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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aqueous Reactions of Organic Triplet Excited States with Atmospheric Alkenes" *by* Richie Kaur et al.

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Please note that our response is given below each question or comment from the reviewers. We have also uploaded our responses as a separate pdf file. Please note that line numbers in the revised version will be different due to changes in the manuscript.

Anonymous Referee #1 Received and published: 4 February 2019

Major comment: The authors present a nice study on the reactions of a model triplet species with various alkenes and reveal which features (e.g. one electron reduction potential, double bond location) have a higher reactivity towards triplets. When reading the manuscript, I was curious whether or not the authors could confirm that the rate

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constants for triplet benzophenone are similar to those generated from brown carbon/ natural organic matter (NOM). Although beyond the scope of this study, a discussion of how the rate constants for the 17 model compounds might be different for triplet NOM, or how they might vary if NOM is also present, might be useful.

Author Response: We thank this reviewer for their thorough review and detailed, helpful comments. Based on our two studies to date, NOM triplets in fog and airborne particles are about as reactive as the triplets of 3'-methoxyacetophenone (3MAP) and 3,4-dimethoxybenzaldehyde (DMB). For the few alkenes where there are rate constants for both these triplets and triplet benzophenone, the latter is approximately 25 times more reactive. This information is in Section 3.4 of the manuscript.

Minor comments: 1. Abstract/Intro Is brown carbon something that needs to be defined here (like in line 46)? Or is it a fairly common term in atmospheric chemistry literature?

Author Response: The reviewer is correct – brown carbon is a fairly common term used in atmospheric chemistry. However, taking the reviewer's question into account, we have included a brief description in the abstract in line 13.

2. Is "a.k.a" commonly used?

Author Response: This refers to line 13 (first line of the abstract). We think it is a commonly used abbreviation, but we have replaced it with "or" to avoid any confusion.

3. Line 76: what are the steady-state concentrations of OH radicals and triplets? Are the concentrations of benzophenone and alkenes used in this study environmentally relevant?

Author Response: For this study, our goal was to measure rate constants for the BP triplet with alkenes, which does not require that the triplet concentration is environmentally relevant. Since we used a relative-rate approach, initial concentrations of the reactants do not impact the outcome. But to answer the question, we estimate that 3C* concentrations in our solutions are 10–14 to 10–15 M (see answer to Q5 for more

details) which is similar to fog triplet concentrations (Kaur and Anastasio, 2018). In comparison, our alkene concentrations are probably higher, by a factor of at least 10, compared to a fog drop. (But, as stated earlier, this does not impact our determination of the rate constant.) Some hydroxyl radical (âĂćOH) was probably generated during our experiments. However, we estimate that the âĂćOH concentration is small and has no significant impact on our rate constants; we discuss this issue in more detail in response to question 5 below.

4. Methods. Why was a pH of 5.5 selected?

Author Response: The pH of 5.5 was based on the average pH we measured in fog waters in a recent study of 5.6 ($\pm$ 0.9) (Kaur and Anastasio, 2017). We have added this information in line 101.

5. Does irradiating the benzophenone solution generate other oxidants? Can you confirm all reactions due to 3BP*? Similarly, do any of the test alkenes or reference compounds degrade due to direct photoreactions when BP is not present?

Author Response: This is a good question. The two most likely other oxidants formed in our system are singlet oxygen (1O2*) and hydroxyl radical (âĂćOH).

1O2* is formed by reaction of triplets with O2 (Zepp et al., 1977; Haag and Hoigné, 1986); for 3BP*, the 1O2* yield (i.e., fΔ) for this reaction is 0.35 (Wilkinson et al., 1993). Based on our measured alkene decays, the triplet BP concentration in our solutions was typically 1 $\times$ 10–15 M. As described by McNeill and Canonica (2016), the singlet oxygen concentration can be estimated by

[1O2*] $\approx$ 2 fΔ [3C*]

For 3BP* this gives a singlet oxygen concentration of nearly 1 $\times$ 10–15 M. For the three alkenes (HxAc, HxO, and MeJA) where we have rate constants with both 3BP* (this work) and 1O2* (Richards-Henderson et al., 2014b), the average value of kALK+1O2* / kALK+3BP* is 4.0 $\times$ 10–4; i.e., rate constants for alkenes with triplet BP are approx-

imately 2500 times faster than with singlet oxygen. Thus, since the concentrations of 3C* and 1O2* are likely similar in our solutions but 1O2* reacts much more slowly with alkenes, singlet oxygen should be a negligible sink for the alkenes in our experiments. We have added this idea to the end of section 2.2.

