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Comment

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

Anonymous Referee #1

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Overview.

The goal of the work is to examine the importance of direct photolysis as a sink for carbonyls in a cloudy atmosphere. To do this, the authors calculate or estimate the rates of three processes for a range of carbonyls: aqueous photolysis, reaction with aqueous hydroxyl radical (OH), and gas-phase photolysis. Because there are insufficient literature data to determine many of these rates, the authors also estimate a number of the required inputs, such as molar absorptivities. The main finding is that aqueous photolysis is a minor sink for all but 3 of the carbonyls examined. This is an important, and somewhat surprising, result in the quest to understand the aqueous processing of organics.

Overall, the science in the manuscript is very interesting and noteworthy; unfortunately,
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the presentation and explanation of the science is often weak and too terse. Before this manuscript is published, the results need to be more clearly and thoroughly described. In addition, more of the primary data needs to be included in the supplemental material as an aid to readers interested in the fate of carbonyls. These, and other concerns, are described in more detail below.

Major Comments.

1. As described above, the science in the manuscript is very interesting, but the presentation and explanation of the science is often too short. Here are some examples:

(a) The discussion of Figure 2 could be improved. Under the assumption that $J(aq) = J(gas)$, the position of a given compound on Figure 2 is determined by the product $X(aq) \times F(Carb)$, where $X(aq)$ is the fraction of total (carbonyl and hydrated) compound present in the aqueous phase and $F(Carb)$ is the fraction of aqueous compound present as carbonyl. The $Z = 1$ line represents $X(aq) \times F(Carb) = 0.5$; for compounds with $X(aq) \times F(Carb) > 0.5$ (i.e., to the right of the $Z = 1$ line) aqueous photolysis might be significant. Given the primary importance of $X(aq)$ on Z , I recommend that a line for $X(aq)$ be included on the graph and the idea be incorporated into the discussion.

(b) There is almost no discussion of Fig. 4. What are the main points from this figure? The propanal/acrolein couple is suggested as an example of the impact of alpha-beta carbonyl-alkene unsaturation, but nothing is said about the actual result from the Figure.

(c) Literally nothing is said about Fig. 7 in the text. The Figure is called out, but that's the full extent. This figure gives some important information about the uncertainty in the computed absorption spectra so it should be kept, but it needs to be discussed.

(d) Table 1. Some of the SP and MD calculated values for $\lambda(max)$ are similar to measured values, but a few are significantly blue-shifted (e.g., aqueous pyruvic acid), which will greatly lower $j(aq)$. The impact of this underestimate of $\lambda(max)$ on the results should be quantified.

(e) Overall, some of the manuscript is well written, but many parts appear to have

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been hastily prepared. (See examples above, and under Minor Comments below.) I encourage the authors to re-read the entire manuscript with the goal of improving the writing.

2. The authors should add some information about gas-phase OH as a sink. If it is not a significant sink, this should be discussed. If it is a significant sink, this should be indicated for specific compounds. The main focus is on aqueous photolysis, but of course readers will also want to know the dominant sink for a given carbonyl.

3. More data should be provided in the Supplement, analogous to the spectral data in Tables S1 and S2. This should include: (a) Henry's law constants, (b) Hydration constants, and (c) second-order rate constants with OH. It would be useful to include both experimental and predicted data (e.g., for Henry's law constants) to assess the skill of the predictions since they were used for many of the compounds.

4. The manuscript has very little treatment or discussion of uncertainties in each model parameter or in the resulting rates and ratios Q and Z. It makes clear that the results are order-of-magnitude estimates, but it would be useful to give a semi-quantitative estimate of the typical uncertainty in each parameter and the propagated uncertainties in the ratios Q and Z. Where are the largest uncertainties? The uncertainty caused by parameterizing the carbonyl peak(s) (eq. 4) should be included in this discussion. For compounds with measured spectra, how different is the parameterized spectra when compared as the integral of actinic flux times absorption coefficient in equation (5)?

