in terms of extinction coefficients and quantum yields (Leermakers and Vesley, 1963). This should be clarified in the text, giving an example.

- **Results and discussion**:
  - P. 10917 lines 22-25: this phrase is too long and confusing.
  - P. 10918 lines 11-15: the comparison between propanal and acrolein is very interesting and relevant. One would like to see on that figure other similar comparisons, especially with α, β unsaturated carbonyls, such as methacrolein and methylvinyl ketone, which are atmospherically relevant as the primary reaction products of isoprene. One would also like to see the α, β unsaturated carbonyls mentioned in Fig. 3.
  - P. 10918 lines 23-29 and P. 10919 lines 1-4: Figure 5 is very interesting and potentially show clearly the relative importance of aqueous phase photolysis compared to OH-oxidation. However, as it is presented, very little can be ruled out from it, and the corresponding text is not clear. I suggest modifying the figure showing the actual compounds with 2 points for each (one for k_{OH} and one for $<\phi>.\varepsilon_{max}$) linked with an arrow pointing towards k_{OH}, and modifying the text

    accordingly. The resulting figure should show clearly the compounds for which photolysis matters (descending arrows). In the new figure, again, the α, β unsaturated carbonyls should be of high interest!
  - P. 10919 line 14: replace “Z” by “Q”
  - P. 10919 line 15: replace “Q” by “Z”
  - P. 10919 line 28: replace “3-oxopropanoic acid” by “3-oxopropanal”
  - P. 10920 line 7: the up-to-date version of the SAR by Doussin and Monod, 2013 would give the following values for the rate constants of OH-oxidation in the aqueous phase: $2.16 \times 10^{8}\ M^{-1}s^{-1}$, $1.83 \times 10^{8}\ M^{-1}s^{-1}$ and $1.09 \times 10^{9}\ M^{-1}s^{-1}$ for pyruvic acid, 3-oxobutanoic acid and 3-oxopropanoic acid respectively (using hydration constants of 1.4, 0.2 and 28.8 respectively).

- **Tables and Figures**: in general, the terminology used for molecule names are not always consistent, see for example levulinic acid, which should be replaced by 4-oxopentanoic acid.
  - **Table 1**:
    - it should help the reader to add 1 column with the molecular structures.
    - The experimental λ_{max} are not always consistent with the values indicated in Table S1 (especially for aqueous acetone and for aqueous pyruvic acid)
    - Add in the legend: see references indicated in Table S3 for each compound.
  - **Fig. 2**:
    - In the legend, replace “Henry’s law constants” by “hydration equilibrium” and vise et versa
    - Try to make all the points readable (zoom out the top right of the figure).
  - **Fig. 3**: for compound , was the keto-enolic equilibrium considered in the calculations ?
  - **Fig. 5**: as mentioned above, Figure 5 is very interesting and potentially shows clearly the relative importance of aqueous phase photolysis compared to OH-oxidation. It should be very useful for experimentalists. However, as it is presented, very little can be ruled out from it. I suggest modifying the figure showing the actual compounds with 2 points for each (one for k_{OH} and one for $<\phi>.\varepsilon_{max}$) linked with an arrow pointing towards k_{OH}. The resulting Figure should show clearly the compounds for which photolysis matters (descending arrows). In the new Figure, it would be useful to show the intermediate values for k_{OH}. Finally, showing on that Figure α, β unsaturated carbonyls for which experimental k_{OH} are available should be of high interest.
  - **Fig. 6**: some points are hidden such as oxoacetic acid (hidden by the legend). Figures S9 and S10 explore the sensitivity of the results to the very relevant parameters SZA and $[OH_{aq}]$. I suggest to add also a sensitivity study to LWC, which is known as a very sensitive parameter to air/water mass transfers.
- **Supplementary material**:
  - **Fig. S4**: is water vapour interfering on this region of FTIR spectra ?

- **Fig. S5**: below the figure, the text should read “hyperchromic” instead of “hypochromic” (?)
- **Fig**. **S6**: below the figure, “small aliquots” should be more precise : the reader would like to see the ratio between glyceraldehyde and derivatisation agent concentrations needed.
- **Fig**. S7: the figure lacks a legend. Why is it so difficult to quantify the derivatized products with ESI-MS?
- **Fig**. S8: what is the reaction time investigated?
- **Tables S1 to S4**: it should be worth adding a table with the molecular structures of all the molecules investigated in the study.

References:

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