In the case of OH, we cannot estimate its formation rate or steady-state concentration, which makes it impossible to quantify its contribution to alkene loss. However, there is at least one piece of evidence that argues against OH as a significant oxidant in our samples. OH reacts with most alkenes at very similar, near diffusion-controlled, rates. For example, the second-order rate constants for OH with allyl alcohol (AlO) and methyl jasmonate (MeJA) are 6.0 $\times$ 109 M–1 s–1 (Simic et al., 1973) and 6.7 $\times$ 109 M–1 s–1 (Richards-Henderson et al., 2014a), respectively. This is a difference of only 11%. In contrast, our measured rate constant for MeJA with 3BP* is more than 30 times higher than the value for AlO with 3BP*. This suggests that OH has no significant impact on our measured rate constants.

Finally, direct photodegradation of all alkenes was examined in illuminated solutions without BP: no direct loss was detected for any of the compounds. We added this information to section 2.2.

6. How does 100 uM BP and 50 uM alkene compare to brown carbon concentrations and alkene concentrations, respectively, in fog droplets/aqueous particles?

Author Response: Dissolved organic carbon concentrations can range between 1200 and 2700 μM-C in Davis fog drops (Anastasio and McGregor, 2001; Zhang and Anastasio, 2001; Kaur and Anastasio, 2017) and can be several orders of magnitude higher in particles. As for the alkenes, we haven't seen concentrations reported, but they are probably at least 10 times lower than our concentration. However, as mentioned above, when determining rate constants with the relative rate method the species do not need to be at atmospherically relevant concentrations.

7. What irradiation time or times were used? Did they vary?

Author Response: Irradiation times were typically between 60 and 150 minutes, with the length dependent upon the reactivity of the alkene. We have included a statement about this in Section 2.2.

8. Is oxygen consumed in sealed quartz cell during this time, impacting rates?

Author Response: We do not think there was significant consumption of dissolved O2 since the solutions started saturated with air (corresponding to 284 μM of dissolved O2) and the cell was opened multiple times during illumination when aliquots were removed. If dissolved oxygen had been significantly consumed during the course of the experiments, the concentration of BP triplet would have increased since O2 is the main sink of triplets. In that case, the rate constants for loss of alkene and reference compound would have increased with illumination time. We did not observe this: the loss of alkenes and reference compounds were always first order and the slope of the ln(C/C0) vs. time plot did not change with time. Thus, our evidence indicates that oxygen was not significantly consumed during the experiments.

9. I imagine benzophenone and NOM have different absorbance (A) spectra? It would be interesting to compare A spectra multiplied by irradiance for benzophenone and for brown carbon (or something similar to figure S1).

Author Response: While these action spectra for light absorption would be interesting, whether the BP and NOM results are similar or different wouldn't have any effect on our results. This is an interesting question, but it does not fit within the scope of our study.

10. Fig. S1 is a bit confusing showing %transmittance for the light source and not its irradiance through the filters? I think showing the irradiance the sample sees would be more useful for a comparison to solar irradiation. I imagine the photon dose the sample sees impacts the formation of triplets, can the authors confirm that this does this not matter for the competition kinetic experiments performed here?

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Author Response: We thank the reviewer for this feedback. We measured the irradiance of our system and used this data to revise Figure S1 (updated figure attached).

Since we are using a relative rate method, where both the reference compound and test alkene are seeing the same concentration of 3BP*, regardless of changes in lamp flux, the irradiance does not affect the second-order rate constant that we determine. While absolute loss rates of the test and reference species are affected by the photon dose, the ratio of pseudo-first-order reaction rate constants are independent of photon flux.

11. Line 115-117: Where was the aluminum wrapped dark in relation to the irradiated sample? If the two samples are side by side there will certainly be issues since aluminum foil is a hard reflector and could increase photon dose in irradiated sample.

Author Response: We appreciate the reviewer's thoughtfulness here. The aluminum-wrapped "dark" cuvette and the illuminated sample were in the same chamber but not kept side by side. The dark cuvette was placed in a corner, not in the path of the light beam so that it was subjected to the same temperature and other conditions as the illuminated sample. We have included this clarification in the Section 2.2.

12. Results/Discussion Lines 311-333: As the authors note, adjusting 3BP* constants is uncertain, but I also now wonder if 3MAP and DMB triplets are more representative of triplets from NOM? Or is that unknown?