5. Section 3.3 is confusing and appears to be out of place.

(a) It is not clear why the TDDFT modeling was performed. The first sentence indicates that the modeling was used "To predict the importance of aqueous photolysis for compounds where no spectroscopic data is available..." but data for all the compounds in Fig. 6 was either from the literature (for a few) or assumed (for most), as described in Supplemental Table S1. For which figures were the modeled spectra used to deter-

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mine aqueous- and gas-phase photolysis rates? Fig. 3? For other figures but not Fig. 6? Only for the d-limonene and isoprene SOA? This needs to be clearly explained and consistent with the supplemental figures of the TDDFT results.

(b) If the TDDFT results are only to estimate aqueous photolysis for the d-limonene and isoprene SOA products, then this section should be renamed (e.g., 3.3 d-limonene and isoprene SOA) and more clearly explained. (If the TDDFT results were used more broadly, then this section should be moved to earlier in the manuscript, before the photolysis results are discussed.) Procedural information (e.g., sentences 3-5 of the first paragraph in section 3.3 and the first 3 sentences of the second paragraph) should be put in the Methods section. Details on TDDFT (e.g., lines 18-21) should be put as footnotes in Table 1.

(c) Page 10921, lines 2-3. The sentence “In solution, MAE amount to . . .” glosses over the significant blue-shifting of $\lambda(\text{max})$ by the SP and MD calculations for acetone and pyruvic acid. This needs to be pointed out and discussed, as it has important implications for photolysis lifetimes. I believe that measured (and not computed) absorption values were used for both of these compounds; either way, the source of their spectral data should be indicated.

6. Fig. 6. This is a very interesting figure that is the heart of the manuscript, but it takes significant time for a reader to understand. Additional explanation on the figure would help.

(a) It would be very helpful to have clear, explicit definitions of Q and Z on the figure. The current caption description has this information, but not in a way that makes it clear which quantity is in the numerator and denominator.

(b) Adding text to the unlabelled axes would help the reader understand the figure much more quickly; e.g., on the right-hand y-axis there could be a dividing line at $Q = 0$, with text above the line indicating “ $A_{\text{q. OH}} > A_{\text{q. h}\nu}$ ” and text below the line indicating the opposite. A similar demarcation and analogous text would go along the top of the figure to explain Z.

(c) The figure is not easy to read because the lines are too faint and axis numbers and

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all fonts are too small.

(d) It would be useful to distinguish the relative importance of gas-phase photolysis and aqueous-phase OH in the upper-right hand quadrant by including (and discussing) a $Q = Z$ line. It's interesting that there is a fairly clear distinction between the more soluble, more functionalized compounds in this quadrant (e.g., dialdehydes and ketoaldehydes), which are destroyed mostly by aqueous OH, and the mono-aldehydes and ketones, which are destroyed mostly by gas-phase photolysis.

(e) It would be useful to understand how important gas-phase OH is as a sink for the compounds with $Z > 1$. I recommend that compounds where gas-phase OH is the dominant sink be denoted in the figure (e.g., by adding a prime character on the number).

(f) The symbol for the 2-carbon aldehydic acid is hidden under the legend box.

Minor Comments.

1. There are numerous instances where the writing is unclear, repetitive, or contains typographical errors:

(a) Abstract, page 10906, lines 10 – 12. This sentence essentially repeats a portion of the previous sentence and could be deleted.

(b) Page 10908, line 19 through first line of next page. This is too much information about the glyceraldehyde quantum yield and other details, especially since you later decide not to try to estimate quantum yields for each compound. This text should be moved to the discussion of the glyceraldehyde results.

(c) Page 10918, line 13: a dash is missing after “acrolein” (to complete the dash before the word).

(d) Page 10918, line 24: “and a larger photolysis quantum yields”. Delete “a”.

(e) Page 10920, lines 3-4. This sentence essentially repeats the text that was 2 sentences earlier. Rearrange the paragraph structure to avoid this repetition.

(f) Page 10921, line 24. Period should be after parentheses (not before).

(g) Page 10922, line 8. Problem with the citation: “see Refs. (Leermakers and Vesley,

1963; Larsen and Vaida, 2012; Guzman et al., 2006, 2007).”