Author Response: Based on our recent work (the only two studies that have measured triplets in atmospheric samples, as best we know), the NOM triplets in fog and PM are typically most similar to 33MAP* and 3DMB*. This is why we adjusted the 3BP* rate constants to what we would expect for an average of 33MAP* and 3DMB*. This is described in Section 3.4.

âĂČ Anonymous Referee #2 Received and published: 6 February 2019

In this very ambitious study, the authors measured the kinetics of oxidation of a series

of alkenes by the triplet excited state of benzophenone, which they use as a model compound for triplet excited states in atmospheric waters. They then looked for correlations between the kinetic data and various properties of the alkenes, some of which were derived using density functional theory (DFT) calculations. They found a fairly good correlation between the rate constants and the one-electron oxidation potential for the alkenes, and used that to develop a quantitative structure-activity relationship (QSAR). They used the QSAR, and more DFT calculations, to infer triplet oxidation rates for several biogenically derived alkenes. Finally, they perform some estimates of the potential importance of triplet chemistry in atmospheric waters. I recommend publication in ACP after some minor points are addressed.

Author Response: We thank this reviewer for their thoughtful review, encouraging comments, and specific suggestions for improvement of the manuscript.

Minor comments: 1. - It is not mentioned in the main text how many times each kinetic experiment was repeated - I only knew this after looking at Table S1.

Author Response: We have added this information to Section 2.2.

2. - Can the authors discuss and provide some estimate of the error/uncertainty for the parameters derived from the DFT calculations? How does this impact the discussion of the outliers for the QSAR?

Author Response: We think the reviewer is inquiring about the CBS-QB3 method specifically, as this was the method used for calculations of BDEs, BDFEs, and OPs. In the article describing this method, the authors state that the errors for CBS-QB3 have a mean absolute deviation of 1.10 kcal/mol on a test set they used. This is comparable to other post-Hartree-Fock ab initio methods (such as MP2, a method we used to calculate HOMOs/SOMOs), which have mean absolute deviations of 0.94 -1.21 kcal/mol on the same test set. This error of roughly 1 kcal/mol corresponds to only 0.04 V in OP, so does not account for the over- or under-prediction of the outliers in Figure 3, which are off by greater amounts. We have added a description of these errors to Section

2.3.

3. I note from Table S1 that several different reference probes were used. The reason for this should be discussed. The reference rates and the uncertainty in those rates should be listed/discussed. Were the uncertainties included in the reported uncertainties in k, and considered in the development of the QSAR?

Author Response: We used several probes so that the loss rates of the test and references alkenes were similar. If the loss rates are very different it is difficult to get good rate constants for both species during the same illumination time. The reference rates and the uncertainties are given in Table S1. We have included a statement about this in Section 2.2. The standard errors in the slope and reference rate constant were propagated to obtain the uncertainties listed for each replicate in parentheses in Table S1. Since each experiment was performed in triplicate, we used the standard deviation of the mean for the QSAR Figure 3. The uncertainties were not considered in the development of the QSAR.

4. - Just a suggestion: Fig. 4 and some of the discussion of these calculations could be moved to the SI, since the article is already quite dense with information and this line of inquiry was ultimately inconclusive.

Author Response: We appreciate the reviewer's comment about the article being dense with information. However, we feel that Figure 4 provides a good example of the computational work that was performed and illustrates an interesting difference in the reactivity of the alkenes we studied. Even though the transition state structures and associated thermodynamics didn't end up being predictive of rate constants, we have kept the figure in the main text because this is an important negative result.

5. - A little more information about the atmospheric lifetime calculations should be provided. Are you considering repartitioning of the OVOCs between the gas and aqueous phases as the reaction proceeds? Or are the calculated rates basically initial rates?

Author Response: This is a good question. Since we are only providing rough estimates, we have not considered repartitioning of the OVOCs between the phases and only considered the initial rates. We added a clarifying “initial” in the first paragraph of Section 3.4.