(h) Page 10923, line 6. A second citation problem: “. . .suggested in Ref. in Vione et al. (2006). . .”.

(i) Page 10923, line 20. “clouds” should be singular.

(j) Page 10923, line 23. k(hyd) should be K(hyd).

(k) Page 10923, line 24. “. . .if quantum yield experiments will product pertinent results. . .”. QY experiments will certainly produce pertinent results (i.e., that pertain to the issue of the atmospheric fate of carbonyls). Whether they’re important is a different matter, as you imply in the last part of this sentence. Fix the wording of this sentence.

2. Page 10906, Abstract. Adding a one-sentence summary of Figure 2 would be helpful for readers.

3. Page 10906 and throughout the manuscript. When “gas-phase” or “aqueous-phase” (or any other two-noun phrase) is used as an adjective it should be hyphenated. Thus it is “gas-phase compound” rather than “gas phase compound”.

4. Page 10907, lines 26-30. (a) Define “hypsochromic” or use a more self-explanatory term. (b) All of the reference compounds in Table 1 show a red shift for the aqueous spectrum relative to the gaseous data, which is the opposite of the Xu et al. (1993) result cited in the introduction. Certainly some compounds show a blue shift in solution, but perhaps for many of the carbonyls examined here this is not significant? This part of the introduction should be modified, as it might overly downplay aqueous-phase photolysis relative to gas-phase photolysis.

5. Page 10908, line 5. More recent data indicates the in-drop actinic flux is enhanced by a factor of 1.5 compared to the surrounding gas-phase. See Mayer and Madronich,

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6. Page 10908, line 8. $O_3 + O_2^-$ is generally a minor source of OH in cloud and fog drops that are acidic. See modeling work by Herrmann and co-workers.

7. Page 10909, line 24. Actinometry was performed before and after photolysis. How different were the two determinations on a given day?

8. Page 10910, equation (1).

(a) It should be made clear that $K(H)$ is the effective Henry's law constant. It would be good to distinguish it from the physical Henry's law constant, e.g., by including an asterisk on the effective value.

(b) The equation accounts for the hydrated carbonyl in the gas-aqueous partitioning by using the effective Henry's law constant, but then the hydrated form of the carbonyl is "removed" from consideration by the term $(K(\text{hyd}) + 1)$ in the numerator. A simpler, equivalent formulation of equation (1) replaces the effective $K^*(H)$ with the physical Henry's Law constant and removes the factor of $(K(\text{hyd}) + 1)$ from the numerator. I recommend that this alternate form of the equation be added to the manuscript as it is often simpler to determine, requiring only the physical $K(H)$ (which is sometimes easier to find than the effective value) but not the hydration constant.

(c) The authors should examine whether a similar simplification could be accomplished for the dicarbonyl equation in the supplement.

(d) It would help the reader understand equation (1) if it was first shown as an equality with the aqueous-phase and gas-phase rate constants shown explicitly. Then the assumption that $J(\text{gas}) \gg J(\text{aq})$ should be explicitly stated, leading to the current form of equation (1).

(e) As formulated in eqn (1), $LWC(v)$ is the volumetric liquid water content (e.g., L-aqueous/L-air) and not the mass-based LWC as stated.

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9. Page 10912, line 6. It should be indicated that $k(\text{OH})$ is a second-order rate constant.
10. Page 10913, lines 10-11. The wording “As an approximation, we treat the photolysis quantum yield as an average value over all relevant wavelengths:” is somewhat misleading since there is little treatment of quantum yields in the subsequent text. In most cases it is assumed that $\text{PHI} = 1$.
11. Page 10916, line 18. The authors assume that $\text{PHI} = 1$. They should add a few sentences of discussion here about literature values for aqueous carbonyls beyond hydroxyacetone and glyceraldehyde. Is this assumption better for certain classes of carbonyls?
12. Page 10917, line 7. “maximum” here should be “minimum” (since the lifetime was calculated with $\text{PHI} = 1$).
13. Page 10919, lines 8 – 10. Indicate the number of compounds where an upper estimate for the maximum molar absorptivity was used. Also indicate the total number of carbonyl compounds considered.
14. Page 10919, lines 20-21. “Reproductions of Fig. 6 under other relevant atmospheric conditions are presented in the Supplement.” This is too vague to be very helpful. It would be better to explicitly list the different conditions considered and the corresponding supplemental figure number.
15. Page 10919, line 28. It doesn't appear that 3-oxopropanoic acid is the correct compound. Based on the symbol type this should be the 3-carbon ketoaldehyde (2-oxopropanal, aka, methylglyoxal), rather than the 3-carbon ketoacid (which was already called out in the bottom left quadrant).
16. Page 10922, lines 13-15, “The same functional groups that allow for photolysis at actinic radiation and increased solubility in water can also increase the rate of hydrogen abstraction in the molecule.” Specifically, which functional groups do you mean? Given that this paper didn't consider unsaturated carbonyls, I assume it's referring to