âĂČ References for the Author’s Responses:

Anastasio, C., and McGregor, K. G.: Chemistry of fog waters in California’s central valley: 1. In situ photoformation of hydroxyl radical and singlet molecular oxygen, Atmos. Environ., 35, 1079-1089, 2001. Haag, W. R., and Hoigné, J.: Singlet oxygen in surface waters .3. Photochemical formation and steady-state concentrations in various types of waters, Environ. Sci. Technol., 20, 341-348, 1986. Kaur, R., and Anastasio, C.: Light absorption and the photoformation of hydroxyl radical and singlet oxygen in fog waters, Atmos. Environ., 164, 387-397, 2017. Kaur, R., and Anastasio, C.: First Measurements of Organic Triplet Excited States in Atmospheric Waters, Environ. Sci. Technol., 52, 5218-5226, 2018. McNeill, K., and Canonica, S.: Triplet state dissolved organic matter in aquatic photochemistry: Reaction mechanisms, substrate scope, and photophysical properties, Environ. Sci. Process. Impact., 18, 1381-1399, 2016. Richards-Henderson, N. K., Hansel, A. K., Valsaraj, K. T., and Anastasio, C.: Aqueous oxidation of green leaf volatiles by hydroxyl radical as a source of SOA: Kinetics and SOA yields, Atmos. Environ., 95, 105-112, 2014a. Richards-Henderson, N. K., Pham, A. T., Kirk, B. B., and Anastasio, C.: Secondary Organic Aerosol from Aqueous Reactions of Green Leaf Volatiles with Organic Triplet Excited States and Singlet Molecular Oxygen, Environmental Science & Technology, 49, 268-276, 2014b. Simic, M., Neta, P., and Hayon, E.: Reactions of hydroxyl radicals with unsaturated aliphatic alcohols in aqueous solution. Spectroscopic and electron spin resonance radiolysis study, J. Phys. Chem., 77, 2662-2667, 1973. Wilkinson, F., Helman, W. P., and Ross, A. B.: Quantum yields for the photosensitized formation of the lowest electronically excited singlet state of molecular oxygen in solution, J. Phys. Chem. Ref. Data, 22, 113-262, 1993. Zepp, R. G., Wolfe, N. L., Baughman, G. L., and Hollis, R. C.: Singlet

oxygen in natural waters, Nature, 267, 421-423, 1977. Zhang, Q., and Anastasio, C.: Chemistry of Fog Waters in California's Central ValleyâĂŤPart 3: Concentrations and Speciation of Organic and Inorganic Nitrogen, Atmos. Environ., 35, 5629-5643, 2001.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-1259/acp-2018-1259-AC1-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1259, 2018.

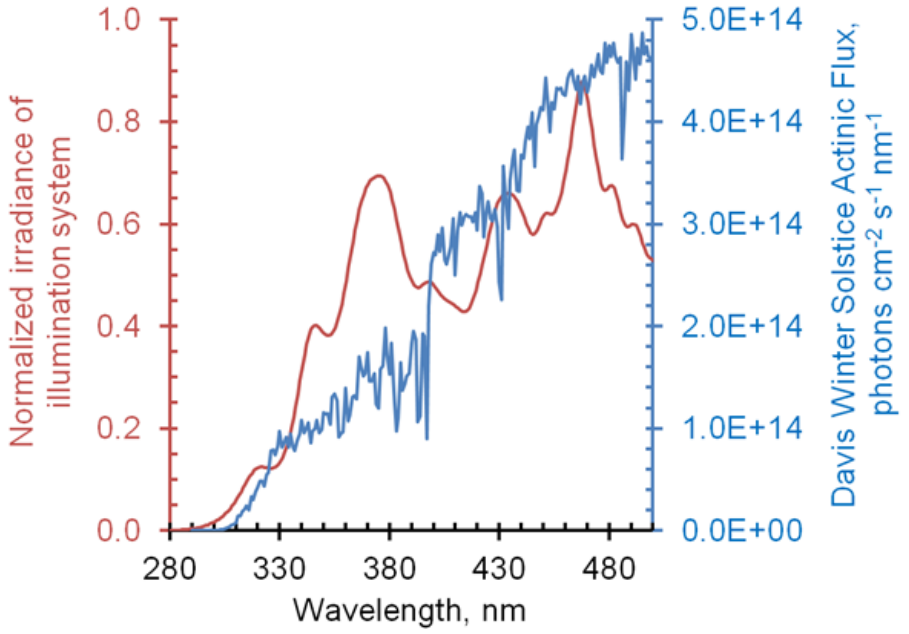

Figure S1. Comparison of the normalized irradiance from our illumination system (red line) and Davis, midday, winter solstice sunlight from the TUV model (blue line; Madronich et al. (2002)). Our illumination system irradiance was measured using a TIDAS spectrophotometer (counts cm^{-2} nm^{-1} s^{-1}) and normalized so that the area under its curve is equal to the area under the TUV actinic flux curve. Input parameters for the TUV model were: solar zenith angle: 62°, measurement altitude: 0 km, surface albedo: 0.1, aerosol optical depth: 0.235, cloud optical depth: 0.00.

Fig. 1.

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