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additional carbonyls and/or alcohols. But does the addition of a carbonyl to a molecule increase its OH rate constant? Does the addition of an alcohol group increase absorption of solar radiation appreciably?

17. Page 10923, line 1. “higher” should instead be “lower”, i.e., lower solar zenith angle, which corresponds to a higher actinic flux.

18. Page 10923, line 8. (a) The supplemental figure should be S10, not S6 as stated in the text. (b) The caption for Figure S10 indicates that the aqueous OH concentration is $1\text{E-}14\text{M}$, while the text here lists the concentration as $2.5\text{ E-}14\text{M}$. Which is it? (I’m guessing the latter based on the S10 results, which are not consistent with the stated concentration.)

19. Fig. 3. It would be helpful to have the names of the compounds included in the caption or in the supplemental material.

20. Fig. 4. (a) I believe the photolysis lifetime calculation assumes a constant actinic flux. If so, 10 days of this condition is more than 20 days of actual time. Either way, this should be explained in the text. (b) The acetone symbol (A) in the figure is not consistent with Figure 7. $\lambda(\text{max})$ in Fig. 4 is 265 nm, while the Fig. 7 value is at least 10 nm larger. Also, $\text{PHI}^*\epsilon$ is nearly 20 in Fig. 4, while the Fig. 7 molar absorptivity sets an upper bound of 14. (c) “ethanol” in the caption (line 5) is not correct. Should it be ethanal?

21. Fig. 5. I believe each line corresponds to $Q = 1$ for a given value of $k(\text{OH})$. If so, this should be indicated in the text and/or figure caption.

22. Fig. 7. (a) This figure (and the implications of the MD underestimation of light absorption by acetone) needs to be discussed in the text. (b) The actinic flux for $\text{SZA} = 20$ deg should be included in the figure to show the importance of $\lambda(\text{max})$. (c) The blue-shift in $\lambda(\text{max})$ for the MD simulated spectra relative to measured values for acetone is troubling since this will lead to an underestimate of the photolysis lifetimes.

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The aqueous shift makes a huge difference: while the measured molar absorptivities modestly overlap with the solar spectrum, the MD result has essentially no overlap. (d) To make the curves more visible, I recommend that you restrict the y-axis range to 0 - 14.

23. Table 1. References for the measured data in Table 1 should be moved from Table S3 to the main text.

24. Supplemental Table S1. As I understand it, this approach was only used to calculate rates of aqueous photolysis, but not gas-phase photolysis. This should be made clear.

25. (a) It would help the reader wade through the sea of names if the authors added a supplemental table with IUPAC and common names for the compounds in Table S1, at least up to carbon number 4 or 5. (b) Structures should be shown for the compounds in Table S4. (c) Structures should be included on Figures S12 – S21. (d) If you really want to help the reader navigate the sea of organic compounds, adding a figure with the structures corresponding to the names in Table S1 would be a great help.

26. (a) Far too many significant figures are presented in the molar absorptivity values and uncertainties in Table S6. (b) What does the uncertainty represent? 1 standard error?

Overall Assessment.

This manuscript makes an important contribution to our understanding of the atmospheric fate of carbonyls. The concepts in the manuscript are interesting and the results are comprehensive. Once the text is expanded and clarified this has the potential to be a great paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 10905, 2013.

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